

Storage of Charge in  
Redox Conductive Polymers  
Probed with  
Electron Spin Resonance Spectroscopy

**Ilia Romanovich Kulikov**

Im Fachbereich Physik der Freien Universität Berlin eingereichte  
Dissertation zur Erlangung des Grades eines  
Doktors der Naturwissenschaften

Berlin  
June 2024

---

Erster Gutachter: Prof. Dr. Jan Behrends  
Zweiter Gutachter: Prof. Dr. Kirill Bolotin  
Tag der Disputation:

# Contents

<b>1</b>	<b>Introduction</b>	<b>7</b>
1.1	Rechargeable Electrochemical Cells . . . . .	8
1.1.1	Organic Radical Battery . . . . .	9
1.2	Experimental Techniques for Characterizing Battery Materials . . . . .	9
1.3	Redox Conductive Polymers . . . . .	10
1.3.1	Charge Transport in a Polymer Electrode . . . . .	11
1.4	Thesis Structure . . . . .	12
<b>2</b>	<b>Fundamentals of EPR</b>	<b>13</b>
2.1	The Spin Hamiltonian . . . . .	13
2.2	Continuous-Wave Electron Paramagnetic Resonance . . . . .	16
2.2.1	cwEPR spectrometer . . . . .	17
2.3	Fundamentals of Pulsed EPR Spectroscopy . . . . .	20
2.3.1	Bloch Equations . . . . .	20
2.3.2	Refocused Spin Echo . . . . .	20
2.3.3	Spin Relaxation Times . . . . .	20
2.3.4	Spin Packets . . . . .	20
2.3.5	Pulsed EPR Instrumentation . . . . .	20
2.3.6	Pulse Sequences and Measurement Techniques . . . . .	20
<b>3</b>	<b>Materials and Devices</b>	<b>23</b>
3.1	Organic Electrochemical Cells . . . . .	23
3.1.1	Cell Electrodes . . . . .	23
3.1.2	Three-Electrode Cell . . . . .	24
3.1.3	Reference Electrode . . . . .	25
3.1.4	Electrolyte . . . . .	25
3.1.5	Characteristics of Rechargeable Batteries . . . . .	26
3.2	Electrochemical Instrumentation . . . . .	28
3.2.1	Cyclic Voltammogram . . . . .	28
3.2.2	Charge-Discharge Cycling . . . . .	29
3.3	Organic Electrode Materials . . . . .	31

---

3.3.1	Semiconducting Polymers . . . . .	31
3.3.2	TEMPO . . . . .	33
3.3.3	PTMA . . . . .	35
3.3.4	NiSalen . . . . .	35
3.3.5	Poly-Di-TEMPO-Salens . . . . .	35
3.3.6	Electro-polymerization of TEMPO-Salens . . . . .	37
3.4	TEMPO-Salen Films for EPR Spectroscopic Measurements . . . . .	38
3.5	Electrochemical Cells for EPR spectroscopy . . . . .	42
3.5.1	Cells Based on a Modified EPR Sample Tube . . . . .	42
3.5.2	Fabrication of the modified tube . . . . .	44
3.5.3	Q-factors and cwEPR spectra for p-DiTS in standard and modified tube . . . . .	45
3.5.4	Reference Electrode . . . . .	46
3.5.5	Electrochemical Cells with a Separator . . . . .	46
3.5.6	Electrochemical Cells with Solid Electrolyte . . . . .	47
3.5.7	Energy Diagram of an Electrochemical Half-Cell . . . . .	47
<b>4</b>	<b>EPR Spectroscopy of TEMPO-Salen Electrochemical Cells</b>	<b>55</b>
4.1	cwEPR Spectroscopy of TEMPO Containing Molecular Fragments . . . . .	55
4.1.1	Room Temperature Spectra of TEMPO <sup>•</sup> Solutions . . . . .	56
4.1.2	Spectra of TEMPO <sup>•</sup> /TEMPO <sup>+</sup> Films . . . . .	58
4.1.3	Spectra of NiSalen Films . . . . .	59
4.2	cwEPR Spectroscopy of a Charging Electrochemical Cell . . . . .	60
4.2.1	cwEPR Spectra During a Charge-Discharge Cycle . . . . .	61
4.3	p-DiTS in-operando redox series . . . . .	63
4.3.1	Spectral Simulations . . . . .	66
4.3.2	Quantitative Analysis of Potential-Dependent EPR Spectra . . . . .	66
4.4	EPR-Detected State Of Charge . . . . .	67
4.4.1	Formation of Singlet Spin States in a Reduced Cathode Film . . . . .	67
4.5	Monitoring of Degradation Processes . . . . .	68
4.6	Monitoring of Self Discharge . . . . .	71
4.7	Low Temperature Measurements . . . . .	71
4.7.1	p-DiTS . . . . .	71
4.7.2	p-NiMeOSalen . . . . .	72
4.7.3	Tube Based Cells . . . . .	73
4.8	Pulsed EPR spectroscopy of TEMPO-Salens . . . . .	73
4.8.1	Pulsed EPR Spectra of TEMPOL solutions . . . . .	73
4.8.2	Pulsed EPR Spectroscopy of a charged pDiTBuS Cathode film . . . . .	73
4.8.3	Field Swept Echo of a charged pDiTBuS Cathode film . . . . .	75
4.8.4	Instantaneous Diffusion in Charged pDiTBuS . . . . .	75

## Contents

---

<b>5 Results and Discussion</b>	<b>95</b>
5.1 Instantaneous Diffusion in pDiTS . . . . .	95
5.2 Simulations of the EDFS Spectra Considering Instantaneous Diffusion . . . . .	97
5.2.1 EDFS in 50 mM TEMPOL Measured with Narrow-Band Pulses	97
5.2.2 EDFS in 50 mM TEMPOL Measured with Broad-Band Pulses . . . . .	97
5.2.3 EDFS in PDiTBuS at ESOC 85% Affected by Instantaneous Diffusion . . . . .	98
5.2.4 EDFS in PDiTBuS at ESOC 95% Affected by Instantaneous Diffusion . . . . .	99
5.2.5 Estimation of Local Spin Concentrations with Instantaneous Diffusion . . . . .	100
5.3 Spin Relaxation in a charged pDiTBuS Cathode Film . . . . .	100
5.3.1 Temperature Dependence of Pulse Spectra of Charged pDiTBuS	103
5.3.2 Limitation on Shortest Detectable $T_m$ by the Spectrometer Dead Time . . . . .	104
5.4 Padé-Laplace Deconvolution of Polyexponential Decay Signals . . . . .	104
5.4.1 Padé-Laplace Deconvolution of the Echo-Decay and Inversion-Recovery Transients . . . . .	107
5.4.2 Detection of Domains with Poor Conductivity . . . . .	113
5.4.3 Towards Electron Resonance Imaging of Spin Concentrations in Battery Electrodes . . . . .	113
<b>6 Conclusions and Outlook</b>	<b>115</b>

---

$\vec{e}_x, \vec{e}_y, \vec{e}_z, t$	Laboratory frame of reference
$\vec{\hat{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$	Spin operator
$h = 6.62607015 \times 10^{-34} \text{ J} \times \text{s}$	Planck constant
$g_e = -2.00231930436118(27)$	Electron g factor
$\mu_B = 9.2740100783(28) \times 10^{-24} \text{ J/T}$	Bohr magneton
$\mu_0 = 1.25663706212(19) \times 10^{-6} \text{ N/A}^2$	Permeability of free space
$\varepsilon$	Relative dielectric permittivity
$\vec{B}_0 = B_0 \vec{e}_z$	Static magnetic field
$\omega_L$	Larmor frequency
$\vec{B}_1(\vec{r}, t)$	Microwave field
cwEPR	Continuous wave electron paramagnetic resonance
pEPR	Pulsed electron paramagnetic resonance
DUT	Device under testing
ORB	Organic radical battery
WE	Working electrode (cathode, "+")
CE	Counter electrode (anode, "-")
RE	Reference electrode
$V_{OC}$	Open circuit potential
SoC	State of charge
ESOC	EPR-detected state of charge
SoH	State of health
CV	Cyclic voltammogram
GCD	Galvanostatic charge-discharge
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
pDiTS	Poly-di-TEMPO-Salen
RCP	Redox conductive polymer
pDiTBuS	Poly-di-TEMPO-Butyl-Salen
PTMA	Poly-TEMPO-methacrylate
EDFS	Echo-detected field sweep
ID	Instantaneous diffusion
$\langle n \rangle$	Mean spin concentration
$C$	Local spin concentration
$T_1$	Spin-lattice relaxation time
$T_m$	Phase memory time
$t_d$	Microwave detector dead time

---

Table 1: List of abbreviations

# Chapter 1

## Introduction

This chapter introduces the concept of an organic radical battery, the electrochemical processes in the battery electrodes, the structures of organic electrode materials based on redox conductive polymers and their electrochemical performance. Necessary electrochemical characterization techniques are described. Charge transport models for particular electro-active conjugated polymers are reviewed.

Energy storage systems such as fuel cells, supercapacitors and batteries are crucial elements for powering portable electronics, vehicles, and for balancing a power grid with a renewable energy source [46]. Stable, capacious and powerful batteries have become of great demand for today's energy driven society [125, 121, 83]. The capacity of installed battery storage systems is predicted to increase upto 400 GWh by 2030 [28]. The advances in lithium ion technology for rechargeable batteries have enabled energy densities that make it possible to battery-power a wearable Internet-of-things device [64, 72], an airplane [50] or a house [19, 42]. Still, the application of lithium ion batteries is limited by irreversible processes [62, 30, 130] that occur upon extreme operating conditions such as high power demand [129, 35] or over-discharge [71]. Such degradation processes limit the performance of a battery by lowering its safe operating power, resulting in lower power density and longer charging times. The challenge to overcome these limitations, together with low abundance of Lithium, Cobalt and rare earth metals [121, 46], the toxicity of the manufacturing process [93, 91] and the bio-hazardous nature of the inorganic electrode materials [12] is motivating research and development of advanced, organic-based battery technologies [17]. This requires understanding of charge transport and degradation pathways in energy storage materials as well as exploring novel materials such as materials based on organic precursors [69, 54].

## 1.1 Rechargeable Electrochemical Cells

Two opposite electric charges separated from each other can store energy in an electrostatic field. It is possible to accumulate many charges on the plates of a capacitor and store some energy [38], but due to the technological difficulties, electrochemical cells are commonly used instead [28]. An electrochemical cell is an energy storage device and a power source that undergoes a chemical reaction to transfer some electric charge from one of its components to another through an external circuit.

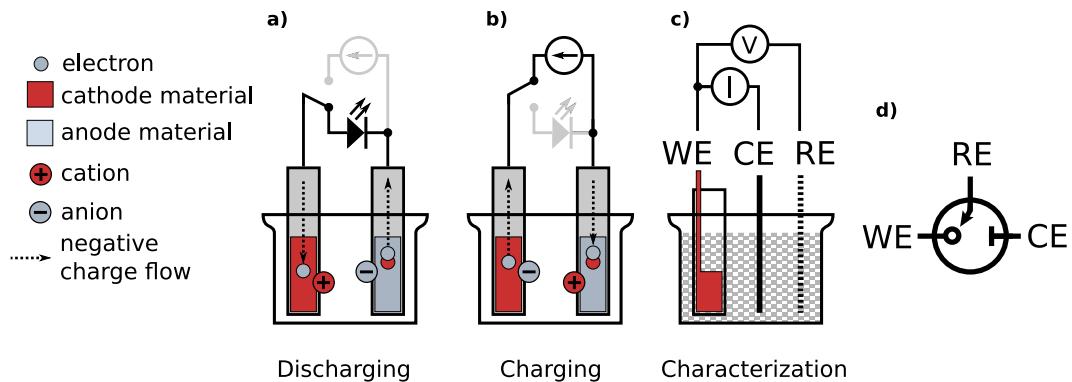


Figure 1.1: Rechargeable electrochemical cell connected to an external circuit for discharging a) and charging b). c): Three-electrode half-cell used for electrochemical characterization and charging of the cathode material. d): symbol for an electrochemical cell used in electric diagrams.

A simple electrochemical cell consists of three elements: two spatially separated materials called electrodes, and a solution of mobile ions between them called electrolyte. The two electrodes have different work functions, or, chemically speaking, reduction-oxidation (redox) potentials. The potential difference between the two electrodes is called the open-circuit potential of the cell,  $V_{OC}$ . When the electrodes are connected through an external circuit, as shown in Figure 1.1 a), the charge flows from one electrode to another through the circuit and the ions in the electrolyte rearrange to maintain charge balance [75]. While the cell delivers the electric current to the circuit, a chemical reaction is happening on its electrodes: the positively charged electrode, called cathode, is being reduced, obtaining electrons from the negatively charged anode through the external circuit. At the same time, the anode loses electrons and is being oxidized. If the electrodes can undergo a reversible redox reaction, a current applied to the cell restores its charged state, as shown in Figure 1.1 b).

### 1.1.1 Organic Radical Battery

Batteries based on redox conductive polymers containing stable radical fragments as high-capacitance groups represent a promising class of future electrochemical power sources - organic radical batteries (ORB) [76, 81, 119, 95]. ORB combine the advantages of high-power supercapacitors, namely high discharge rates, and the high energy density of conventional lithium-ion technology. In contrast to the lithium-ion battery, the charging of an organic battery does not involve intercalation of metal ions into the electrodes. This reduces the structural change of the electrode upon repeated recharging which allows for a longer cycle life of ORBs. The electrolyte ions in an ORB do not chemically react with the electrodes, but rearrange to compensate the charges in the electrode, that improves the safety and lifetime of ORBs as compared to the Li technology. The amorphous and swollen structure of organic electrodes allows the electrolyte ions to diffuse into the electrode, which allows for oxidizing or reducing the electrode within its volume - this also increases the charge/discharge rates of ORBs [82]. A further beneficial property of organic materials over traditional inorganic materials is their availability and the low cost of the starting materials for the synthesis of the target polymers in conjunction with good mechanical properties [46, 75, 29]. The large knowledge base on polymer processing allows for inkjet printing, roll-to-roll processing and other low-cost manufacturing techniques for making low-cost, flexible and light-weight integrated devices, including flexible plastic batteries [46, 82].

## 1.2 Experimental Techniques for Characterizing Battery Materials

The flexible molecular design together with questions regarding unresolved charge-transport- and performance limiting mechanisms have inspired a variety of characterization techniques to be developed and applied to both energy storage materials and energy storage devices, operando (during the operation of a device) and ex-situ. Together with electrochemical characterization as the standard method for studying the properties of energy storage materials [4, 109, 128], operando optical microscopy [74], neutron imaging [71], mass spectroscopy [25] and X-ray diffraction [94] were applied to monitor irreversible structural deformations of the components of Li cells during extreme charging conditions.

UV and IR spectroscopy turned out to be particularly useful for studying organic energy-storage materials. For instance, with UV-Vis spectroscopy, it was possible to observe formation of positive polarons in the conductive molecular backbone for ORBs upon its oxidation [20]. Since the electrochemical processes happen within the bulk of the energy storage material and involve changes in the spin states, imaging techniques

based on magnetic resonance [80, 73, 65, 7] can be applied to obtain structural information on the battery electrodes at the molecular level. NMR was used to study dendrite formation, electrolyte dynamics and intercalation of Li ions [60, 34] in Li cells, including operando imaging [103].

Operando continuous-wave electron paramagnetic resonance spectroscopy(cwEPR) was applied to study electron transfer rates and electrolyte decomposition in redox-flow batteries [132], redox kinetics of inorganic battery cathodes [79], radical formation and spin densities in redox polymers [20] and in organic electrochemical cells [44, 57, 51].

Pulsed EPR (pEPR) provides an even more powerful toolbox for material studies with the electron spin as a microscopic structural probe. In particular, pEPR provides access to the dipolar coupling between neighboring electron spins and thus the possibility to determine distances between adjacent redox-active centers using dipolar spectroscopy [97] as in spin-labelled proteins [49, 112]. In addition, the hyperfine coupling between electron and nuclear spins in close vicinity can be measured by the electron spin echo envelope modulation (ESEEM) and the electron nuclear double resonance (ENDOR) techniques and can thus elucidate the degree of delocalization for charge carriers in ORB materials in a similar way as in organic semiconductors [26].

### 1.3 Redox Conductive Polymers

Redox active macromolecules or polymers [106] are known since 1940s due to the works of Lauth and Cassidy [13] on electron exchange polymers. After the discovery of the conductivity of polyacetylene by Shirakawa, Heeger and McDiarmid in 1977 [104], organic semiconducting polymers with sufficient charge carrier mobilities ( $\mu > 1 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$ ) were synthesized [43], and the field of organic electronics had emerged [39, 12]. Electron and hole mobilities in modern organic semiconductors have reached the values as high as  $\mu > 10 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$  [43] and, theoretically, can be above  $\mu > 100 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$  for organic molecular co-crystals [134], which enables efficient charge transport in fast-switching organic electronic circuits. Organic solar cells [63], organic field effect transistors [55, 123], e-papers [43] and organic electrochemical neurons [37] contain conjugated polymers that have electrical properties of semiconductors, yet can be easily printed in form of thin flexible films without using high temperatures, can be bio-integrated and undergo an environmentally friendly recycling [82]. A combination of conductive polymers with charge-bearing organic radicals [109] has formed the class of redox conductive polymers [12] and lead to the concept of an organic radical battery [95, 81, 76, 120] - the last missing component needed for making an electronic device fully organic.

### 1.3.1 Charge Transport in a Polymer Electrode

Charge transfer within a RCP electrode governs the speed, reversibility, physical conditions and release of by-products of the redox reaction in an organic electrochemical cell, that are the key factors that define the charging rate, cycling stability, self-discharge rate and the area of application of the cell.

The transfer of charge between the metallic substrate of the electrode and the surface-bound molecules of the electrode can be described in terms of the electrode workfunction, the HOMO and LUMO levels of the electrode molecule and the applied potential [4]. On the contrary, the transfer of charge between the molecules within the volume of the electrode is a complex process that involves hopping and time-dependent delocalization of the charge carriers in the percolated network of the porous electrode material. Furthermore, the number of available charge bearing groups and the resulting local electric fields in the electrode are changing depending on the state of charge of the electrode, that implies that the conductivity of the RCP strongly depends on its state of charge [131]. The microscopic structure of the electrode affects the diffusion of the electrolyte ions, that also affects the charge transport properties of the electrode [56, 38].

Molecular systems for electrochemical charge storage are inherently disordered materials and the electric performance of a film containing those molecules is strongly dependent on the deposition method, as well as on the molecular structure [120, 131]. Some charge transport models have been developed, that are applicable to certain classes of polymers. The charge transfer between the radicals in non-conductive redox polymers is described with the diffusion cooperation model that involves charge hopping between the charge bearing fragments as well as their Brownian motion [99]. Mixing the non-conductive redox polymers with conductive additives such as activated carbon [115, 15] allows for efficient transport of charges through the conductive additive. The carbon mesh makes it possible to oxidize most of the redox active groups in the electrode and allows for the electrolyte to diffuse into the electrode, but also adds a significant amount of “dead mass” that decreases the specific capacity of such electrodes. In RCPs, the conductive mesh is created by the semiconductor polymer backbone - that reduces the dead mass and allows for higher specific capacities. The transport of charge in such materials includes direct hopping between the charge bearing groups, transfer of charge between the charge-bearing group and the conductive polymer backbone, transport of charge through the backbone, and transport of electrolyte ions inside the polymer mesh. Those many factors affecting the performance of an RCP with a certain molecular structure lead to unexpected results, such as the decrease of the electrode conductivity with the increase of the number of charge-bearing radicals per monomer unit in a Poly (3-hexylthiophene)/TEMPO RCP [131].

## 1.4 Thesis Structure

The rest of this thesis is structured as follows:

Chapter 2 introduces the phenomenon of electron paramagnetic resonance - the phenomenon that is used throughout the studies to obtain information on the local molecular environment inside the organic battery cathodes. Physical interactions of the electron spin with the external electromagnetic fields and with its local molecular environment are summarized in the spin Hamiltonian. The experimental techniques based on the electron paramagnetic resonance are presented, as well as the used hardware solutions.

# Chapter 2

## Fundamentals of EPR

In this chapter, the phenomenon of electron paramagnetic resonance is briefly described with details that are required to interpret the spectra of a charging electrochemical cell containing nitroxide radicals attached to a conjugated polymer backbone. After the introduction of the spin Hamiltonian, an experimental procedure to observe the corresponding spin transitions with continuous microwaves is described. The characteristic spectra of nitroxide radicals in various environments are described. Finally, the fundamentals and the experimental techniques of the pulsed EPR spectroscopy are introduced.

### 2.1 The Spin Hamiltonian

**Electron Spin** In the Poincaré group of special relativity [92], rotations are considered together with the relativistic boosts [23] and there emerges an additional quantity that is associated with rotation and is preserved together with the orbital angular momentum. This additional quantity is retained for point objects and it is called spin [59]. A particle is said to have a spin if the quantum mechanical states of the particle in its own rest frame are eigenstates of the square of the angular momentum operator [113]. Spin is quantized [32]; it can take values in integer- or half-integer multiples of the Planck's quantum of action  $\hbar$  up to a certain magnitude  $S$ . The electron, as a fundamental particle and a fermion, bears a half-integer spin with a magnitude of  $S = 1/2$  [32, 96].

An isolated electron has two degenerate spin states - spin-up  $|\uparrow\rangle$  and spin-down  $|\downarrow\rangle$  - that are eigenfunctions of the square of the spin operator  $\hat{s}^2$  with the same (degenerate) eigenvalue  $\hat{s}^2|\uparrow\rangle = \hat{s}^2|\downarrow\rangle = \frac{3}{4}\hbar^2|\uparrow\rangle = \frac{3}{4}\hbar^2|\downarrow\rangle$ . The states  $|\uparrow\rangle$  and  $|\downarrow\rangle$  are also eigenfunctions of the  $z$  component of the spin operator, but correspond to different (non-degenerate) eigenvalues  $m_s = \pm\hbar/2$  [96]:

$$\hat{s}_z|\uparrow\rangle = +\frac{\hbar}{2}|\uparrow\rangle \quad (2.1)$$

$$\hat{s}_Z |\downarrow\rangle = -\frac{\hbar}{2} |\downarrow\rangle$$

**g factor** Spin combines with the charge of the electron to endow the electron with a magnetic moment  $\mu_{spin} = \gamma S$ , where  $\gamma = \frac{g_e \mu_B}{\hbar} \approx 28 \text{ GHz/T}$  is the gyromagnetic ratio of the electron,  $\mu_B = \hbar e/m_e$  is the Bohr magneton and  $g_e \approx 2$  is the electron g factor [10]. The g factor connects the spin of a particle with a magnetic moment that the particle expresses through interactions with external fields [102]. The Dirac quantum theory of the electron predicts  $g_e = 2$  [89]. However, up to date,  $g_e = 2.00231930436256(35)$  has been measured to the unprecedented accuracy of 0.13 ppt [24]. This measurement lies at the frontier of modern particle physics and the accordance of the measured  $g_e$  with the value obtained with quantum electrodynamics [102, 24] is the triumph of the quantum field theory [27].

Depending on the local environment of an electron, its g factor can change from  $g_e$  due to the spin-orbit coupling that changes the observed magnetic moment of the electron [10]. The magnetic moment of an electron can therefore be used as an extremely sensitive probe of the electron's local environment. The g factor of an electron localized in a molecular orbital can be anisotropic, depending on the shape of the orbital. Anisotropic g factor is represented by a  $3 \times 3$  **g** matrix that can almost always be diagonalized [10] by an appropriate rotation of the molecular coordinate system.

**Zeeman Splitting** When an electron is placed in a static magnetic field  $\vec{B}_0 = B_0 \vec{e}_z$ , its magnetic moment experiences a torque and precesses in the  $xy$  plane about the field axis with the Larmor frequency  $\omega_L = \gamma B_0$ . The magnetic moment of the electron has two possible projections on the magnetic field axis, according to 2.1. The two corresponding eigenvalues  $\pm \frac{\hbar}{2}$  define the energy difference between the states  $|\uparrow\rangle$  and  $|\downarrow\rangle$  when the spin couples to the external magnetic field, that is known as the Zeeman splitting. The energy difference between  $|\downarrow\rangle$  and  $|\uparrow\rangle$  in a magnetic field is the Zeeman energy.

The energy of an isolated electron placed in the external magnetic field  $\vec{B}_0$  is the energy of the electron's magnetic moment in that field, that is given by the eigenvalue of the spin Zeeman Hamiltonian:  $\hat{H}_{EZ} = \frac{\mu_B}{\hbar} \vec{B}_0 g_e \vec{s}$ . In the laboratory frame of reference  $\vec{B}_0 \parallel \vec{e}_z$ ,  $[\hat{H}_{EZ}, \hat{s}_z] = 0$ , so  $\hat{H}_{EZ}$  and  $\hat{s}_z$  share the two eigenfunctions  $|\uparrow\rangle$  and  $|\downarrow\rangle$ . The energies of the corresponding states are  $E_{EZ}^{\pm} = \pm \frac{1}{2} \mu_B g_e B_0$  (see Figure 2.2), and their difference is the Zeeman splitting:

$$\Delta E_{EZ} = \mu_B g_e B_0 \tag{2.2}$$

The measurement of the magnetic moment of an electron can be done by measuring its Zeeman energy. The local molecular environment affects the electron's magnetic moment through spin-orbit coupling which can be seen as a deviation in the electron's g factor, and therefore, in the measured Zeeman energy [10].

## 2.1 The Spin Hamiltonian

---

**Nuclear Spin and Nuclear Zeeman Splitting** A proton has a half-integer spin  $S = 1/2$  that results in a magnetic moment  $\mu_p = \mu_e \frac{m_e}{m_p}$ , that is  $\frac{m_p}{m_e} \approx 1836$  times smaller than the electron's magnetic moment. A neutron bears no charge but also has a half-integer spin  $S = 1/2$ . An atomic nucleus that consists of protons and neutrons has a magnetic moment which is a vector sum of the aligned spins of its protons and neutrons. The spin of a nucleus is defined by the arrangement of its nucleons and by the nuclear charge. A nitrogen nucleus has 7 protons and 7 neutrons that total in a nuclear spin  $I = 1$  which, with the g factor for the nitrogen nucleus  $g_N$ , results in the nuclear magnetic moment of  $\mu_N = \mu_B \frac{m_e}{m_N} g_N I$  that splits each of the electron Zeeman level into three nuclear Zeeman energy sublevels corresponding to the three possible projections of the nuclear spin on the magnetic field axis,  $m_I = -1, 0, +1$ , analogously to the electron with  $m_S = 1/2, -1/2$ . The two splittings are shown in the energy diagram in Figure 2.1. The nuclear Zeeman splitting is more than two orders of magnitude weaker than the electron Zeeman splitting because of the difference in the masses of the particles.

**Hyperfine Interaction** The magnetic moments of an electron and a magnetic nucleus, such as nitrogen, couple in the hyperfine interaction:  $H_{HF} = \vec{s}\vec{\mathbf{A}}\vec{I} = H_F + H_{DD}$  with the hyperfine coupling tensor  $\mathbf{A}$ . The isotropic part  $H_F = a_{iso}\vec{s}\vec{I}$ , or the Fermi contact interaction, scales with the probability density of the electron at the position of the nucleus  $a_{iso} = \frac{2\mu_0}{3\hbar} g_e \mu_e g_n \mu_n |\psi(0)|^2$  [101]. The anisotropic part  $H_{DD} = \vec{s}\vec{\mathbf{T}}\vec{I}$  with the dipolar coupling tensor  $\mathbf{T}$  takes into account the anisotropic magnetic dipole coupling between the magnetic moments of the electron and the nucleus.  $\mathbf{T}$  depends on the shape of the electron orbital, its  $3 \times 3$  Cartesian matrix representation depends on the molecular frame of reference and can be diagonalized by rotating the coordinate system. The matrix representation of the hyperfine coupling tensor  $\mathbf{A}$  can be written as the sum of its isotropic and anisotropic parts:  $\mathbf{A} = a_{iso}\mathbb{1}_3 + \mathbf{T}$  [117]. In its diagonal matrix representation  $\mathbf{A}$  reduces to the three principal components  $[A_{xx}, A_{yy}, A_{zz}]$ . The values of  $\mathbf{A}$  are typically given in MHz.

**Exchange Interaction** In a system of closely placed electrons, such as in a film of densely packed radicals, the electron orbitals may overlap significantly and the radicals may exchange electrons. The energy required to exchange the electrons is called the exchange coupling  $H_{exch} = \vec{s}_1 \mathbf{J} \vec{s}_2$ , that becomes considerably large at inter-spin distances below  $r < 1.5$  nm or with a large spin delocalisation [101]. The positive  $\mathbf{J}$  corresponds to a weak coupling between  $s_1$  and  $s_2$  which leads to an antiferromagnetic or antiparallel alignment of spins with a total  $S = 0$ , whereas the negative  $\mathbf{J}$  causes the strong inter-spin coupling which leads to a ferromagnetic alignment with  $S = 1$  [101].

**Nuclear Quadrupole Moment** The nitrogen nucleus has a spin greater than 1/2 which alters the charge distribution within the nucleus which gives rise to a non-vanishing nuclear electrical quadrupole moment  $Q$  [101]. The interaction between the asymmetrically distributed charge and the gradient of the electric field at the nucleus is given by the nuclear quadrupole Hamiltonian  $H_{NQ} = \vec{I}\vec{\mathbf{P}}\vec{I}$  with the nuclear quadrupole tensor  $\mathbf{P}$  that describes the coupling of the nuclear quadrupole moment to the electric field gradient.

**The Spin Hamiltonian** For the interactions considered in this thesis, the following Hamiltonian will be applied to describe the interactions of unpaired electron spins with their local environments, ranging by their magnitude:

$$H = H_{EZ} + H_{HF} + H_J + H_{NZ} + H_{NQ} \quad (2.3)$$

The electron Zeeman term  $H_{EZ}$  defines the requirements on the hardware and sets the range of the magnetic fields used in the spectroscopic experiments. The hyperfine interaction term  $H_{HF}$  allows for reconstruction of the hyperfine coupling tensor from the recorded spectra which is used as a marker to identify the molecular structure and dynamics of the mobile molecular fragments that are released during the operation of an electrochemical cell. The exchange interaction term  $H_J$  scales with the concentration of the electrons, so the information about  $\mathbf{J}$  can be used to characterize the packing of the molecular fragments in the electrode. The nuclear quadrupole interaction term may lead to spectral distortions in a highly charged cathode where electric fields may be sufficiently strong to introduce noticeable nuclear quadrupole couplings to the nitrogen nuclei.

## 2.2 Continuous-Wave Electron Paramagnetic Resonance

First observed in 1945 [127, 126, 98], the phenomenon of electron paramagnetic resonance had quickly become a tool for probing local molecular environments in species that contain unpaired electron spins. A free electron, that does not interact with its environment and has  $g = g_e$ , experiences a Zeeman splitting of  $\Delta E = g\mu_B B_0$ , that corresponds to the energy of a photon with a frequency of  $\nu = \Delta E/h$ . A microwave photon can drive a magnetic dipole transition between the Zeeman-split spin states - this is called electron paramagnetic resonance (EPR). An X band microwave photon (IEEE X band,  $\nu = 8 - 12$  GHz,  $\lambda = 2.5 - 3.8$  cm, Figure 2.2, left) can drive the magnetic dipole transition between  $|\uparrow\rangle$  and  $|\downarrow\rangle$  at  $B_0 \approx 0.3$  T. In a continuous-wave electron paramagnetic resonance (cwEPR) experiment, the microwave frequency and power is kept constant while  $B_0$  is scanned and the microwave absorption is observed. EPR happens around the  $B_0$  values given by the spin resonance condition:

$$\mu_B g_e B_0 = h\nu \quad (2.4)$$

## 2.2 Continuous-Wave Electron Paramagnetic Resonance

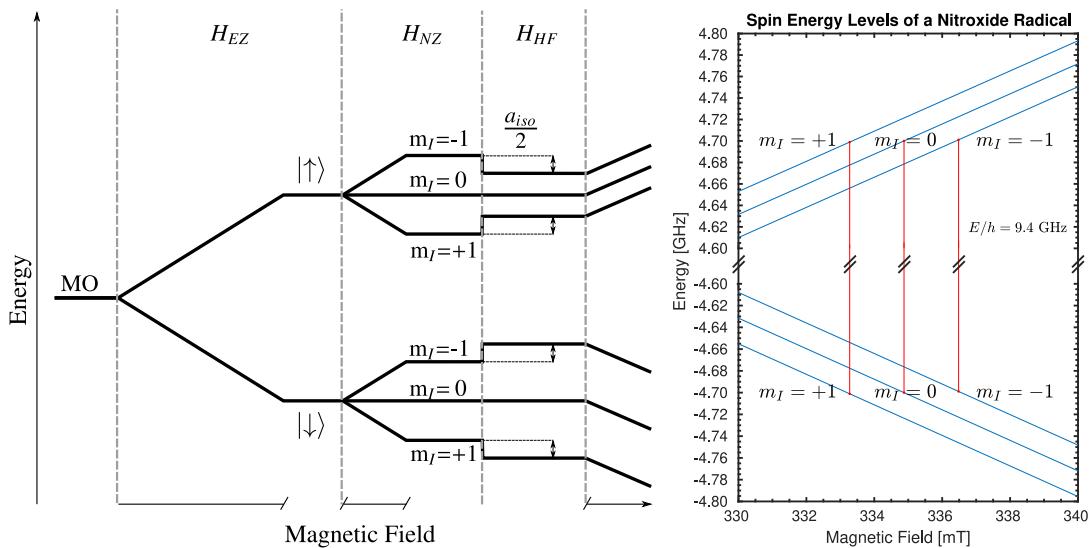


Figure 2.1: Energy diagram of the spin Hamiltonian showing the contributions to the energy level of an unpaired electron in a molecular orbital in the presence of Nitrogen. The energy of the unpaired electron at the molecular orbital (*MO*) splits into two electron Zeeman spin levels  $| \uparrow \rangle$  and  $| \downarrow \rangle$  in the magnetic field. The electron Zeeman spin levels further split into three nuclear Zeeman sublevels, due to the nuclear Zeeman interaction of the Nitrogen nucleus with three projections of the nuclear spin ( $m_I = -1, 0, +1$ ). The hyperfine interaction between the electron spin and the nuclear spin depend on the relative orientations of the spins of the particles. The parallel alignment adds  $a_{iso}$  to the energy level and the anti-parallel alignment subtracts  $a_{iso}$  from it. The energy scale for a typical X-band EPR spectrometer is shown on the right. The allowed electron spin transitions corresponding to  $\Delta m_s = \pm 1$ ,  $\Delta m_I = 0$  are shown in red vertical lines on the right.

When  $B_0$  reaches the value that satisfies Eq. 2.4, the sample starts absorbing microwaves. The absorbed microwave power recorded as a function of  $B_0$  is the cwEPR spectrum (Figure 2.2, right, dashed). By construction, cwEPR spectrometers typically record the derivative of the microwave absorption vs.  $B_0$  (Figure 2.2, right, solid). Advanced spin resonance techniques methods that involve coherent spin dynamics and pulsed microwave fields are discussed in Section 2.3.

### 2.2.1 cwEPR spectrometer

A basic cwEPR spectrometer consists of a magnet, a microwave source, a resonator and a microwave detector. Figure 2.3 depicts those elements with more details, including the sample - an electrochemical cell that is placed inside the microwave resonator and its SoC controlled with an external potentiostat.

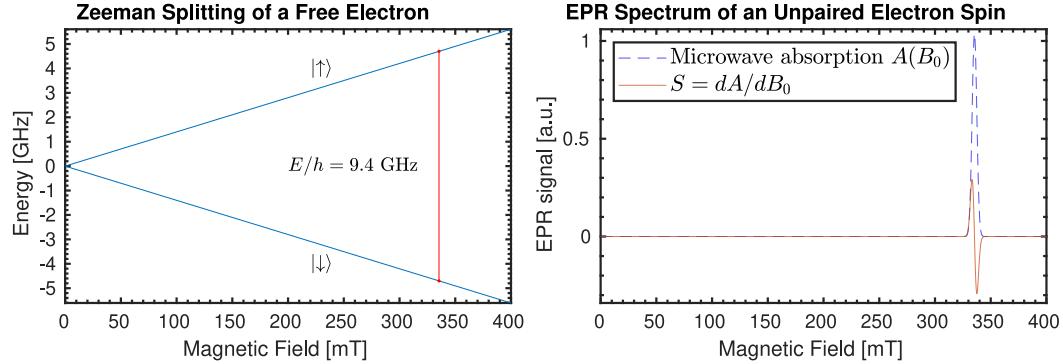


Figure 2.2: Left: Zeeman splitting for the energies of the two states of an isolated electron spin in a static magnetic field computed with EasySpin [107]. Vertical line is the magnetic dipole transition driven by a 9.4 GHz microwave photon. Right: Microwave absorption and its derivative as a function of the static magnetic field for an unpaired electron spin with a 5 mT Gaussian broadening.

Continuous microwaves are generated with a klystron (MW source in Figure 2.3) and directed towards the resonator (resonating cavity) through the signal arm that contains a variable attenuator and a circulator. The circulator directs the microwaves from the source to the cavity and passes the microwaves reflected from the cavity further to the microwave detector. The adjustable coupling iris between the circulator and the resonating cavity allows one to match the impedance of the cavity to the impedance of the signal arm so that minimal microwave power is reflected back from the cavity at a non-resonant field  $B_0$ . That impedance matching is called critical coupling. At the microwave detector, the microwaves reflected from the cavity are compensated by the microwaves with fixed microwave power and an adjustable phase, that pass through the reference arm. The signals from the two arms interfere destructively at the detector, so that there is no signal at the detector for non-resonant  $B_0$ .

When the resonance condition (Eq. 2.4) is met, the incident microwaves are being absorbed by the sample and the resonator's  $Q$  factor slightly changes. The change in the  $Q$  factor decouples the resonator from the signal arm, that causes additional reflections in the signal arm. The microwaves in the signal arm that are not compensated by the reference arm become detected by the microwave detector - a biased semiconductor diode that has a linearly changing conductivity in the range corresponding to the incident microwave power. A phase sensitive detection with shallow modulation of  $B_0$  increases the signal-to-noise ratio (SNR) and yields the derivative of the microwave absorption profile vs.  $B_0$ . The typically high  $Q \gg 1$  factor of the resonator further increases the SNR, as the decoupling of a resonator with higher  $Q$  leads to a larger reflected microwave power.

To ensure that only the magnetic component of the microwave is interacting with

## 2.2 Continuous-Wave Electron Paramagnetic Resonance

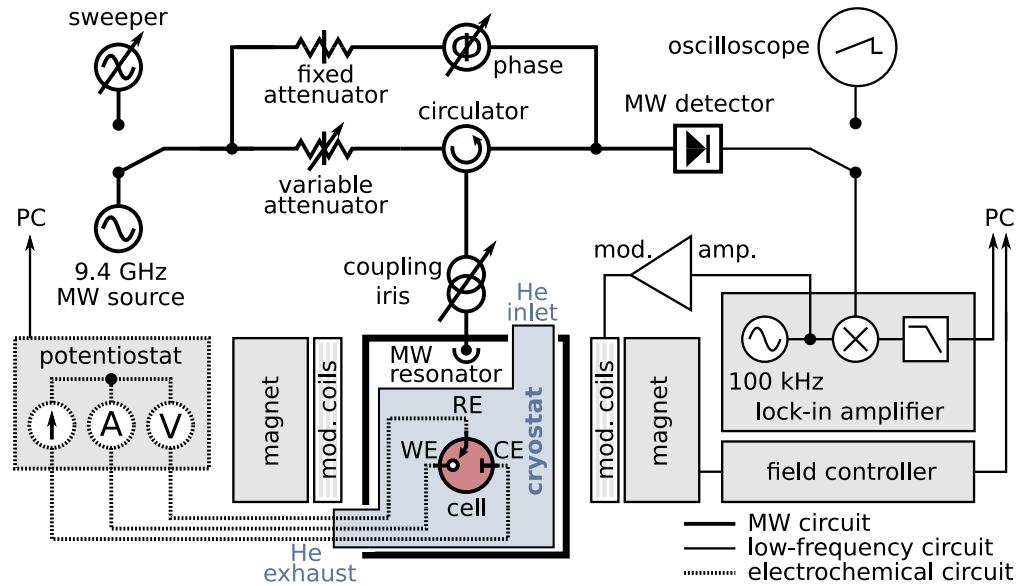


Figure 2.3: Diagram of an X band cwEPR spectrometer combined with an electrochemical setup.

the sample, a standing microwave is formed in the resonating cavity. In the center of the cavity, the magnetic component of the microwave is maximized and the electric component is quenched. When a small sample is inserted in the center of the cavity, it is mostly the magnetic component of the microwave that is interacting with it. That allows one to drive magnetic dipole transitions without heating up the sample by the electric component. For larger samples as, for example, working electrochemical cells, the separation between the electric and magnetic microwave components does not hold within the full sample volume. Furthermore, the insertion of a cell containing metal electrodes and polar electrolyte into a resonator changes the distribution of the microwave field in it and lead to a non-resonant microwave absorption.

**Line Broadening** The lines in the EPR spectra have finite widths. The lines of the liquid samples are broadened mostly by the dynamic effects (relaxation, tumbling, chemical exchange), while the lines of solid state samples are broadened by static effects (orientational disorder, unresolved hyperfine splittings, distributions in **g**, **A**, and **D** values) [107].

According to the stochastic, gaussian random modulation theory of exchange narrowing, the width of a strongly exchange narrowed EPR line (HWHM) is given by

$$\Delta B_0 \approx \frac{10}{3} \left( \frac{H_p^2}{H_e} \right) \quad (2.5)$$

and the resonance lineshape is lorentzian.  $H_p$  is the mean square dipolar field and  $H_e$  is an effective exchange field which is proportional to the mean exchange integral  $J$  [85]

## 2.3 Fundamentals of Pulsed EPR Spectroscopy

The motion of the magnetization vector  $\vec{M}(t, \vec{r})$  precessing in a static magnetic field  $B_0$  is convenient to consider in the rotating frame of reference that has its  $\vec{z}'$  axis fixed to the magnetization vector  $\vec{z}' \parallel \vec{M}$  so that the  $x'y'$  plane rotates around  $\vec{M}$  at the Larmor frequency  $\omega_L = \gamma B_0$  when viewed from the laboratory frame  $\vec{x}, \vec{y}, \vec{z}$ , where  $\gamma$  is the gyromagnetic ratio for electrons described in Section 2.1. In the rotating frame, the macroscopic magnetization stays constant as long as the spin system interacts only with the static field  $B_0$ . When the spin system is excited with a linearly polarized microwave field  $\vec{B}_1(t, \vec{r}) \perp \vec{B}_0$ , its evolution is described with the set of equations that is known as the Bloch equations (Eq. 2.8). A microwave field of frequency  $\omega_1$  and amplitude  $B_1$  propagates along  $\vec{z}'$  and it is polarized in the  $xz$  plane:  $\vec{B}_1(t, \vec{r}) = B_1 \vec{x} \cos(\omega_1 t)$ . The total magnetic field  $\vec{B} = \vec{B}_0 + \vec{B}_1$  then causes a time-dependent torque on the  $\vec{M}$  which leads to its precession - this time in the rotating frame of reference.

### 2.3.1 Bloch Equations

$$\frac{dM_x(t)}{dt} = \gamma (\vec{M}(t) \times \vec{B}(t))_x - \frac{M_x(t)}{T_2} \quad (2.6)$$

$$\frac{dM_y(t)}{dt} = \gamma (\vec{M}(t) \times \vec{B}(t))_y - \frac{M_y(t)}{T_2} \quad (2.7)$$

$$\frac{dM_z(t)}{dt} = \gamma (\vec{M}(t) \times \vec{B}(t))_z - \frac{M_z(t) - M_0}{T_1} \quad (2.8)$$

### 2.3.2 Refocused Spin Echo

### 2.3.3 Spin Relaxation Times

### 2.3.4 Spin Packets

### 2.3.5 Pulsed EPR Instrumentation

### 2.3.6 Pulse Sequences and Measurement Techniques

#### The Hahn Echo Sequence

The Hahn Echo sequence consists of two pulses, the  $\pi/2$  pulse and the  $\pi$  pulse, separated in time by  $\tau$ :  $\pi/2 - \tau - \pi - \tau - echo$ . Initially, the macroscopic magnetization of

## 2.3 Fundamentals of Pulsed EPR Spectroscopy

---

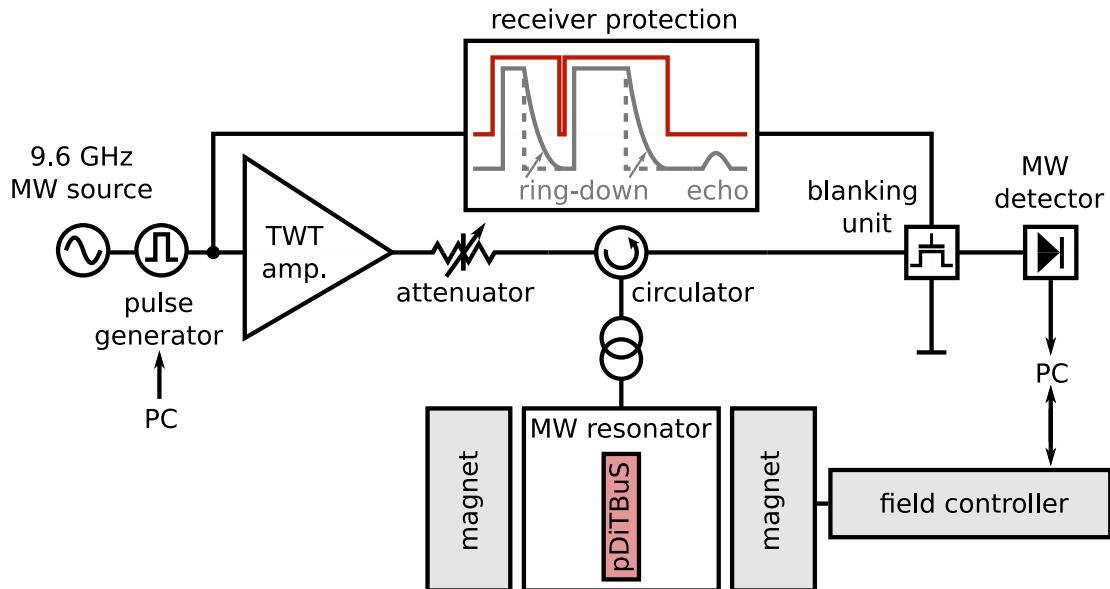


Figure 2.4: Diagram of a pulsed EPR spectrometer.

the spin system is aligned along  $\vec{B}_0$ :  $\vec{M}_0 = M_Z \vec{e}_Z$ . The  $\pi/2$  microwave pulse has such length  $t_{\pi/2}$  and amplitude  $B_1$  that, during the pulse,  $\vec{M}$  nutates to the  $xy$  plane, where it keeps precessing about  $\vec{e}_Z$  after the end of the pulse. The difference in local environments for each individual spins in the spin packet, as well as the interactions between the spins, that make up  $\vec{M}$ , leads to slightly different precession frequencies  $\omega_L^i$  of the spins. After some time  $\tau$ , the difference in the precession frequencies translates into the differences in phases so that the vector sum of the excited spins averages down to  $\vec{0}$  for sufficiently long  $\tau$ . In other words, the excited spin packet dephases with time. The dephasing due to different local spin environments can be reversible if the deviations of the precession frequencies do not depend on time, as is the case for separated electrons in an inhomogeneous solid. In such case, a  $\pi$  pulse can be applied to the spin system to flip every single spin in the dephased spin packet by 180deg in a plane containing  $\vec{e}_Z$ , so that the spins keep precessing in the  $xy$  plane, but the direction of precession is inverted for them, leading to the effect that is opposite to the initial dephasing. So a  $\tau$  after the  $\pi$  pulse excites the spin packet, the accumulated phase differences become the smallest and the packet recovers its macroscopic magnetization  $\vec{M}$  that oscillates in the  $xy$  plane with  $\langle \omega_L^i \rangle$  and can be detected. The recovered  $\vec{M}$  at  $t = \tau$  after the  $\pi$  pulse is called the refocused spin echo. The difference in  $\omega_L^i$  leads to a further dephasing of the considered spin packet and to the vanishing of  $\vec{M}$ .

**Spin Echo Decay and Phase Memory Time**

$T_2$

**Inversion Recovery and Spin-Lattice Relaxation Time**

$T_1$

# Chapter 3

## Materials and Devices

In this chapter, the redox conductive polymers are presented and a preparation of organic electrochemical half-cells suitable for electron spin resonance spectroscopy is described.

### 3.1 Organic Electrochemical Cells

#### 3.1.1 Cell Electrodes

The electrode of an ORB is made of a conductive (metallic) lead and a layer of redox active (organic) molecules adsorbed to the metal [8] with a bond that allows for electrical conductivity. The charge transfer between the conductor and the redox active molecule in the electrode can be described in terms of the molecular orbitals of the cathode molecule and the Fermi energy of the electrode [105, 118, 8]. The oxidation potential of a molecule correlates with the energy of its highest unoccupied molecular orbital (HOMO) [108, 118]. A simple organic cathode consists of a metallic lead and one redox active molecule attached to it. When the electric potential  $V$  of the metallic lead is set lower than the HOMO of the cathode molecule, and the other end of the molecule is “grounded” with the electrolyte to the anode, an electron can be transferred from the cathode molecule to the lead. The cathode molecule loses an electron, acquires a positive charge and its electronic energy lowers. The induction of a positive charge in the molecule simultaneously attracts a negative ion from the electrolyte. No charge transfer happens between the ion and the charged molecule, but the movement of the ion causes a DC current to flow through the electrochemical cell, closing the electrical circuit shown in Figure 1.1 a). In a cathode containing more than one layer of redox active molecules, together with the polymer-metal charge transfer, an intermolecular charge transfer has to take place in order to oxidize the next molecular layer.

A symmetric reaction on the anode is reducing the anode molecule and changing its

state from HOMO to LUMO. These two redox reactions describe the charging of an electrochemical cell. The opposite reaction is discharging. Upon discharging, the cathode is reduced and the anode is oxidized. Excessive charging and discharging may lead to an irreversible chemical reaction in the electrodes and the reactions to the electrolyte, that is undesirable, so the  $V_{OC}$  of the cell has to be observed during its operation.

### 3.1.2 Three-Electrode Cell

It is possible to study the redox reaction only at one electrode of the cell, e.g. the cathode, using a chemically inert second electrode. A cell with only one redox active electrode is called a half-cell. The studied electrode is called the working electrode (WE). The opposite electrode, called the reference electrode (RE), is made of a known material that maintains a constant composition and has a reproducible potential difference at the electrode-electrolyte interface called the standard potential. Any change in the potential difference between the WE and RE of the half-cell setup is therefore attributed to the processes in the WE only [4].

However, when a half-cell is being charged and the current is flowing through the RE, a chemical reaction can take place at the RE, changing its composition and the standard potential. The chemical reaction on the RE changes the parameters of the half-cell and shifts the observed potential difference unpredictably [4, 105]. For this reason, a three-electrode half-cell shown in Figure 1.1 c) is used for characterizing battery electrodes that are designed for significant charging currents.

In the three-electrode half-cell, the charging current is applied between the WE and a chemically inert counter electrode (CE). The oxidation of the WE is accompanied by the formation of a double layer of the electrolyte molecules at the surface of the CE. The electric potential of the WE is measured as a potential difference between the WE and the calibrated RE, inserted in the electrolyte close to the CE. The potential difference between WE and RE is measured with a high impedance voltmeter that ensures minimal charge flow through the RE. That is, RE does not undergo a chemical reaction during the charging of WE, its chemical environment does not change during the experiment and the measured potential difference between WE and RE corresponds to the potential of the WE. Due to the finite dimensions of the electrodes and the finite thickness of the double layer around the CE, the RE cannot be inserted at the position of the CE, so the measured potential has a constant offset as the electrolyte between the points where WE, RE and CE are inserted, acts as a voltage divider [4].

### 3.1 Organic Electrochemical Cells

---

#### 3.1.3 Reference Electrode

The potential  $E$  of the cell electrode is measured with respect to a calibrated, inert RE. The potential of the RE is chosen as  $E = 0$ . A general RE is the standard hydrogen electrode ( $\text{Pt}/\text{H}_2/\text{H}^+$ ), or SHE. The main difference between the various RE is their operation range and a constant potential shift with respect to the SHE depending on the workfunction of the RE material. The couple  $\text{Ag}/\text{AgNO}_3$  is commonly used in electrochemistry [4]. It exhibits a shift of 0.7991 V vs. SHE. For the couple  $\text{Ag}/\text{AgCl}$ , the shift is 0.2223 V against SHE [4, 105], although these values can only be used if the electrode configuration is strictly equivalent to the one used for determining them. In other cases, like in the case with a thin electrolyte layer in the modified sample tube, the exact shifts of the RE might differ [105].

#### 3.1.4 Electrolyte

Electrolyte is an ionic conductor [4] - an electrically conductive solution of oppositely charged ions that are typically products of dissociation of the corresponding salts. The dissociation of a salt in a solvent implies that the solvent has high enough dielectric constant  $\epsilon$  to polarize the salt molecule and to separate it into a positive ion (cation) and a negative ion (anion) by creating solvation shells around them. High mobility of the electrolyte ions is needed for the efficient ion diffusion into the battery electrodes, so that the redox reaction can take place along the entire surface of the electrode material that is soaked into the electrolyte. The ionic mobility also influences the Ohmic losses and polarization of electric double layers, governing, together with the electronic properties of the electrodes, the power density of a battery [77].

#### Liquid Electrolyte

Tetraethylammonium tetrofluoroborate ( $\text{Et}_4\text{NBF}_4$ , Figure 3.1 a) is a crystalline salt that dissociates into a  $\text{Et}_4\text{N}^-$  cation and a  $\text{BF}_4^-$  anion in polar solvents such as Acetonitrile ( $\text{CH}_3\text{CN}$ , Figure 3.1,b) and Propylene Carbonate ( $\text{C}_4\text{H}_6\text{O}_3$ , Figure 3.1,c).  $\text{Et}_4\text{NBF}_4$  is a small molecule with a relatively high dissociation energy, so the solvents have high dielectric constants ( $\epsilon \approx 40$  for Acetonitrile and  $\epsilon \approx 64$  for Propylene Carbonate). Propylene Carbonate has higher density than Acetonitrile, has higher viscosity and is less volatile. A 100 mM solution of  $\text{Et}_4\text{NBF}_4$  in Acetonitrile or in Propylene Carbonate ensures sufficient ionic transport for the organic electrochemical cells described later in this section.

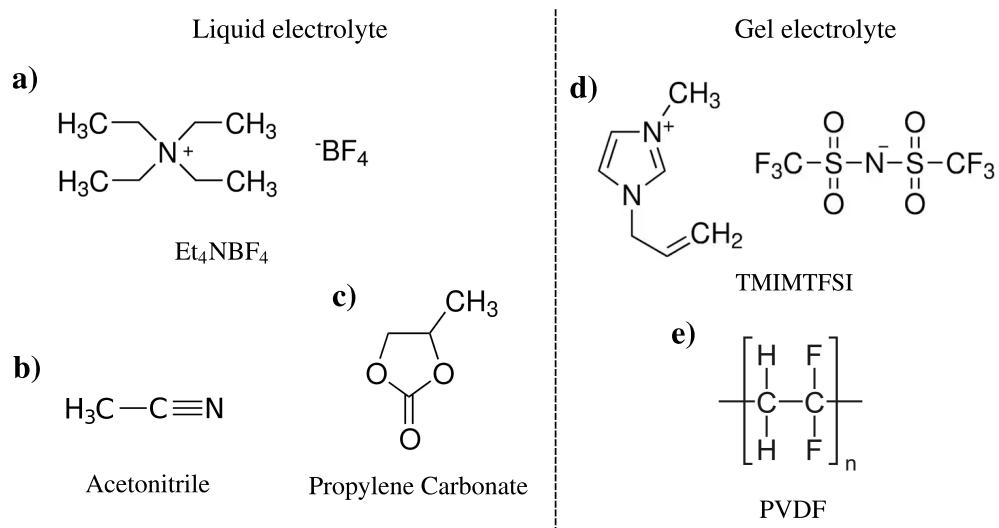


Figure 3.1: Ionic salt ( $\text{Et}_4\text{NBF}_4$ , a) and the corresponding solvents (Acetonitrile (b) and Propylene Carbonate (c)) for liquid electrolytes. Ionic liquid (TMIMTFSI, d)) and polymer matrix (PVDF, e)) for the gel electrolyte.

### Polymer-based Gel Electrolyte

The use of ionic liquids and the suitable polymer matrix allows for fabrication solid-state electrolytes that are used for making organic electrochemical neurons [37] and solid-state Li batteries [90]. PVDF (Figure 3.1 e) was used as a polymer matrix. TMIMTFSI (Figure 3.1 d) was the ionic liquid. The polymer grains were dissolved in Chloroform at  $80^\circ\text{C}$  and the ionic liquid was mixed in at a ratio 1 : 4 : 20 (polymer : ionic liquid : solvent). The polymer electrolyte was used to manufacture an all-polymer organic radical battery described later in this section.

### 3.1.5 Characteristics of Rechargeable Batteries

Depending on the redox potentials of the used electrodes, the output voltage of a cell ( $V_{OC}$ ) ranges between 0 and 5 V [46]. Most applications require higher voltages, so multiple cells are connected in series to form a battery.

**Energy and power density, C-rate and State Of Charge** The capacity of a cell  $C$  is measured in mAh. It is the maximal electric charge that can be stored in it. Different electrode materials can store different amounts of charge depending on their chemical composition and microscopic structure. Due to the unavoidable losses of charge caused by the finite shunting resistance between the cell electrodes, one distinguishes between the charging capacity and the discharging capacity. The capacity of 1 g of an electro-

### 3.1 Organic Electrochemical Cells

---

active material is its gravimetric capacity, it is measured in  $\text{mA}\text{hg}^{-1}$ . The volumetric capacity is the corresponding value with respect to the volume of the material that is measured in  $\text{mA}\text{hl}^{-1}$ . The energy stored in a cell is a product of its capacity and its voltage. The ratio of the stored energy to the volume of a cell is its energy density. The energy density of a cell depends on the capacity of the electrodes and the potential difference between the electrodes [67]. The fraction of charge left in a cell with respect to the full charge that can be stored in that cell in percent is called the state of charge or SoC. The SoC of a fully charged battery is 100%.

A battery is typically charged with a constant DC current. The magnitude of the charging (or discharging) current relative to the battery capacity determines the rate at which a battery is charged (or discharged). The charging rate, or C-rate is the charge or discharge current in Amps divided by the battery capacity in Ampere-hours. For a modern rechargeable Li-polymer battery a safe charging C-rate cannot exceed 1 C [129]. That means, the safe charging time for a Li-polymer battery cannot be shorter than 1 hour. The discharge rate of the same battery, however, can be as high as 100 C that corresponds to a discharge current larger than the charging current by a factor of 100. The power that a battery can deliver depends on its maximal discharging C rate and equals to the product of its short-circuit current and its voltage. The organic radical batteries can have charging and discharging C rates close to 3000 C and gravimetric discharge capacities upto  $111 \text{ mA}\text{hg}^{-1}$  [114, 29, 128, 115, 58, 110]. While the capacities of the organic electrode materials are smaller than for the Li metal electrodes ( $3850 \text{ mA}\text{hg}^{-1}$ ), the organic electrode materials allow for much higher C rates that already exceed the C rate of the conventional inorganic cells by orders of magnitude [19].

**State Of Health** The capacity of a battery may decrease upon repeated charge-discharge cycling, especially at high C rates [35, 86], over-discharge [71] and extreme environmental conditions [129]. The ratio of the maximum battery charge to its rated as-manufactured capacity expressed in percent is called state of health (SoH). SoH is a measure of the remaining life time of a battery. The decrease in SoH indicates the intensified irreversible processes that take place in an electrochemical cell, such as a physical damage [31], degradation of the electrode material [71, 57], side reactions at the electrode-electrolyte interface [110], or decomposition of the electrolyte [25]. A damaged cell, especially that can store significant amount of charge, represents a major hazard [71]. Accurate measurements of SoH can prevent hazardous battery malfunctions such as explosions.

## 3.2 Electrochemical Instrumentation

### 3.2.1 Cyclic Voltammogram

The complete electrochemical behavior of a redox active molecular system can be obtained with a series of transient current responses to potentials, applied step-wise to the electrochemical cell containing the system. However, for a basic electrochemical characterization, a current response during a linearly swept potential is sufficient [4]. During the linear-potential-sweep chronoamperometry, or linear sweep voltammetry, the potential  $E$  applied to the electrochemical cell is swept in a linear manner between the values  $E_{min}$  and  $E_{max}$ , upwards and downwards, with a rate  $v$  ( $\text{mVs}^{-1}$ ):  $E(t) = E_0 \pm vt$ . During the sweep, the current is recorded as a function of the applied potential as shown in Figure 3.2 b).

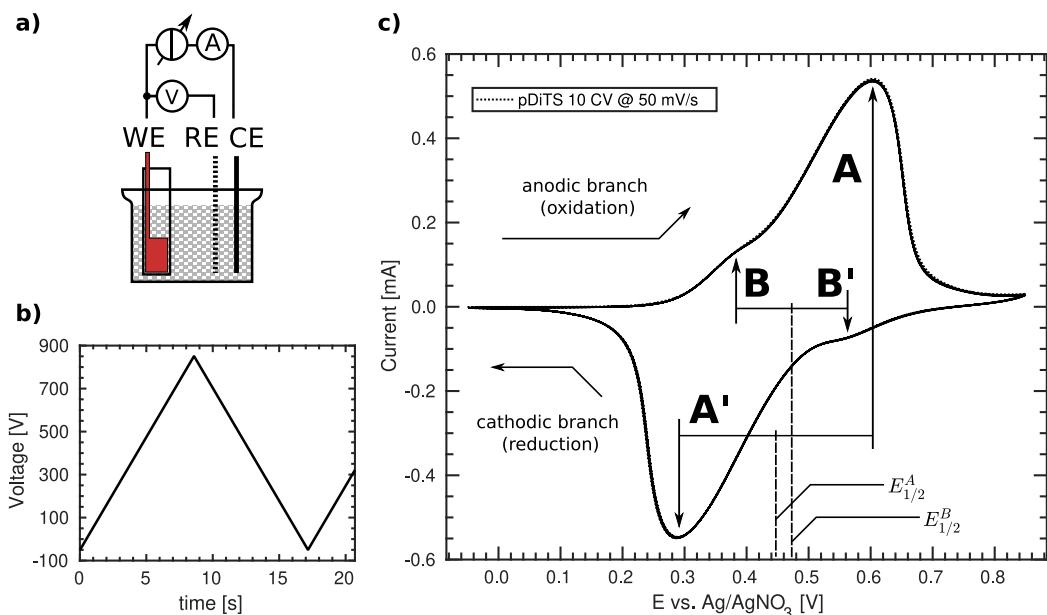


Figure 3.2: a): Electrochemical setup for measuring a cyclic voltammogram. b): Linear voltage sweep at a  $50 \text{ mVs}^{-1}$  rate. c) Cyclic voltammogram of an electro-active polymer cathode film. Oxidation and reduction of the charge-bearing fragments of the film corresponds to the A and A' redox peaks, respectively. Oxidation and reduction of the conductive polymer backbone of the film corresponds to peaks B and B'. The standard oxidation potential of the charge-bearing fragments,  $E_{1/2}^A$ , lies close to the standard oxidation potential of the backbone,  $E_{1/2}^B$ .

The resulting plot  $i(E)$  is the cyclic voltammogram (CV). The upward potential sweep corresponds to the anodic, or charging branch of the CV and the downward sweep

## 3.2 Electrochemical Instrumentation

---

corresponds to the cathodic, or discharge branch. A CV of a three-electrode electrochemical cell with an electro-active polymer film on the WE is shown in Figure 3.2 c). When  $E$  reaches the oxidation potential of the working electrode, charge transfer happens and the current through the cell increases. This corresponds to the oxidation peak in the anodic branch. The width of the peak is determined by the temperature of the cell and the number of electrons  $n$  transferred in a single oxidation reaction ( $n = 2$  for poly-di-TEMPO-Salen, the redox conductive polymer described in Section 3.3). The negative current peak in the cathodic branch of the CV curve corresponds to the reduction of the WE. The difference between the potentials of the oxidation and reduction peaks arises because of the finite electric capacity of the electro-active film and a finite voltage sweep rate. For higher sweep rates the difference in peak potentials is higher, as the scanning time becomes comparable to the RC time constant of the cell.

The area under the anodic branch can be used to calculate the charge that was transferred from the WE upon its reduction from the fully oxidized state. The applied voltage is swept at a known rate, so the anodic branch  $i(E)$  can be plotted vs. time  $i(t)$ , hence the transferred charge equals to the integral under the curve:  $q = \int_{E_{\min}}^{E_{\max}} i(t) dt$ . By knowing the  $q$  and considering the corresponding chemical reaction (how many electrons are transferred for one molecule) one gets the amount of substance in the electrode  $v = qF$  [mol] and the number of electrochemically active molecules  $N_{echem} = vN_A$  with  $F \approx 9.46853 \times 10^4 \text{ C} \times \text{mol}^{-1}$  for the Faraday constant and  $N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$  for the Avogadro constant [78]. Given the molecular weight  $M$ , the total mass of the electrochemically active molecules of the film can be calculated. Together with the information on the density of the film, its dimensions can be estimated. However, as demonstrated in Section 4.3.2 and in Refs. [115, 57, 58], the number of electrochemically active molecules in a polymer cathode film can be much lower than the total number of molecules in it.

### 3.2.2 Charge-Discharge Cycling

A constant-current characterization technique called galvanostatic potentiometry [4] can be used in combination with the cyclic voltammetry to study the redox behavior of the electrochemical system quantitatively. The setup for galvanostatic charge-discharge cycling is shown in Figure 3.3 a). The cell is excited with a DC current as shown in Figure 3.3 b) and the potential of the cell is measured as a function of time, as shown in Figure 3.3 c). Upon positive (charging) current, the working electrode of the cell is oxidized. The voltage required to provide the charging current gradually increases, resulting a galvanostatic charging curve shown in Figure 3.3 c). The shape of the charging curve can be approximated by considering two major effects: the Faradic current and the displacement current [4]. The Faradic current is caused by the oxidation of

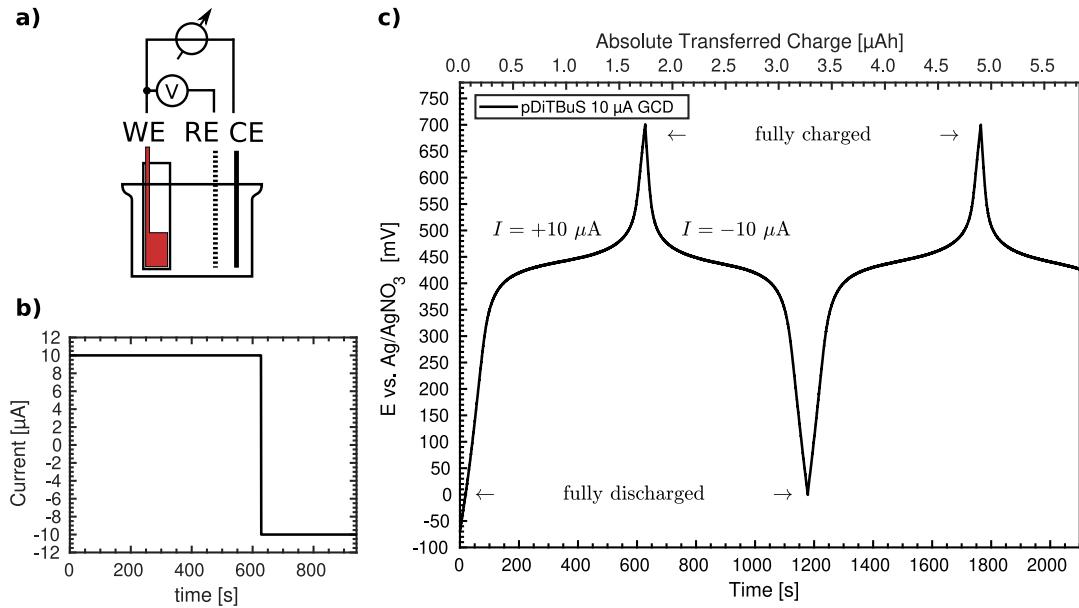


Figure 3.3: a): Electrochemical setup for galvanostatic charge-discharge cycling. b):  $\pm 10 \mu\text{A}$  DC current applied to record the cycling. c) Chronopotentiometry of an eelctrochemical cell containing electro-active polymer film cathode. Full charging is recognized by the steep increase of the charging curve after passing the plateau.

the redox active species in the WE. It defines the plateau regions in the middle of the charging and discharging curves. The displacement current is the result of the charging of a double layer around the WE and CE. It explains the capacitor-like response of the charging and discharging curves before and after the plateau region [4]. In this regard the electrochemical cell with only one redox active electrode can be treated as a pseudocapacitor [38, 115]. When all redox active species of the WE are oxidized, the voltage required for providing the charging current steeply increases, that is seen in the end of the charging curves in Figure 3.3 c) and 3.14. Eventually, upon charging, the potential of the cell grows beyond the oxidation peak of the WE, according to the cyclic voltammogram (Figure 3.2). Then the charging is stopped and the transferred charge is calculated from the charging time. The same strategy is applied for the discharging curve to determine the discharging capacity of the cell. The reproducibility of the charge-discharge curve indicates the stability of the electrochemical cell. SoH of the cell can be estimated by observing the decrease in the period of the charge-discharge curve.

A cell can also be charged by applying a constant voltage to it and by letting the applied current to change upon charging, this mode is called potentiostatic chronoamperometry. A positive voltage applied to a discharged cell will initially result in a large

### 3.3 Organic Electrode Materials

---

current. Upon potentiostatic charging, the charging current decreases with time, as most of the molecules in the electrode are oxidized and the cell voltage approaches the applied voltage.

## 3.3 Organic Electrode Materials

ORB based on redox polymers containing stable radicals [76] have been shown to compete with or even outperform conventional Li based batteries in terms of power densities [109] with the additional benefit of being free from rare precursors, inheriting mechanical properties of plastics and electrical properties of semiconductors [29, 11, 33]. Advanced molecular design techniques allow for tuning of the electrochemical properties of the redox polymers [47], that brings in a rich variety of organic energy storage materials [120, 115, 48] and creates a large room for their optimization.

### 3.3.1 Semiconducting Polymers

The key for polymer conductivity is the  $\pi$ -conjugated network, a system of overlapping  $\pi$  orbitals of carbon in a chain of alternating single and double carbon-carbon bonds that allows for charge delocalization along the polymer backbone [39, 61, 12]. An example of a  $\pi$  conjugated network is polyacetylene shown in Figure 3.5b. Polyacetylene exhibits a band structure in the electron energy levels (between its band-like  $\pi$  and  $\pi^*$  orbitals) and represents a molecular semiconductor [39].

A simple organic molecule, ethylene, shown in Figure 3.4, contains two carbon atoms and four hydrogens. Each carbon atom has six electrons. The four unpaired electrons of carbon - one at the  $2s$  orbital and three at the  $2p$  orbital - interact to form two  $sp^2$ -hybridized orbitals and one unhybridized  $p_z$  orbital, as shown in Figure 3.5a.

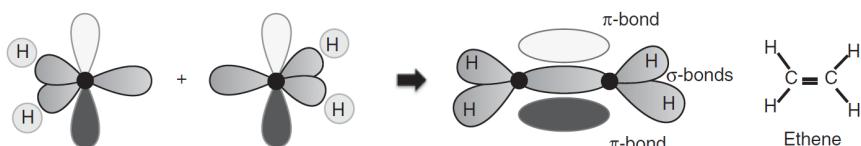
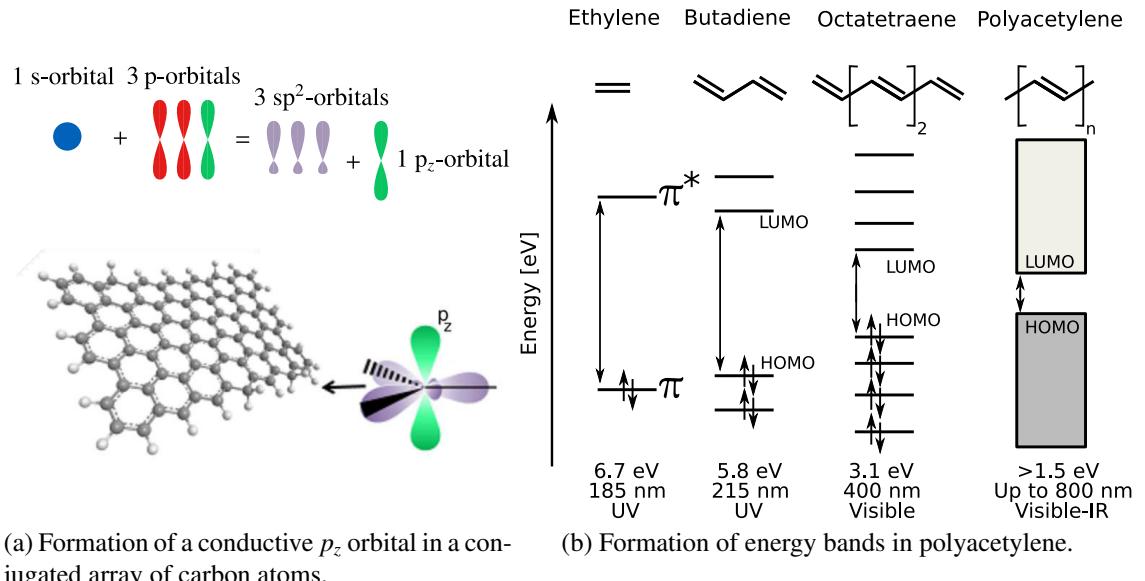


Figure 3.4: Ethylene molecule with  $\sigma$  and  $\pi$  bonds [61].

The hybridized  $sp^2$  orbitals form  $\sigma$  bonds between adjacent carbon atoms. The  $\sigma$  bonds keep the carbon atoms together in the molecule. The remaining  $p_z$  orbitals interact with each other and form a  $\pi$  bond so that  $p_z$  electrons are shared between the carbon atoms. The interaction between  $p_z$  orbitals results in two molecular orbitals, the



(a) Formation of a conductive  $p_z$  orbital in a conjugated array of carbon atoms.

(b) Formation of energy bands in polyacetylene.

Figure 3.5: Formation of a band gap in a conjugated polymer. Figures adapted from [84].

bonding ( $\pi$ ) and the antibonding ( $\pi^*$ ) orbitals [18]. A  $\pi$  orbital is described by a symmetric wavefunction and  $\pi^*$  orbital is described by an antisymmetric wavefunction. A  $\pi$  orbital has a lower energy than  $\pi^*$ , as shown in Figure 3.5b. The symmetric  $\pi$  orbital is more energetically favorable, so the electrons occupy it at the equilibrium. Because of that, the  $\pi$  orbital is called the Highest Occupied Molecular Orbital (HOMO) and  $\pi^*$  is the Lowest Unoccupied Molecular Orbital (LUMO). There is a forbidden energy zone between HOMO and LUMO which is equivalent to a bandgap of a semiconductor.

In a longer molecule, the  $\pi/\pi^*$  states are delocalized over many carbon atoms. This is known as conjugation and the number of conjugated atoms determine the conjugation length. As conjugation length increases, the HOMO and LUMO levels for each pair of carbon atoms in the molecule become slightly different. In a polymer with a very large conjugation length, many energy levels around HOMO and LUMO overlap which forms energy bands, as shown in Figure 3.5 [61, 84]. At a finite temperature, there is a non-zero population of electrons above the LUMO level which allows them to move freely along the chain of overlapping  $p_z$  orbitals and makes conjugated polymers conductive [39].

Even though conjugated polymers have band-like energy structure and a bandgap, their charge-transport properties are different from crystalline semiconductors. Real polymer chains have finite lengths that brings disorder to an organic semiconductor

### 3.3 Organic Electrode Materials

(Figure 3.6 a). The disorder causes localization of electronic wave functions, that is known as charge carrier trapping, and hinders the electrical transport in semiconductors [124, 73], so when an external electric field is applied, a charge needs additional energy to hop from one localized state to another for electric current to flow (Figure 3.6 b). In Figure 3.6 c) it is shown how a charge moves through a disordered organic semiconductor choosing the optimal path in both energy and space domains. This mode of charge transport is referred to as the hopping transport [111].

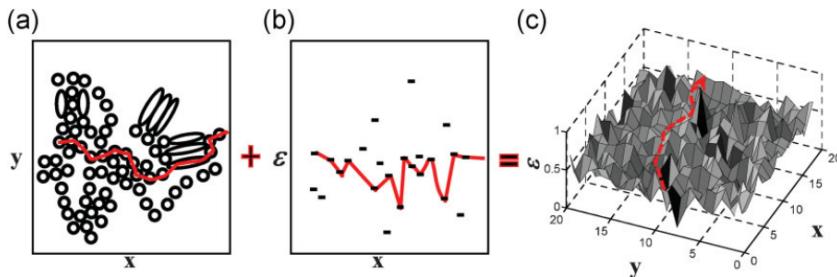


Figure 3.6: Transport of charge through localized energy sites distributed both in space (a) and in energy (b). The line describes a possible path that a charge carrier takes while hopping through a conjugated polymer under an external electric field. The trajectory is affected by the energy distribution (c). The picture is taken from Ref. [111].

Redox conductive polymers (RCP), besides being conductive, are able to store a charge. Typically, a RCP has a large concentration of charge bearing fragments that are interconnected by the polymer backbone [12]. Storage of charge implies that the stored charge carriers are localized and cannot freely move within the polymer, unless the appropriate electric field is applied to release them to the conjugated network. In this regard, the charge bearing fragments of an RCP can be viewed as charge carrier traps. The high concentration of the charge carrier traps in a conductive polymer makes neither the hopping-charge transport model [99], nor the band-like transport model [61] applicable to describe the electric transport in these materials, so alternative models were developed.

#### 3.3.2 TEMPO

TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) shown in Figure 3.7 a) is a small molecule and a stable radical that can undergo a fast and reversible redox reaction between  $\text{TEMPO}^\bullet$  and  $\text{TEMPO}^+$  [116], with an electron self-exchange rate constant of  $k_{ex} \approx 10^{6-8} \text{ M}^{-1} \text{ s}^{-1}$  [14]. TEMPO is an inexpensive organic compound [115] produced from acetone with liquid ammonia, hydrazine and peroxide [12]. TEMPO radicals are widely used as spin labels in the studies of biological systems with electron spin resonance [9], because the unpaired electron of  $\text{TEMPO}^\bullet$  has a well defined spectral signature that

changes when the local environment of a TEMPO fragment changes. TEMPOL is a TEMPO with an OH group. It is soluble in many organic solvents and forms crystals. Solutions of TEMPOL with various concentrations can be used for the reference spectroscopic measurements, as by varying the concentration the strength of inter-spin interactions between the neighboring radicals can be adjusted.

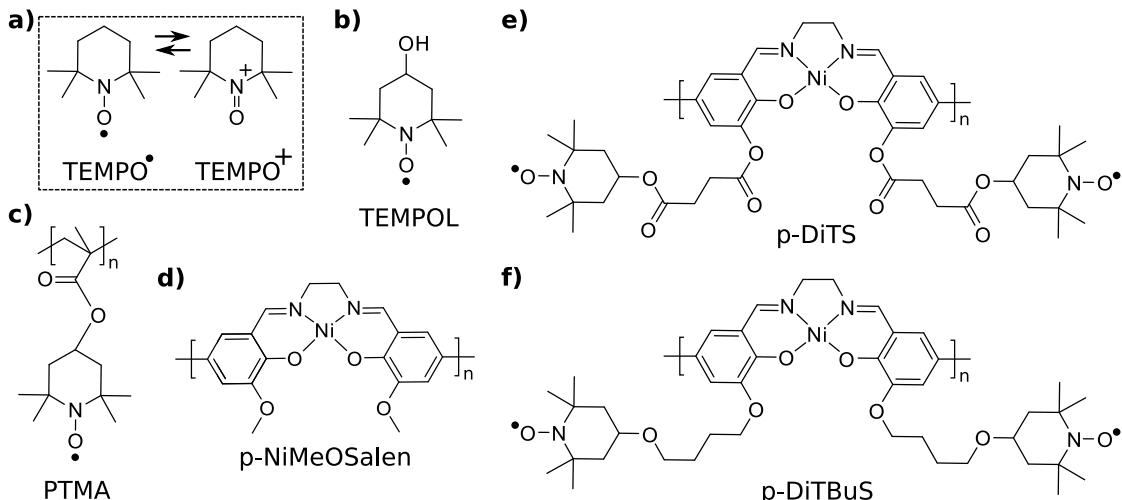


Figure 3.7: Chemical structures of the molecular fragments and polymers that were used for making a battery cathode containing stable nitroxide radicals.

Redox conductive conjugated polymers containing TEMPO redox groups, as pDiTBuS (poly-di-TEMPO-Butyl-Salen) shown in Figure 3.9, demonstrate particularly promising energy and power densities [114]. The pDiTBuS was designed as a cathode material: it is oxidized when the electrochemical cell containing this material is charged. A film of pDiTBuS comprises a high concentration of redox active stable nitroxyl radicals attached to a conjugated polymer backbone that interconnects them as a molecular wire. Such system can be viewed as a highly disordered molecular hole-transporting semiconductor (the poly-NiSalen backbone) that contains a large amount of hole traps (TEMPO groups) attached to it with butyl linkers. When the film is reduced (discharged), the TEMPO groups are in the radical state and act as unfilled traps. Upon oxidation (charging), the TEMPO fragments lose an unpaired electron and acquire a positive charge, so the traps are being filled with holes. The reversible redox reaction in the pDiTBuS film is demonstrated in a cyclic voltammogram shown in Figure 3.2, c) and in the equal charging and discharging capacity of the film in Figure 3.14, c).

While active electrode materials with nitroxide radicals as redox-active groups are ideally suited for organic radical batteries (ORBs) that exhibit high power densities, the broad application of most nitroxide-based materials is limited by their moderate electrical properties. A promising route towards overcoming the conductivity problem is the use of polymers that combine radical-containing moieties and a conductive backbone.

### 3.3 Organic Electrode Materials

---

This strategy was successfully followed in a number of studies focusing on different polymers [88, 3, 52, 122, 2, 100]. The standard redox potential of the NiSalen molecular backbone ( $E_{1/2}^B$  in the middle of the peaks B and B' in Figure 3.2) lay close to the standard redox potential of the attached nitroxide charge-bearing fragments ( $E_{1/2}^A$  in the middle of the peaks A and A' in Figure 3.2) - that ensures an efficient charge transport between the charge-bearing fragments and the conductive backbone and allows for very high charge and discharge rates up to 3000 C [114, 57].

#### 3.3.3 PTMA

A simple organic radical polymer containing TEMPO is poly-TEMPO-methacrylate) (PTMA, Figure 3.7 c). The polymer backbone of PTMA consists of single C-C bonds and therefore is not conductive, so the transport of charge in a PTMA film has to be mediated by adding conductive mesh such as activated carbon. When mixed with conductive carbon additive, PTMA has become a standard cathode material for ORBs and Li-ORBs, providing a discharge cell voltage of  $V_{OC} = 3.5$  V (with a Li anode) and a theoretical discharge capacity of  $C_{theo} = 111$  mAh/g [15]. PTMA is soluble in acetonitrile (AN), chloroform (CF), tetrahydrofuran and dichlormethane. It is claimed to be insoluble in toluene, ethers, carbonates, and alcohols, however it becomes gel-like with some of these solvents [105].

#### 3.3.4 NiSalen

The molecular backbone of a redox conductive polymer has to conduct electric charge. A NiSalen molecule shown in Figure 3.7 d) is a Schiff complex of Ni that has a conjugated path through it. p-NiMeoSalen is polymerized NiSalen with two methoxy groups, that forms the conductive backbone of the corresponding RCPs in e) and f). The pNiSalen backbone is redox active and can store up to 2 positive charges per monomer unit [20]. The conductivity of p-NiSalen depends on its oxidation state. The oxidized polymer has higher conductivity due to a higher concentration of holes [20]. Upon oxidation of a polymeric NiSalen, the formation of positive polarons and bipolarons was observed in it with UV-Vis and EPR spectroscopy [20], that suggests p-NiSalen is a p-type molecular semiconductor.

#### 3.3.5 Poly-Di-TEMPO-Salens

Redox conductive conjugated polymers containing TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) redox groups, as pDiTS [114, 57] (poly-Di-Tempo-Salen) and pDiTBuS [58] (poly-di-TEMPO-Butyl-Salen) shown in Figure 3.7 e) and f), demonstrate particularly promising energy and power densities with charging rates upto 3000 C and gravimetric

capacity up to  $91.5 \text{ mAh g}^{-1}$  for pDiTS [114] and up to  $75 \text{ mAh g}^{-1}$  for pDiTBuS [58]. pDiTS and pDiTBuS have similar molecular structures, except for pDiTBuS has no oxygens in the linkers that connect the backbone to the TEMPO fragments, which has led to its higher electrochemical stability and a more efficient electro-polymerization, that allows for growing thicker films. pDiTS is a charge storage material that consists of TEMPO redox active molecular fragments [115, 49, 36] interconnected by a redox conductive conjugated NiSalen backbone [114, 20]. DiTS and DiTBuS monomers were synthesized in the Levin group at the Saint-Petersburg State University.

pDiTS was designed as a cathode material: it is oxidized when the electrochemical cell containing this material is charged. A film of pDiTBuS comprises a high concentration of redox active stable nitroxyl radicals attached to a conjugated polymer backbone that interconnects them as a molecular wire. Such system may be viewed as a highly disordered molecular hole-transporting semiconductor (the poly-NiSalen backbone) that contains a large amount of hole traps (TEMPO groups) attached to it with butyl linkers. When the film is reduced (discharged), the TEMPO groups are in the radical state and act as unfilled traps. Upon oxidation (charging), the TEMPO fragments lose an unpaired electron and acquire a positive charge, so the traps are being filled with holes [58].

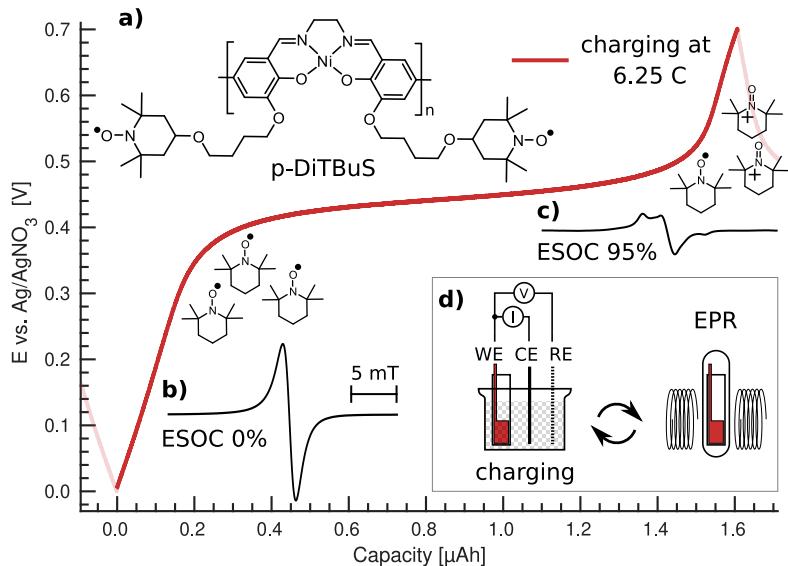


Figure 3.8: Galvanostatic charge-discharge curve for a pDiTBuS cathode film at  $10 \mu\text{A}$  ( $6.25 \text{ C}$ ), chemical structure of pDiTBuS (a), normalized cwEPR spectral signatures for reduced (b) and oxidized (c) states. Scheme of the ex-situ EPR measurement on the pDiTBuS half cell (d).

### 3.3 Organic Electrode Materials

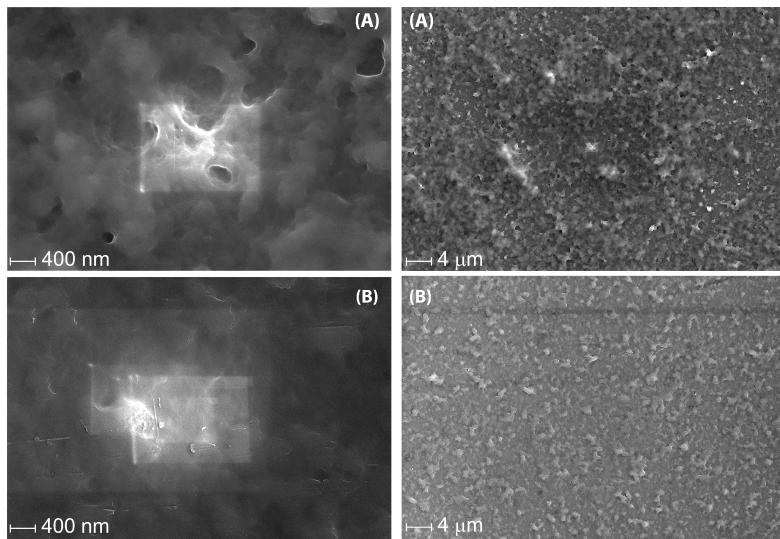


Figure 3.9: Scanning electron microscope images of a pDiTS film in a reduced (a) and oxidized (b) states, image adapted from Ref. [114].

#### 3.3.6 Electro-polymerization of TEMPO-Salens

The process of polymerization is connecting multiple monomer units of one sort to a continuous molecular chain. A polymerization of redox active molecules, such as NiSalen monomer fragments, can be done electrochemically with the setup shown in Figure 3.11. A three-electrode cell is made with a 10 mM solution of NiSalen in the electrolyte. By applying a positive voltage between the WE (Au) and the CE (Pt), NiSalen molecules are adsorbed to the surface of the WE and oxidized. Oxidation of NiSalen leads to a formation of a positive radical in the ring of the NiSalen that can be seen as the opening of the ring, as shown in the diagram in Figure 3.11. The oxidized, open ring attracts the next NiSalen molecule from the solution, then the positive radical is transferred from the ring to the attracted molecule through the conjugated network and the two molecules form a bond [56]. The reaction repeats until the conductivity of the film allows for efficient transfer of the positive radical to its outer surface. Because of charge storing ability of pNiSalen, the film growing from the oxidized monomers has to be periodically discharged to withdraw the positive charges that repel the oxidized monomers and do not allow them to attach to the film. So a pNiSalen film is grown on the WE surface [1, ?].

The electrochemical polymerization of a TEMPO-Salen is done in the same way as for pNiSalen. The electrical screening effect in TEMPO-Salens is much stronger, because the oxidation potential of the charge-bearing TEMPO radicals is close to that of NiSalen and the TEMPO radicals in the film oxidize when the film is oxidized. The

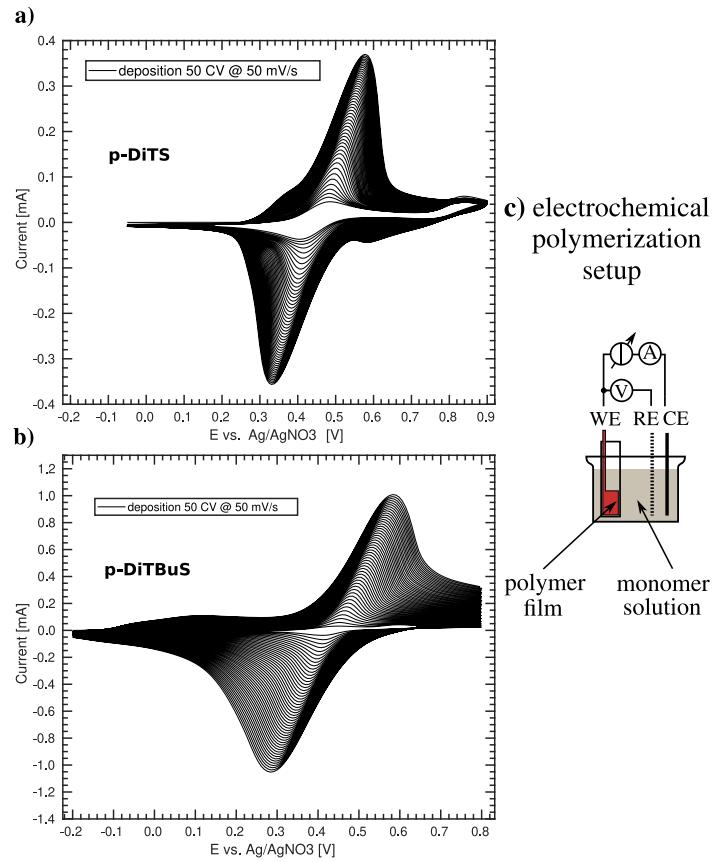


Figure 3.10: Deposition of TEMPO-Salen films with cyclic electrochemical polymerization from 1 mM monomer solutions in the 10 mM Et<sub>4</sub>NBF<sub>4</sub> electrolyte at 50 mVs<sup>-1</sup> and 50 deposition cycles. a): pDiTS, b): pDiTBuS. c) setup for electrochemical polymerization

oxidized TEMPO radicals form a strong Coulombic “shield” that repels the TEMPO-Salen monomer fragments in the solution [114]. To discharge the TEMPO fragments, the growing film has to be periodically discharged, so a cycling voltage is applied to perform a cyclic polymerization of pDiTS and pDiTBuS films [114, 58].

### 3.4 TEMPO-Salen Films for EPR Spectroscopic Measurements

The monomeric DiTS is electropolymerized to p-DiTS and simultaneously deposited onto the 12 mm<sup>2</sup> on-substrate Au WE. The setup for deposition is shown in Fig. 3.9c.

### 3.4 TEMPO-Salen Films for EPR Spectroscopic Measurements

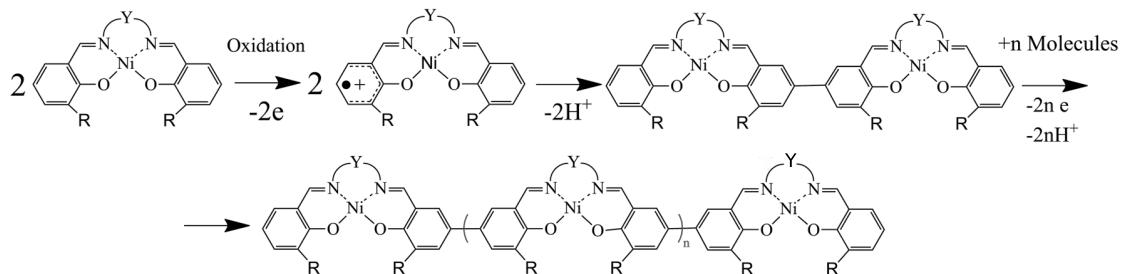


Figure 3.11: A scheme of a two-step cyclic electropolymerization of NiSalen containing electrochemically inactive side groups (R). First, two monomers are oxidized upon application of a positive potential to the cell containing the monomer solution, that induces a cation (hole) in their phenyl rings. The oxidized monomers create a bond by sharing their cations. When the potential is ramped down, the holes are withdrawn from the radicals and they remain connecting by forming a C-C bond instead of closing the bond in their rings.

The CE for the deposition is a coiled Pt wire. Both electrodes are submerged in the electrolyte (0.1 M Et<sub>4</sub>NBF<sub>4</sub> in Acetonitrile (ACN)) containing 1 mM monomeric DiTS. The chemically inert RE for the deposition is a Ag wire in a solution of 10 mM AgNO<sub>3</sub> and 0.1 M tetrabutylammonium tetrafluoroborate in ACN, placed inside a glass tube with a porous CoralPor™ tip. A cyclically changing potential between -50 mV and +900 mV is applied between the CE and RE for 8 to 200 deposition cycles, at a rate up to 50 mV s<sup>-1</sup>. The deposition process is monitored by recording a cyclic voltammogram (CV). This results in the deposition of a thin film of p-DiTS on the on-substrate WE. In studies involving NiMeOSalen films, 10 to 20 deposition cycles led to considerably thicker films ( $\approx 1 \mu\text{m}$ ). p-DiTS has lower conductivity than p-NiMeOSalen [?], therefore the growth of p-DiTS films is hindered after fewer deposition cycles as compared to p-NiMeOSalen. The thicknesses ( $t$ ) of all films used in this study are listed in Section 6 (ESI†). A few representative thicknesses are: for p-DiTS, 8 deposition cycles result in  $t \approx 40 \text{ nm}$ , and 200 deposition cycles result in  $t \approx 500 \text{ nm}$  films; for p-NiMeOSalen, 15 deposition cycles result in  $t \approx 900 \text{ nm}$ .

The most electrochemically stable and pure films came from polymerized systems which were rinsed in ACN followed by propylene carbonate (PC), then rinsing the charged film (900 mV with respect to the Ag/AgNO<sub>3</sub> RE) in a beaker-based cell, and lastly potential-cycling it in the electrolyte. The effects of rinsing and cycling of the polymer films in solvents/electrolyte are described in Section ??.

There are some differences in the CV recorded in a beaker (setup schematic in Fig. 3.9c) as compared to the CV measured in the modified tube (setup schematic in Fig. 3.9d). As seen in Fig. 3.9e, the CV measured in the modified tube (blue curve) shows slightly shifted and broader oxidation and reduction peaks as compared to the in-beaker measurements (solid-brown and crossed-black curves) for the same p-

DiTS film. The shift is mainly due to the use of different reference electrodes, while we attribute the broader peaks to the smaller electrolyte volume used in the modified tube. The electrolyte volume seen by the on-substrate films in the modified tube is significantly smaller than the total electrolyte volume of  $60 - 70 \mu\text{L}$ , as only 0.35 mm of space remains between the inner width of the flattened modified tube and the substrate. Hence, not more than a 0.2 mm layer of electrolyte is seen by the films. The CV in a modified tube shows less distortions with slower scan rates (e.g.  $5 \text{ mV s}^{-1}$  used for studies in Section ??) and also with higher concentrations of the electrolyte, as the former gives more time for the ion diffusion and the latter improves the ionic conductivity of the electrolyte. While the CV in the modified tube is distorted, the oxidation and reduction peaks remain symmetric, suggesting that the reversibility of the redox process is not hindered.

**JMRO** The pDiTBuS film was brought to the desired oxidation state by galvanostatic discharging with a current of  $10 \mu\text{A}$  in a three-electrode electrochemical cell in a 5 ml beaker with the electrodes and the electrolyte described above. Each potential of the film was reached by first fully charging the cell to 700 mV and then discharging it to the desired potential (labeled points in Figure 3.12). When the desired potential was reached, the output relay of the potentiostat was opened so that no current went through the cell after charging. The substrate with the WE and the pDiTBuS film was removed from the charging cell, placed in a 5 mm OD quartz EPR tube, evacuated down to  $< 5 \times 10^{-3} \text{ mbar}$ , filled with He up to a pressure of 500-600 mbar, then flame sealed with a  $\text{H}_2/\text{O}_2$  burner.

After reaching the fully charged state with  $10 \mu\text{A}$  (by  $t = 0$  in Figure 3.13), a  $10 \mu\text{A}$  discharge current was applied to reach the four states of charge considered in this study (a-d in Figure 3.13 and in Figure 3.12). Initially, the full charging capacity of the film was  $1.48 \mu\text{Ah} = 5.11 \text{ mC}$  ( $3.29 \times 10^{16}$  electrons withdrawn upon the full charging). The charging capacity has decreased by  $0.06 \mu\text{Ah}$  (4%) after the four temperature cycles between 300 K and 5 K during the cryogenic EPR measurements.

### 3.4 TEMPO-Salen Films for EPR Spectroscopic Measurements

---

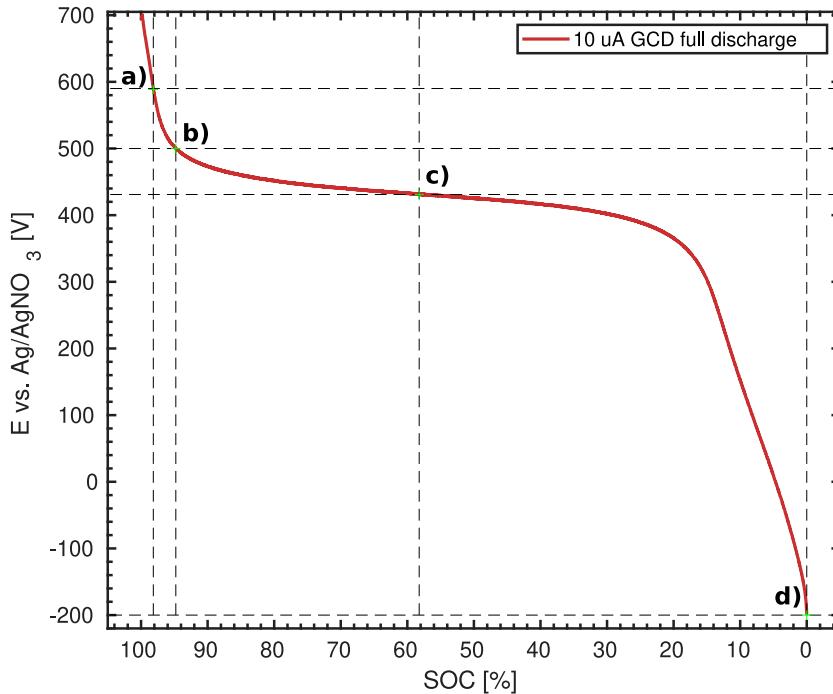


Figure 3.12: Initial galvanostatic discharge curve for the pDiTBuS film with the redox potentials described in the main text. Since the film has lost 12% of its capacity during the temperature cycling, the SoC determined from the potentials mapped to the initial curve are lower than the SoC determined from the individual discharge curves (given in brackets). The SoC values corresponding to the initial (individual) discharge curve are a): SoC 98 (98)%; b): SoC 94 (96)%; c): SoC 57(65)%; d): SoC 0(0)%. (Dis-)charging current: 10  $\mu$ A, charging rate: 6.25 C. After this initial discharging, the pDiTBuS film has undergone 10 charge-discharge cycles and 4 temperature cycles.

From the quantitative analysis of the GCD for each SoC, we calculate the number of elementary charges that are transferred to the film (withdrawn from the film) upon charging (discharging). The GCD and the calculated values of the transferred charge are shown in Figure 3.13. During the full discharge from +700 mV down to -200 mV the pDiTBuS film has gained a total charge of 1.355  $\mu$ Ah=4.88 mC (d), corresponding to  $3.01e+16$  electrons that had been transferred to the film.) The considered SoC correspond to discharging by  $0.020 \pm 0.005$   $\mu$ Ah (Figure 3.13 a,  $(5 \pm 1) \times 10^{14}$  electrons injected),  $0.060 \pm 0.005$   $\mu$ Ah (Figure 3.13 b,  $(1.4 \pm 0.1) \times 10^{15}$  electrons injected),  $0.480 \pm 0.005$   $\mu$ Ah (Figure 3.13 c,  $(1.07 \pm 0.01) \times 10^{16}$  electrons injected) and  $1.360 \pm 0.005$   $\mu$ Ah (Figure 3.13 d,  $(3.05 \pm 0.01) \times 10^{16}$  electrons injected). The SoC values determined from the respective potentials are different when mapped to the initial discharge curve in

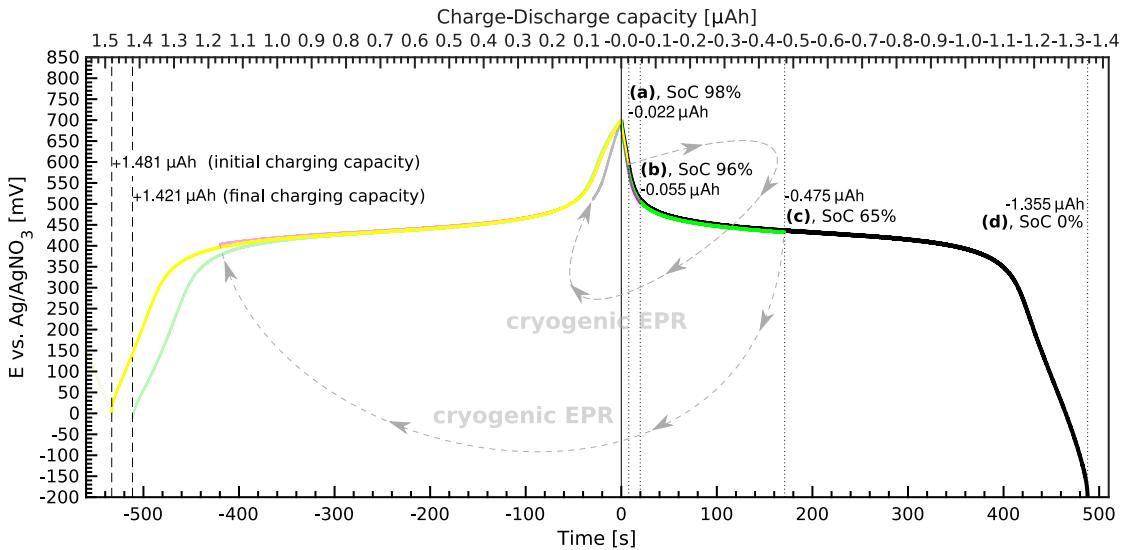


Figure 3.13: Calculation of the number of withdrawn electrons from a pDiTBuS film for the four states of charge. At negative times the pDiTBuS film is charged, corresponding to the withdrawal of electrons from the film. At positive times the film is discharged. The number of transferred electrons during discharging is determined from the four overlaid galvanostatic discharge curves (a-d).

Fig. 3.12 and when considering the individual discharge curves in Fig. 3.13, as the film was gradually losing its capacity during the temperature cycling, so the discharge curves were reaching the considered potentials at shorter times, leading to a lower Coulomb counting, lower discharge capacity and therefore a lower SoC.

## 3.5 Electrochemical Cells for EPR spectroscopy

One significant drawback with spectroelectrochemical EPR spectroscopy is the fact that microwave resonators suffer from substantial microwave damping as a result of introducing metal electrodes, polar solvents and ionic salts (i.e., the electrolyte) needed for successful electrochemistry[?]. Microwave damping can be significantly reduced by using an on-substrate electrode design (see Fig. 3.15) as this limits the amount of metal that is introduced into the resonator, while still allowing for electrode surface areas large enough to deposit sufficient material of interest to observe EPR signals.

### 3.5.1 Cells Based on a Modified EPR Sample Tube

An electrochemical half-cell was constructed inside an X band EPR sample tube. The WE of the cell was electrochemically polymerized on a flat Au electrode formed on a

### 3.5 Electrochemical Cells for EPR spectroscopy

---

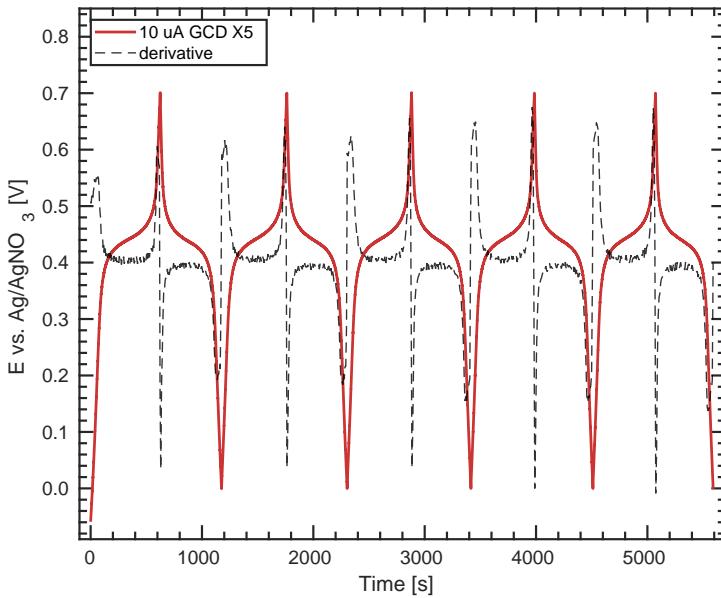


Figure 3.14: Galvanostatic charge-discharge cycling of a pDiTBuS electro-active film with a discharge capacity  $C_{DCG} = 1.6 \pm 0.1 \mu\text{Ah}$  recorded with 10  $\mu\text{A}$  charging and discharging current that corresponds to charging and discharging at a C rate of  $6.3 \pm 0.4 \text{ C}$ .

3.5 mm wide quartz substrate. The second on-substrate Au electrode was used as the CE. The substrate was inserted inside the EPR sample tube. The tip of the tube was flattened to reduce the amount of electrolyte in the half-cell.

The on-substrate electrodes are produced as follows. Cleaned quartz substrates are placed inside a holder and covered with shadow masks. The assembly is transferred into a vacuum chamber equipped with a thermal evaporator (MBraun ProVap 5G PVD System). At a pressure of  $7 \times 10^{-7} \text{ mbar}$ , 10 nm of Chromium (Cr) adhesion layer is evaporated, followed by 180 nm of Gold (Au). In this way the on-substrate working and counter electrodes are formed (WE and CE respectively). The reference electrode (RE) is not evaporated on substrate for electrochemical stability reasons. Instead, a 250  $\mu\text{m}$  Ag wire is used, either as is or, for additional stability, coated galvanically with a AgCl layer.[?] See Section ?? in the ESI† for details of the sample preparation.

The above procedure provides a WE active area of  $12.0 \text{ mm}^2$  which allows one to deposit an electrochemically active film that is large enough to yield a clear EPR signal. The flat electrode design provides the possibility to increase the WE area for samples with particularly small EPR signals while still maintaining certain film thicknesses. This also allows for studying EPR properties as a function of film thickness. In cases where

the electrochemical process is thought to deposit material on both the WE and CE, the distance between the on-substrate electrodes can be adjusted such that only one of the electrodes is positioned in the active volume of the microwave resonator, allowing for selective EPR probing of either of the electrodes.

The on-substrate electrodes reduce microwave damping. However, a substantial amount of microwave damping occurs due to the electrolyte, made of polar solvent and ionic salts. Therefore, we further optimize our setup by modifying conventional 5 mm outer diameter (OD) quartz EPR tubes by flattening the bottom 1.3–1.6 cm (cf. Fig. 3.15b and Section 3.16 in the ESI†), thereby reducing the active electrolyte volume needed to submerge both the WE and CE on the substrate as well as the RE wire, from ~120  $\mu\text{L}$  to ~60–70  $\mu\text{L}$ .

The flattened tube and the thin-film electrode setup have an additional benefit in that the sample is moved away from the maximum of the electric field distribution in the Bruker ER 4122-SHQE resonator ( $\text{TE}_{011}$  mode cavity for cwEPR), thereby further increasing the resonator quality factor (Q-factor, given by  $Q = \frac{\nu_{res}}{\Delta\nu}$ ,  $\nu_{res}$  = resonance frequency,  $\Delta\nu$  = FWHM of the resonance dip) and hence sensitivity. Further improvements can be made using the flat electrode setup in a  $\text{TM}_{110}$  mode cwEPR cylindrical cavity such as a Bruker ER 4103-TM (developed for studying samples exhibiting high dielectric constants), where the flattened cell can be aligned to further reduce coupling to the microwave electric field. The modified tube is compatible with commercial Bruker ER 4118X-MD5 resonators, most commonly used for advanced pulse EPR measurements at X-band frequencies ( $\nu = 9 - 10$  GHz).

### 3.5.2 Fabrication of the modified tube

The volume of the cell used in this study had to be minimized, as the high dielectric constant of the electrolyte does not allow for the critical coupling of the resonator. The volume of the electrolyte was minimized by flattening the tip of the quartz (melting point  $T_m = 1660 - 1710^\circ\text{C}$ ) tube accommodating the cell. For that, a tungsten (W,  $T_m = 3420^\circ\text{C}$ ) rod of a  $3.70 \times 1.35$  mm rectangular cross section, narrowing to the bottom of the tube at a wedge angle of  $\alpha \approx 5^\circ$ , was inserted into the tube (Fig. 3.16). The tube was evacuated and filled with He to a pressure of 100 mbar. The tip of the evacuated tube was molten around the thermally expanded rod with a Hydrogen-Oxygen burner ( $T_f = 3080^\circ\text{C}$ ). The modified tube was then connected to atmosphere and the cooled, contracted rod was removed and later reused for modifying other tubes. The tungsten rod was fabricated from an electrode of a flash lamp of a pulsed Nd:YAG laser.

The modification of the tip of the tube provided a decrease in the volume of the electrolyte down to 45  $\mu\text{L}$ , while the cylindrical part of the tube allowed for fitting the substrate connector and the wiring in. That allowed for the room temperature EPR measurements on the electrochemical cell during charging and discharging. Extensive care

### 3.5 Electrochemical Cells for EPR spectroscopy

---

had to be taken to reproduce the cv curve in the modified tube as the limited volume of the electrolyte was distributed over the large surface area. That caused poor ionic transport in the electrolyte layer.

To establish the extent to which the modified tube improves the resonator Q-factor ( $Q$ ) and therefore sensitivity of the cwEPR experiment, cwEPR spectra and associated Q-factors were recorded for a flat-electrode p-DiTS cell assembled in two different sample tubes. For both cell setups we used enough electrolyte to submerge all three electrodes. This required  $100 \mu\text{L}$  for the standard tube and  $70 \mu\text{L}$  for the modified tube. The effect of the two tubes on the cwEPR spectrum and on the Q-factor was studied for a range of heights ( $H$ ) measured from the center of the microwave resonator to the middle of the WE.

#### 3.5.3 Q-factors and cwEPR spectra for p-DiTS in standard and modified tube

We determine  $Q \approx 7800$  for the empty resonator. Inserting the tube-based cells initially at  $H = 24$  mm reduces the Q-factor for both cases, but more significantly for the standard tube ( $Q_{\text{standard tube}} \approx 4200$ ,  $Q_{\text{modified tube}} \approx 5400$ , see Fig. 3.17). At  $H = 18$  mm the Q-factor drops for both, again more significantly for the standard tube to  $Q_{\text{standard tube}} \approx 300$  while for the modified tube it is still  $Q_{\text{modified tube}} \approx 1200$ , a factor of 4 difference. This difference between the two tubes shows the benefit of using the modified tube and flat electrode geometries for SEC EPR. When the modified tube is inserted as deep as  $H = 14$  mm, the  $Q_{\text{modified tube}}$  is around 400, which still allows for EPR measurements. Coupling the resonator not possible for  $H < 18$  mm (standard tube) and  $H < 14$  mm (modified tube).

The decreasing Q-factor is not the only effect of a high-dielectric sample in an EPR resonator. The interaction between the sample and the electric field distribution of the resonator causes a mixture of absorption and dispersion signals, leading to asymmetric lineshapes in the cwEPR spectra. This makes double integration of the derivative cwEPR signal more complex, thereby making a quantitative analysis more difficult. This effect can be seen in the cwEPR spectra of p-DiTS (Fig. 3.17) measured in the standard 5 mm tube for  $H = 18$  mm where the cwEPR signal is asymmetric. The modified tube yields symmetric lineshapes at the same sample heights. Further details are presented in the following subsection.

The electrochemical cells based on the modified tube allow for higher EPR signals as compared to the normal X-band EPR tube. Fig. 3.18 represents two sets of measurements that describe the enhancement of the EPR signal for the modified tube. When the cell is inserted closer to the resonator's center, the Q factor of the resonator lowers and the EPR signal increases, because the intensity of the magnetic component of the

microwave field  $B_1$  is higher in the center of the resonator. When the cells were inserted closer to the center of the resonator, the Q factor went from  $\approx 6000$  down to  $\approx 400$ , so that the microwave bridge could not be critically coupled to the resonator and no EPR measurements were possible. Depending on the volume of the electrolyte in the cell, it can be inserted more or less deep into the resonator.

The modified tube could be inserted 7 mm deeper into the microwave resonator (see Fig. 3.18). The EPR signal in the modified tube is increased as compared to the normal tube at the same height.

The modified tube also allows for larger cwEPR signal intensities as it can be inserted closer to the resonator center. The signal-to-noise ratio (S/N) for the modified tube is increased by a factor of  $\approx 6$  as compared to the standard tube, both inserted at  $H = 18$  mm. At the maximum sample insertion, the S/N is improved by a factor of  $\approx 8$  for the modified tube.

Using the modified tube we see three major benefits. Firstly, it results in much higher Q-factors and therefore sensitivity when comparing Q-factors for the same sample height. Secondly, the modified tube allows for insertion of the tube closer to the resonator center, allowing for a larger S/N and therefore requiring less averaging time for each cwEPR measurement. This is especially useful for samples where holding the potential for long periods causes unwanted effects or degradation. Thirdly, cwEPR measurements with the modified tube give symmetric cwEPR lineshapes (using the conventional procedure for critically coupling the microwave cavity, the standard tube gives an asymmetric lineshape) which allows for more straightforward quantitative analysis (spin counting), especially useful for in-situ cwEPR with varying redox potentials.

### 3.5.4 Reference Electrode

The Ag/AgCl reference (RE) electrode for the EPR-compatible electrochemical cells described in 3.5.1 was formed by coating a layer of AgCl onto a 250  $\mu\text{m}$  Ag wire galvanically from a 1 M aqueous solution of KCl. For that, the Ag wire and a Pt wire were connected as a cathode and an anode respectively to 10 mL of the KCl solution and a DC potential of 500 mV was applied for 7500 s which resulted in a dark AgCl layer deposited onto the Ag cathode. In the beginning of the galvanic deposition, the current through the KCl solution was changing in a jumpy manner, that indicated the growth of the AgCl layer. The galvanic process was stopped after the current was stable for at least 300 s.

### 3.5.5 Electrochemical Cells with a Separator

Two planar substrates were covered with a 7 nm layer of Cr and a 180 nm layer of Au. One substrates was covered with a redox active pDiTBuS film. The other substrate was

### 3.5 Electrochemical Cells for EPR spectroscopy

---

either covered with pNiSalen (full cell), or was used as is (half cell). The cell preparation is shown in a scheme in Figure 3.14.

#### 3.5.6 Electrochemical Cells with Solid Electrolyte

The electrolyte based on an ionic liquid incorporated in a gel-like polymer matrix has sufficient ionic mobility and diffusion to penetrate the pDiTBuS and pNiSalen surface and allow for partial charging and discharging of the battery electrodes. TEMPO radicals were shown to undergo a redox reaction in ionic liquids with a slightly changed redox potential of the TEMPO<sup>•</sup>-TEMPO<sup>+</sup> reaction [?].

#### 3.5.7 Energy Diagram of an Electrochemical Half-Cell

The transfer of charges in a TEMPO-Salen electrochemical cell can be described in an energy diagram shown in Figure 3.23. The energy scale of the diagram starts at the vacuum level - the energy of a free electron. The potential energy of an electron in the Au lead in this energy scale is the work function of Au which is 5.1 eV [21]. The energy at which an electron in a material can be found with a 0.5 probability is called the Fermi energy. The Fermi energy of a cathode changes with the SoC of the cell.

The redox potential of TEMPO is 0.812 V vs. SHE [133]. The absolute potential of the SHE is 4.44 V vs the vacuum level. The workfunction of Au is 5.1 eV. The electrochemical window of Acetonitrile is between -3.45 V and +2.35 V vs. SCE (+0.268 V vs SHE) [70].

Electrochemical doping of a semicoudacting polymer [45]: Charge transfer, ion insertion. The oxidation and reduction potentials of the ions are separated from the redox potentials of the polymer by several volts, so no charge transfer occurs between the polymer and the electrolyte. The positive charge injected to the polymer from the metal is compensated by the intercalated negative ion. The ionization efficiency in electro-chemically doped films is close to 100% [45].

During the charging of a poly-TEMPO-Salen half-cell, its electrochemically active cathode film is being oxidized: positive charges are being injected into it. If the bias potential of the cathode  $E$  is higher than the oxidation potential of the polymer (see Figure 3.23 a)), a positive charge charge is injected to the pNiSalen backbone. The oxidation potential of pNiSalen was adjusted during the molecular synthesis to be close to the oxidation potential of TEMPO<sup>•</sup>, so that the oxidation of the backbone would lead to a simultaneous oxidation of the charge bearing groups [114]. If  $E$  increases above the oxidation potential of TEMPO<sup>•</sup> and the polymer backbone connecting the metal and the TEMPO<sup>•</sup> fragment is oxidized, the injected hole reaches the TEMPO<sup>•</sup> fragment and oxidizes it to TEMPO<sup>+</sup>. The charge transfer process during the charging of the half-cell is shown in Figure 3.23 a). The oxidation TEMPO<sup>•</sup> leads to a creation of an electric

double layer next to the cathode [6] of A negative  $\text{BF}_4^-$  ion is attracted from the electrolyte solution to the positively charged backbone.

The hole injected into the polymer backbone propagates in the direction of the Fermi energy gradient within the biased polymer until it encounters the unpaired electron on a  $\text{TEMPO}^\bullet$  group and recombines with it. During the recombination, the hole disappears from the backbone and the electron disappears from the  $\text{TEMPO}^\bullet$ . The charge bearing group oxidizes to  $\text{TEMPO}^+$ . This process can be seen as the hole hopping from the backbone to the TEMPO radical. The TEMPO radicals therefore serve as hole traps.

The consequent oxidation of the redox active groups during the biasing of the polymer cathode is shown in Figure 3.24.

### 3.5 Electrochemical Cells for EPR spectroscopy

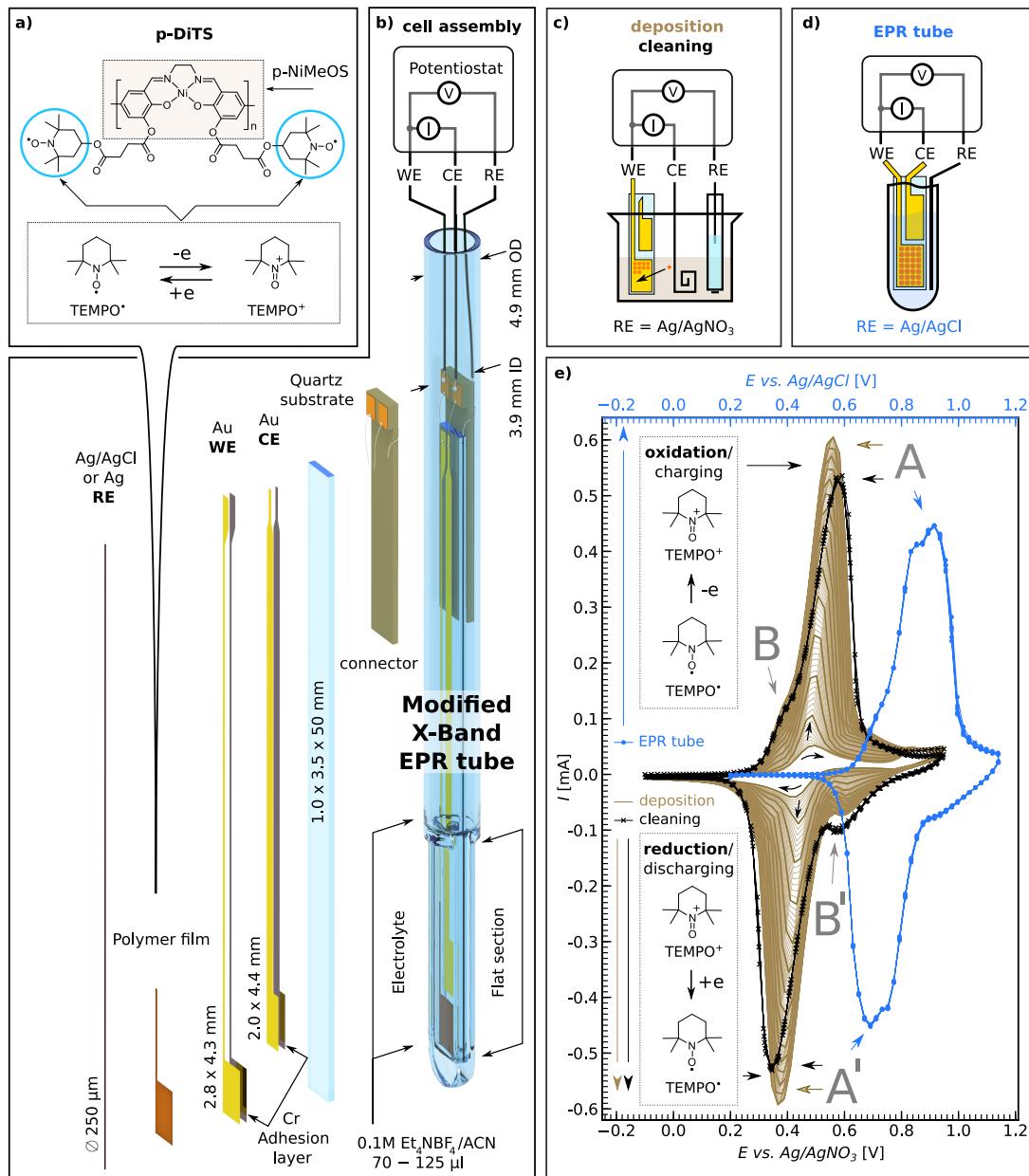


Figure 3.15: Schematic diagram of the electrode design and assembly of the electrochemical cell based on a modified X-band EPR quartz tube. a): Molecular structure of p-DiTS, with the redox reaction of its charge-bearing TEMPO groups; highlighted is the backbone, p-NiMeOSalen. b): Photograph of the modified tube with a flattened bottom section, with the on-substrate electrochemical setup assembled inside, and the process of forming the modified tube. c): Electrochemical setup for deposition and cleaning of polymer films. d): Tube-based electrochemical setup. e): Cyclic voltammograms of a growing p-DiTS film during 100 electropolymerization cycles (solid-brown), during the cleaning process (crossed-black) and in the tube-based setup (dotted-blue). Peaks A/A', B/B' correspond to the oxidation and reduction of the TEMPO fragments and of the p-NiSalen backbone, respectively. All CV were recorded at 50 mV s<sup>-1</sup>.

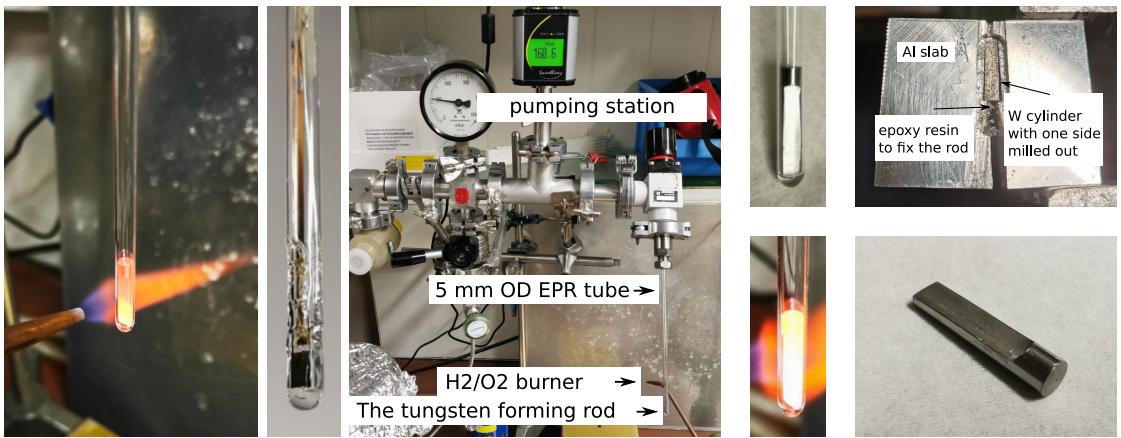


Figure 3.16: Modifying the tip of the standard 5 mm OD quartz EPR sample tube by melting it around a Tungsten (W) forming rod with a H<sub>2</sub>/O<sub>2</sub> burner in an evacuation setup.

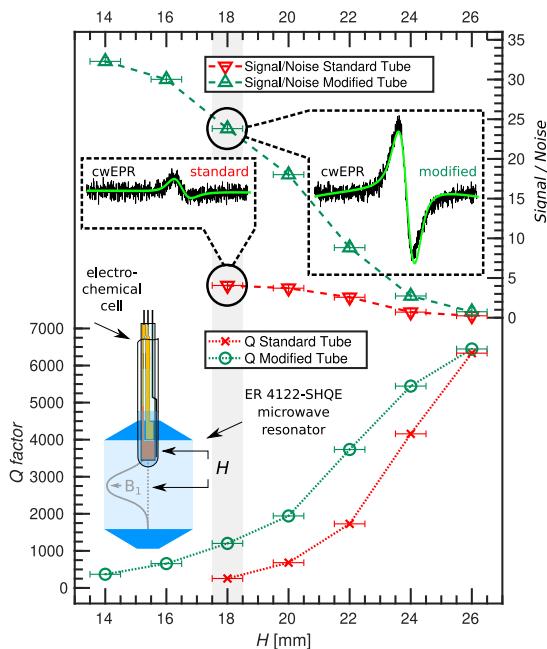


Figure 3.17: Signal-to-noise ratio of the cwEPR spectrum of p-DiTS and the Q-factor of the Bruker ER4122-SHQE microwave resonator measured for an electrochemical cell based on a standard X-band EPR sample tube and for an electrochemical cell based on the modified tube. Data for various heights  $H$  from the center of the resonator. Insets: Representative cwEPR spectra at  $H = 18$  mm, where the signal for the standard tube is the strongest.

### 3.5 Electrochemical Cells for EPR spectroscopy

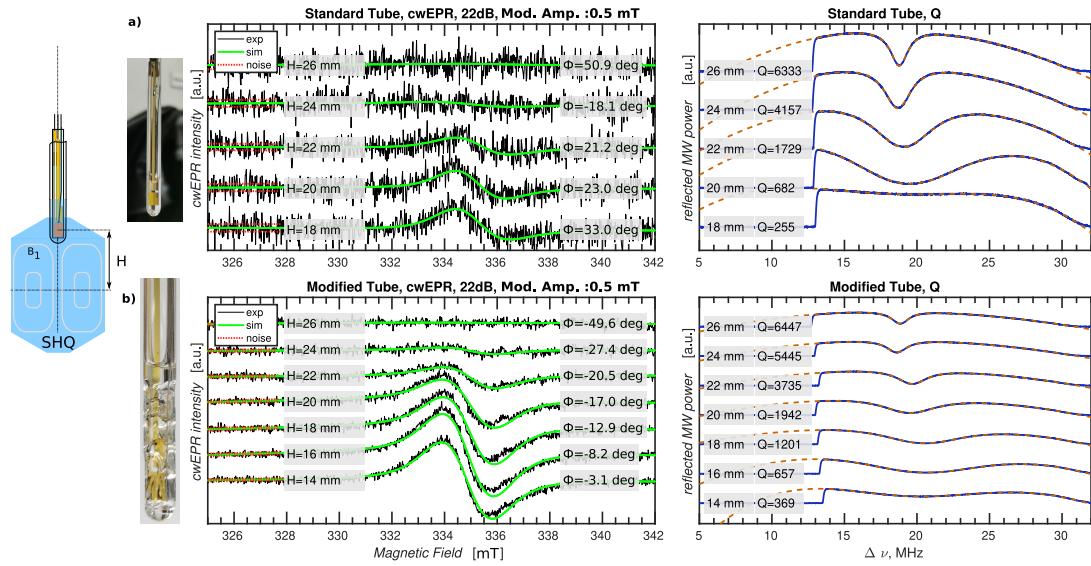


Figure 3.18: cwEPR signal intensity and Q factors for the standard 5 mm OD quartz EPR sample tube and for the modified tube at different heights from the center of the Bruker ER 4122-SHQE resonator.  $\nu = 9.4$  GHz. Simulations of the cwEPR spectra with adjusted microwave phase. Noise analysis.

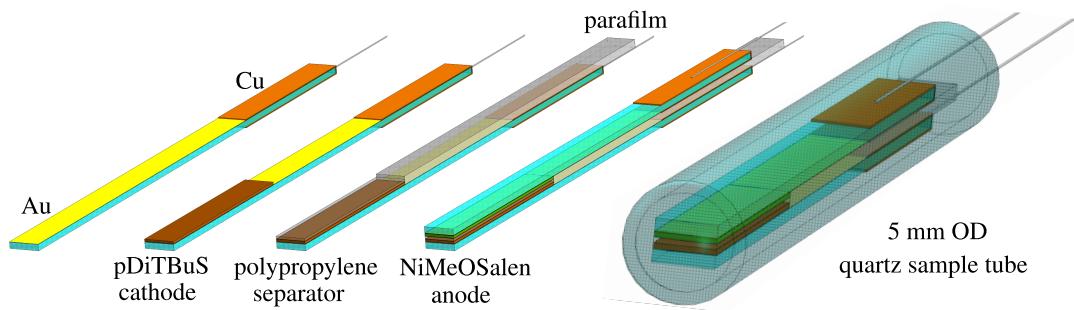


Figure 3.19: Organic radical battery made with two parallel Au-plated substrates and a polypropylene separator soaked in liquid electrolyte.

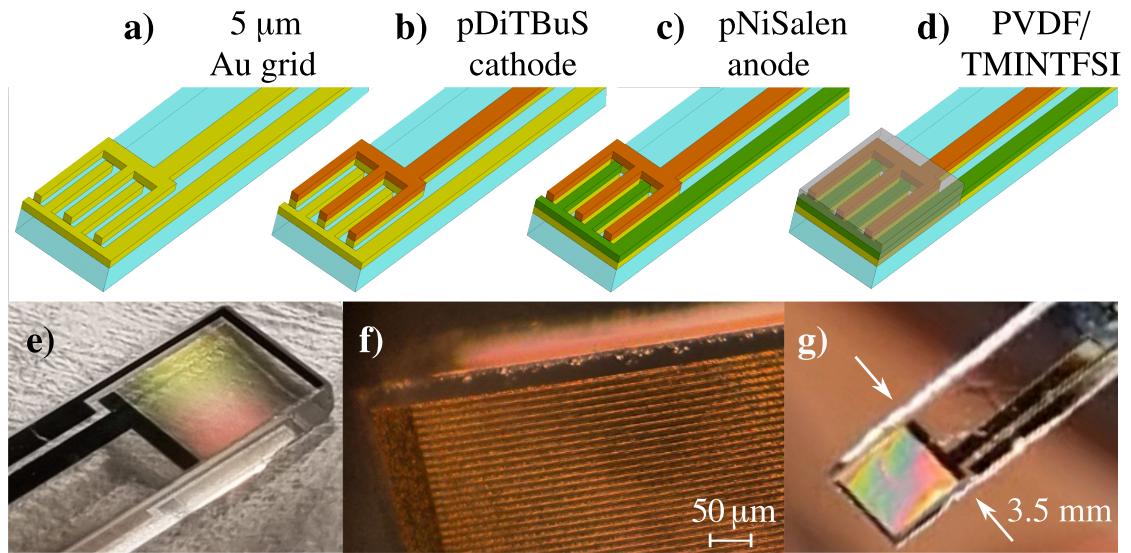


Figure 3.20: All-polymer solid state organic radical battery produced on a  $5 \mu\text{m}$  interdigitated grid.

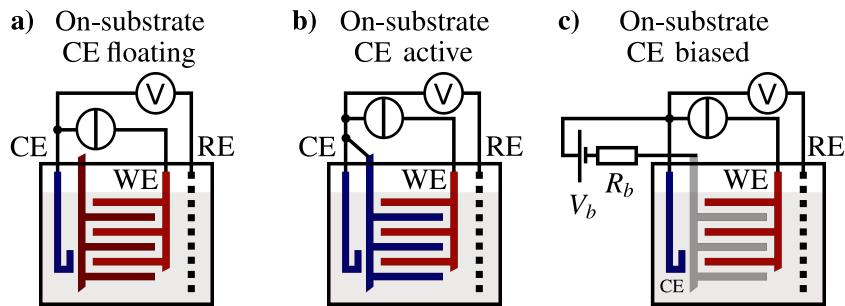


Figure 3.21: Deactivation of the on-substrate CE during the electrodeposition of a pDiTBuS film on the on-substrate WE of a  $5 \mu\text{m}$  interdigitated grid.

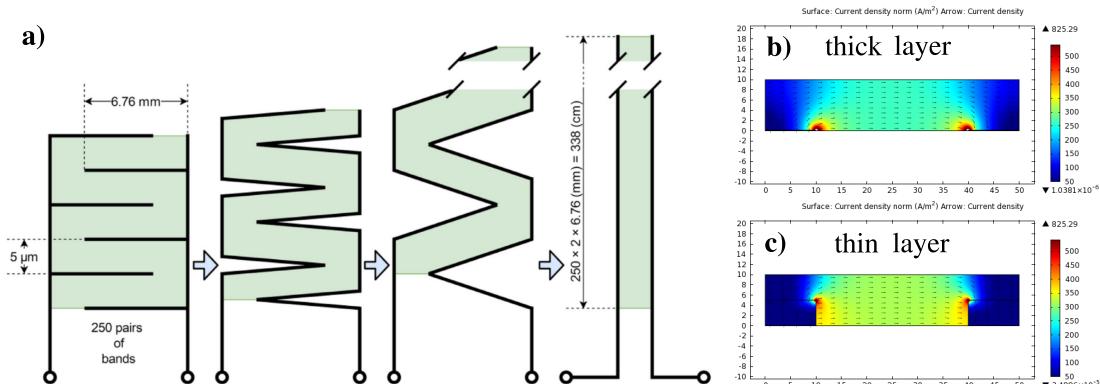


Figure 3.22: Extremely inhomogeneous current density in a closely spaced electrodes of the interdigitated grid. Numerical simulation in Comsol Multiphysics.

### 3.5 Electrochemical Cells for EPR spectroscopy

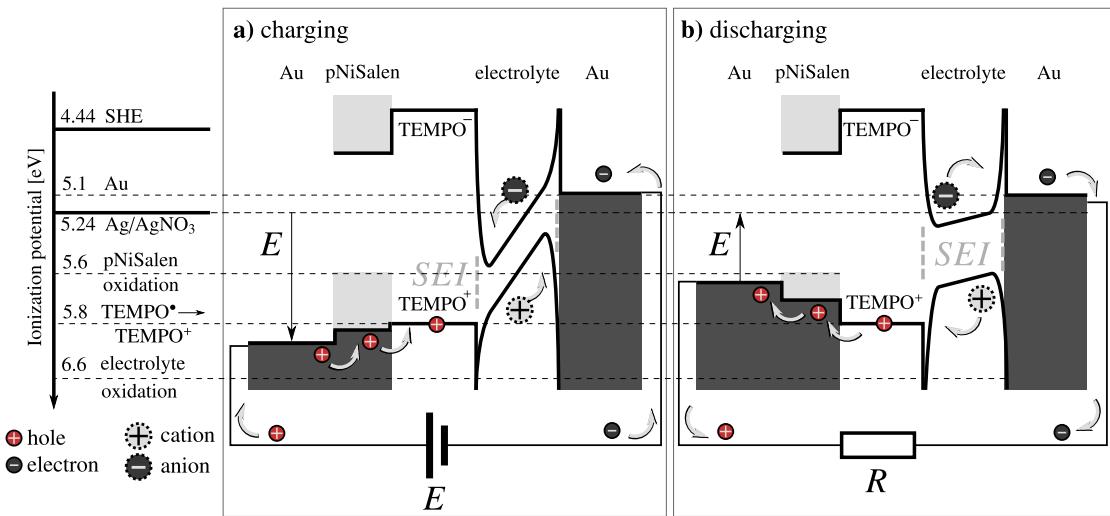


Figure 3.23: Band diagram of a rechargeable electrochemical half-cell with a TEMPO-containing polymer cathode during charging (a) and discharging (b).

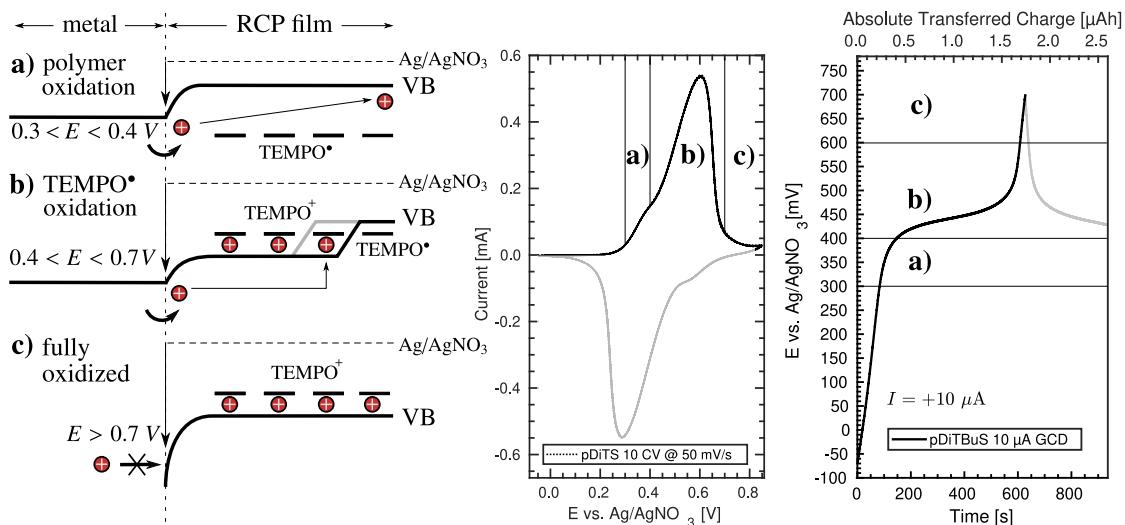


Figure 3.24: Charging of a poly-TEMPO-Salen film by injecting positive charge carriers at different biasing conditions. The Fermi energy for holes in the film is lowering during its electrochemical p-doping. a)  $0.3 < E < 0.4$  V - the biasing potential is above the oxidation potential of the backbone and below the oxidation potential of TEMPO<sup>\*</sup>. b):  $0.4 < E < 0.7$  V - the biasing potential is in the range of the oxidation potentials of TEMPO observed as a current peak in a cyclic voltammogram (middle plot) and a voltage plateau in a galvanostatic charging curve (right plot). c):  $E > 0.6...0.7$  V - the biasing potential is above the oxidation potential of all TEMPO groups in the film. Bending of the conduction band edge at the metal-semiconductor interface due to the Coulomb shielding by the ions stabilizing the TEMPO<sup>+</sup> fragments.



# Chapter 4

## EPR Spectroscopy of TEMPO-Salen Electrochemical Cells

Here the EPR spectra of TEMPO-Salen electrochemical cells are shown under operating conditions and ex situ, for various states of charge, as well as the spectra of the materials that were used to construct the cells. That information is used to decompose the complex spectra of a charging cell and to perform its quantitative analysis to identify the state of charge of the cell and the by-products that are being released during the cell operation.

### 4.1 cwEPR Spectroscopy of TEMPO Containing Molecular Fragments

The stable TEMPO<sup>•</sup> radical is widely used in the EPR spectroscopy as a spin probe and particularly in the EPR studies of TEMPO containing ORB materials [76, 81, 3, 2, 53, 131]. The spin density at the TEMPO<sup>•</sup> radical is localized within the N-O bond [87] and partially resides on the  $I = 1$   $^{14}\text{N}$  nucleus, so to describe the EPR spectrum of an isolated TEMPO<sup>•</sup> one has to take into consideration the electron Zeeman term  $H_{EZ}$ , the nuclear Zeeman term  $H_{NZ}$  and the hyperfine coupling term  $H_{HF}$ . The unpaired electron spin on TEMPO<sup>•</sup> has anisotropic g value, because of the asymmetry of its molecular orbital, so the  $\mathbf{g}$  matrix and the  $\mathbf{A}$  hyperfine coupling tensor are both anisotropic.  $\mathbf{g}$  is diagonal in the molecular frame of reference shown in Figure 4.1. Its principal values are  $[g_{xx} = 2.009, g_{yy} = 2.006, g_{zz} = 2.002]$  [68, 9]. The principal values of  $\mathbf{A}$  in the same frame are  $[A_{xx} = 20, A_{yy} = 20, A_{zz} = 100]$  MHz [68, 9].

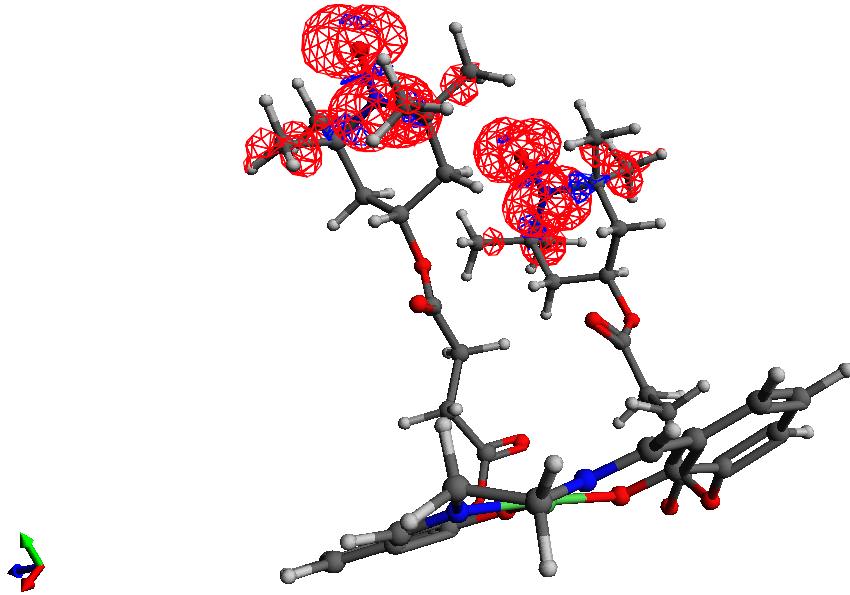


Figure 4.1: Spin density in a DITS monomer with unoxidized TEMPO groups computed with density functional theory. The spin density localized on two neighboring TEMPO radicals, around the Nitrogen nuclei that gives rise to the hyperfine coupling. Calculation by Marcel Gauglitz in ORCA [?] at the high-performance computing cluster Curta of the Free University of Berlin [5]. The def2-TZVP functional basis set was used for the geometry optimization and for the calculations of the spin density.

#### 4.1.1 Room Temperature Spectra of TEMPO<sup>•</sup> Solutions

Solution spectra of radicals are showing averaged values of  $g$  and  $A$  because of the fast molecular tumbling [68, ?]. The observed  $g$  value for a tumbling TEMPO<sup>•</sup> is the average of the principal values of the  $\mathbf{g}$  matrix:  $g = 1/3(g_{xx} + g_{yy} + g_{zz})$ . The anisotropic part of the hyperfine coupling tensor for the tumbling TEMPO<sup>•</sup> also averages to zero, so only the isotropic hyperfine constant  $a_{iso}$  determines the observed hyperfine coupling. CwEPR spectra of a 0.1 mM solution of TEMPOL measured at room temperature are shown in Figure 4.2. The spectral simulation performed with EasySpin [107] yields  $g = 2.0055$  and  $a_{iso} = 43.8$  MHz.

A biradical molecule like Di-Tempo-Salen (Figure 3.7 e) and f)) has two paramagnetic species that are close to each other and therefore exchange electrons. When the exchange coupling between the radicals  $J$  is comparable to the hyperfine coupling  $A$  of each radical to its 'host' nucleus, the superhyperfine interaction [?] takes place, in which

#### 4.1 cwEPR Spectroscopy of TEMPO Containing Molecular Fragments

---

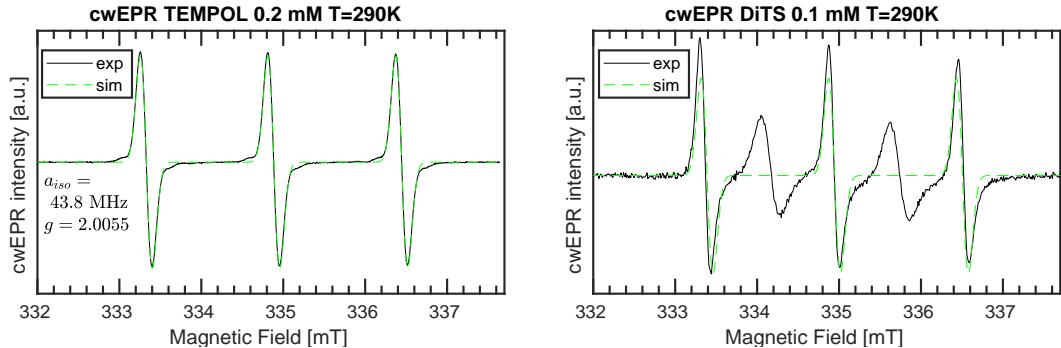


Figure 4.2: Room temperature cwEPR spectra of a low-concentration solutions containing mono- and di-TEMPO molecular fragments. Left: TEMPOL, Right: Di-Tempo-Salen.

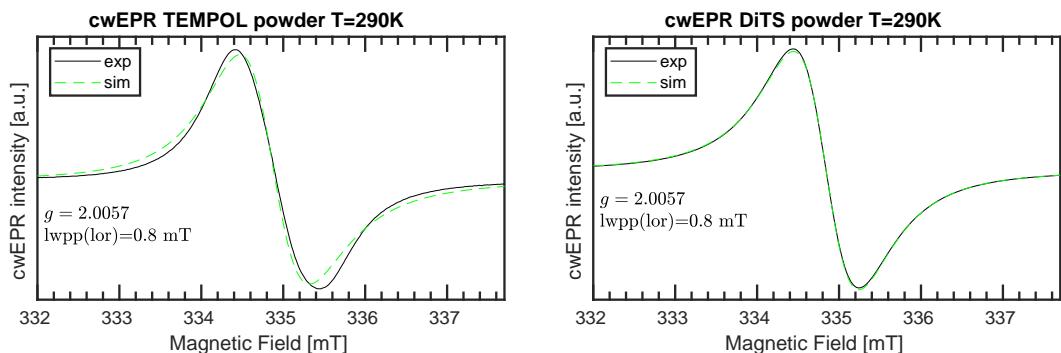


Figure 4.3: Room temperature cwEPR spectra of pure TEMPO-containing powders. Left: TEMPOL, Right: Di-Tempo-Salen.

the radical is interacting to the nucleus of the neighboring radical [22]. Solutions of biradical molecules with magnetic nuclei show more features in cwEPR spectra when the electron-electron exchange coupling  $J$  between the two radicals within the molecule becomes comparable to the hyperfine coupling between the radical and its 'host'  $^{14}\text{N}$  nucleus. tumbling of the molecule and the restricted motions of each radical within the molecule cause a complex molecular motion that affects the dipolar and exchange couplings between the radicals and causes "spectra with alternating linewidths" [22, 10]. A solution of Di-TEMPO-Salen shows a five-line cwEPR spectrum with alternating linewidths (Figure 4.2, right) with the three most intense lines corresponding to the three hyperfine sublevels of  $\text{TEMPO}^{\bullet}$ . The five-line structure in the cwEPR spectrum indicates the presence of a di-TEMPO biradical in the solution.

TOLYAN:

If the TEMPO groups are far away from each other, their cw-EPR signal consists of three lines that are due to the hyperfine interaction between the electron spin and the

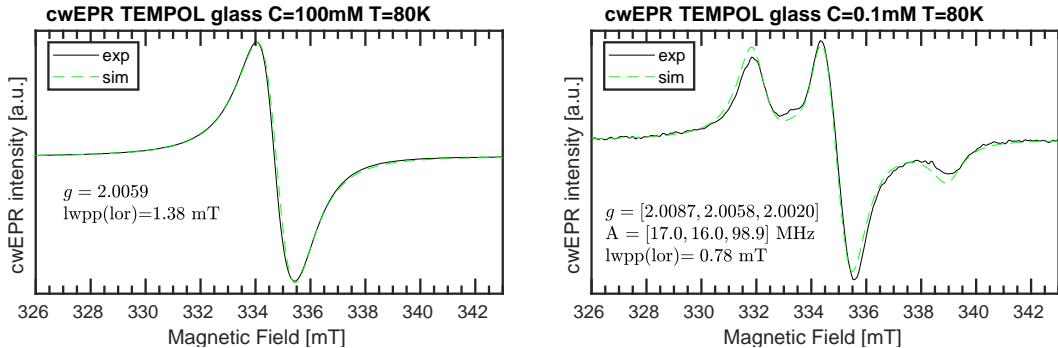


Figure 4.4: Cryogenic cwEPR spectra of TEMPOL at high and low concentration in a Dichloroethane/Acetonitrile glass. Left: 100 mM, Right: 0.1 mM.

spin of the Nitrogen nucleus. When the TEMPO groups are brought closer to each other, their electron orbitals start to overlap, and the exchange interaction ( $J$ ) between the electrons grows. That splits the signal into more lines as it was shown by [10] and represented in Fig. 7. In the case of strong exchange interaction the spectrum consists of five lines with relative ratios 1:2:3:2:1. In the absence of the exchange interaction the spectrum contains only three hyperfine lines of equal intensities. In DiTS, a sum of a three-line spectrum and a five-line spectrum was observed. This may be the evidence that TEMPO-bearing linkers are sufficiently long to allow TEMPO groups to move freely in space around the organometallic complex. That can yield to different  $J$  values depending on the relative orientation of the linkers, similar to [10]. In theory, there are several possible positions of TEMPO groups relative to each other that can change the EPR spectrum. Depending on the angle between the linkers (from  $\pi$  to 0),  $J$  may vary from its minimal to maximal value, that should yield a three- and five-line structures respectively. Since the process of movement is dynamic, we can explain the observed picture as a combination of several positions in space [10]. The five-line structure suggests different preferred conformations of the TEMPO fragments and dynamic interconversion between these states with different exchange coupling  $J$  leads to the observed spectrum.

#### 4.1.2 Spectra of $\text{TEMPO}^\bullet/\text{TEMPO}^+$ Films

A film made of a TEMPO-containing polymer can be brought to a certain oxidation state, depending on how many of the TEMPO groups are in the radical ( $\text{TEMPO}^\bullet$ ) state and how many are in the oxidized ( $\text{TEMPO}^+$ ) state. The densely packed  $\text{TEMPO}^\bullet$  fragments in the film cannot be considered as isolated molecules anymore, and the interactions between the radicals become significant. Microcrystals of TEMPOL are densely packed  $\text{TEMPO}^\bullet$  with a concentration of ??? mM. The cwEPR spectrum of TEMPOL microcrystals in Figure ?? is one broad line centered at  $g = 2.0055$ . A powder of DiTS

## 4.1 cwEPR Spectroscopy of TEMPO Containing Molecular Fragments

---

monomers is showing the same cwEPR spectrum in Figure ???. It is the matter of concentration of the paramagnetic TEMPO fragments that changes the cwEPR spectral shape. In Figure ?? cryogenic (80 K) cwEPR spectrum of a 100 mM solution of TEMPOL in Dichloroethane/Acetonitrile is presented. With a slight shift in  $g$  factor due to the polar molecular environment of the frozen solvent [?] and a broader lineshape due to a weaker exchange narrowing, the spectrum consists on one dipolar-broadened Lorentzian line. In contrast, when the concentration of the solution is lowered to 0.1 mM (Figure ??) - the inter-molecular interactions become weak enough to resolve the  $A$  and  $g$  anisotropy of the nitroxide radical, so the spectrum consists of three lines that can be simulated with the known  $A$  and  $g$  parameters.

A redox-active film containing TEMPO radicals, like the TEMPO-Salen cathode film, shows different cwEPR signatures depending on its redox state. Figure 4.5 represents two cryogenic cwEPR spectra of a  $d \approx 2.2 \mu\text{m}$  DiTBuS cathode film that was discharged to  $E = -50$  mV and charged to  $E = +900$  mV vs. the Ag/AgNO<sub>3</sub> RE as described in Section 3.2.2. The spectral intensities were normalized to represent the signal shape not the magnitude. The discharged film shows one broad cwEPR line in Figure 4.5, left, that reflects on the strong interactions between the non-oxidized TEMPO<sup>•</sup> in the discharged cathode. The linewidth of the discharged film spectrum is smaller than the linewidth of the DiTS monomer spectrum, suggesting a smaller exchange interaction between the TEMPO fragments in the film [114].

The oxidized film in Figure 4.4, right, shows a well resolved spectrum of an isolated nitroxide, similar to the low-concentrated solution of TEMPOL (Figure ??). A series of powers was recorded for both redox states of the film to observe possible microwave saturation effects that are crucial for the pulsed EPR experiments discussed in Chapter 2.3.

### 4.1.3 Spectra of NiSalen Films

The molecular backbone of pDiTS and pDiTBuS is the pNiSalen, a conjugated polymer that exhibits redox behavior [20, 114, 1]. The observations of electrochromicity of pNiSalen films with UV-VIS spectroscopy [20] have revealed the formation of polarons and antiferromagnetically coupled (with total spin S=0) bipolarons in the oxidized state of pNiSalen. A series of cwEPR spectra recorded for a pNiSalen film in various redox states is shown in Figure 4.9. Operando cwEPR spectra of a cell containing a pNiSalen cathode is shown in Figure 4.10.

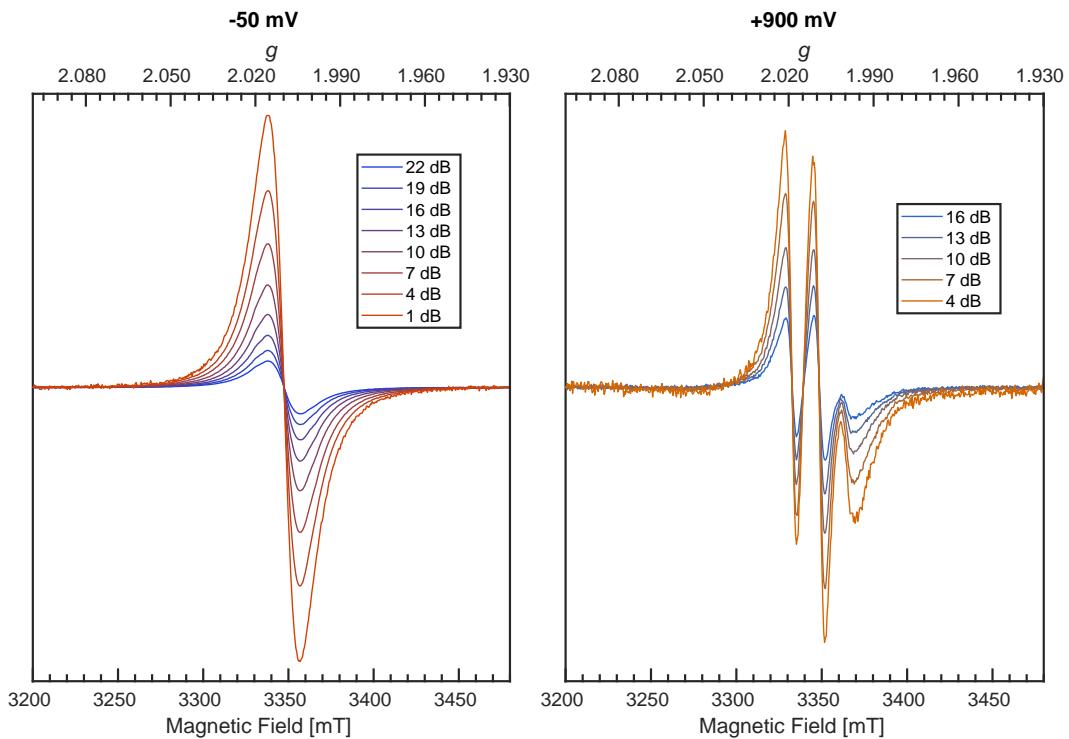


Figure 4.5: Cryogenic (80 K) cwEPR spectra of a pDiTBuS film grown with 200 deposition cycles. Left: discharged film, -50 mV vs. Ag/AgNO<sub>3</sub> RE. Right: Fully charged film, 900 mV vs. Ag/AgNO<sub>3</sub> RE.

## 4.2 cwEPR Spectroscopy of a Charging Electrochemical Cell

There is a number of difficulties when it comes to an EPR experiment on a working electrochemical cell. The cell must contain mobile ions between its electrodes - cations and anions. The ions are normally produced as products of dissociating salts. To overcome the ionic bond in a salt and to break it into the ions, a solvent with large dipole moment is needed. Solvents with large dipole moments, as acetonitrile ( $\text{CH}_3\text{CN}$ ,  $\epsilon \approx 37.5$ ) or water ( $\epsilon \approx 78.4$ ), have large dielectric constants which results in a non-resonant absorption of microwaves. A cell containing liquid electrolyte absorbs microwaves and lowers the sensitivity of the EPR experiment. Furthermore, due to a finite dimension of cell, not only the magnetic component of the microwave is interacting with the electrolyte, but also the electric one - this results in heating of the electrolyte in a similar fashion as in a microwave oven. The heating of the electrolyte leads to a faster degradation of the cell and does not allow for long systematic measurements.

Another general issue with the operando EPR and EDMR experiments is that the de-

## 4.2 cwEPR Spectroscopy of a Charging Electrochemical Cell

---

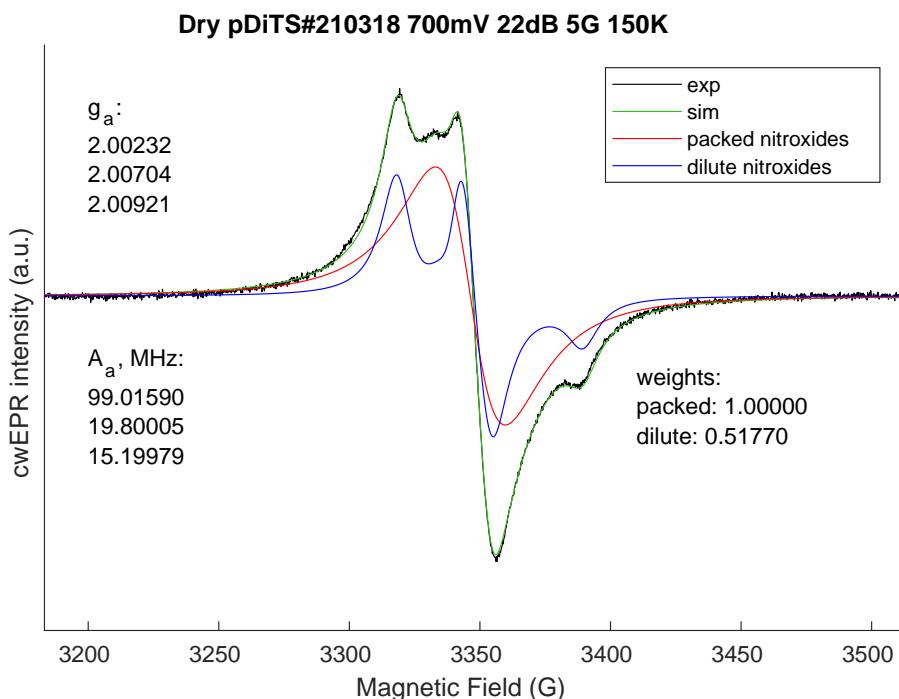


Figure 4.6: A pDiTS film in the intermediate state of charge (700 mV vs. Ag/AgNO<sub>3</sub>) showing a composition of two spectral signatures. The single-line signal from the densely packed nitroxide radicals coexists with the signal of the isolated nitroxide radicals. Two-component simulation.

vice under testing (DUT) has to have metal electrodes that deliver current to it. Metals, placed in a microwave cavity, change the distribution of the electromagnetic field in it - that weakens the magnetic component at the device and at the same time strengthens the electric component. It is the magnetic dipole transition that is causing the magnetic resonance, so the weakening of the magnetic component by introducing the metal electrodes further decreases the magnetic resonance response. The increased electric component causes heating to temperatures that can be critical for the DUT operation.

### 4.2.1 cwEPR Spectra During a Charge-Discharge Cycle

There are four characteristic cwEPR signatures of an electrochemical cell containing di-TEMPO-Salen polymer cathode. The well known signature of a freely tumbling TEMPO<sup>•</sup> exhibits three narrow lines corresponding to the three nuclear sublevels of nitrogen:  $m_I = -1, 0, +1$ .

EPR spectra of electrochemical cells with p-DiTS as active-electrode material can

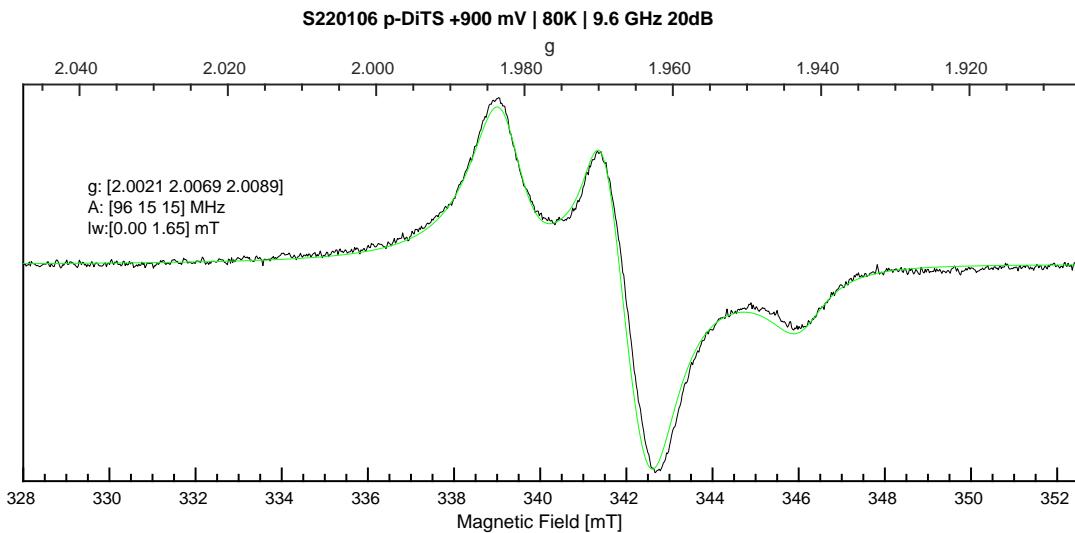


Figure 4.7: Cryogenic (80 K) cwEPR spectrum of an oxidized pDiTBuS film grown with 200 deposition cycles showing a signature of the isolated nitroxide radical with the standard  $g$  and  $A$  parameters, revealed with a simulation.

exhibit a variety of different signals. Before presenting and discussing the experimental results, we will provide an overview about the various characteristic cwEPR lineshapes associated with nitroxides in different environments.

Fig. 4.11a shows the spectrum expected for a *densely packed p-DiTS film* with all nitroxides in the EPR-active reduced state. The broad unstructured line results from the strong dipolar and exchange interaction between both nitroxides of each DiTS monomer as well as between the nitroxides of different monomers. The exchange interaction can lead to either line narrowing or broadening depending on the strength of the interaction,[?] while the dipolar interaction causes broadening. In consequence, the overall cwEPR line width depends on the spin concentration in the film.

*Dilute mono-TEMPO fragments* dissolved in the electrolyte, each containing only one nitroxide, give rise to a three-line spectrum (cf. Fig. 4.11b) which is well known from nitroxide-based spin labels in solution.[68] Tumbling of the molecules in the liquid electrolyte results in an averaging of the anisotropic interaction between the electron spin and the nitrogen nuclear spin ( $I = 1$ ) as well as of the  $g$  anisotropy, leaving only the isotropic part of the hyperfine coupling and the isotropic  $g$  value.

*Dilute DiTS monomers* in the electrolyte generally give a spectrum consisting of five narrow lines (cf. Fig. 4.11c), if each monomer contains two interacting EPR-active nitroxides. The spectrum depends on dynamic effects, specifically the modulation of the exchange interaction between both radicals of each monomer. Thus, depending on the solvent and temperature, the spectrum can be indistinguishable from the three-line

### 4.3 p-DiTS in-operando redox series

spectrum of mono-TEMPO fragments.

The fully charged (oxidized) p-DiTS film can contain electrically isolated domains in which the nitroxides are not connected to the electrode and cannot be oxidized or reduced. These electrically inactive *immobilized DiTS monomers* in the oxidized film display a spectrum as shown in Fig. 4.11d. In contrast to the densely packed p-DiTS film, the dipolar and exchange interactions between neighboring radicals are much weaker. The anisotropy of the nitroxide's hyperfine tensor adds features to the cwEPR spectrum in d) as compared to a). Yet, there is some remaining line broadening that does not allow one to distinguish between immobilized DiTS monomers with either one or two paramagnetic nitroxides.

We note that the oxidized NiSalen backbone can contribute to the spectrum as well. Its EPR signature, which is not shown in Fig. 4.11, is clearly different from the nitroxide/TEMPO-related spectra discussed above.

## **4.3 p-DiTS in-operando redox series**

Here we present the cwEPR spectra at each measured potential during the in-operando redox series for the 8 CV cycle ( $t = 40$  nm) p-DiTS film. We fit the experimental data with a two component fit consisting of component 1 describing the densely packed on film immobilized nitroxide spins and component 2 describing the dilute mobile nitroxide spins in electrolyte. All simulation parameters and relative weights of the two components are shown in Fig. 4.12.

Fig. 4.13 shows the in-operando study on a 150-deposition-cycle  $t = 400$  nm film, that has not undergone the cleaning procedure. Here we see that non-polymerized monomeric DiTS is released into electrolyte, confirmed by measuring the in-operando and used electrolyte cwEPR spectra, along with comparison to a  $100 \mu\text{m}$  sample of monomeric DiTS in solution.

Fig. 4.14 shows more steps in the in-operando study shown in the main text Fig. 5.5

Potential dependent in-operando SEC cwEPR was measured on a  $40 \pm 5$  nm thick (8 deposition cycles) p-DiTS film inside the modified EPR tube at room temperature (see Fig. 5.1). At 0.3 V (vs. Ag) the TEMPO fragments are in the reduced/discharged state. The discharged film exhibits a single Lorentzian derivative lineshape with a peak-to-peak line width of 1.4 mT. The single-line derivative lineshape results from the collapse of the hyperfine structure due to strong exchange coupling in the films with high spin concentration, whereas the broader line width is due to a combination of dipolar and exchange coupling between the nitroxide spins within the film. In this reduced, neutral radical state the number of unpaired electrons in the film was calculated to be  $6 \times 10^{14}$  (with up to 20% error in quantitative cwEPR). This is comparable to the number of electrochemically active TEMPO charges at  $8 \times 10^{14}$ , determined by integration of the reduction branch of the CV of the cell vs. time.

Upon increasing the oxidation potential, there is no significant change in the cwEPR spectra in the oxidation potential range between 0.3 V and  $\sim$ 0.8 V (region I). A representative cwEPR spectrum from region I, taken at an oxidation potential of 0.6 V, is shown in Fig. 5.1c, where the peak-to-peak line width is 1.4 mT. There is no significant change in the number of spins (spin count) contributing to the cwEPR spectra at all potentials in region I, as shown in Fig. 5.1b. The cwEPR signal intensity starts to decrease at 0.8 V, and from 0.85 V to 0.94 V (the maximum potential applied to this cell), the signal intensity drops sharply. The lowest spin count is observed at an oxidation potential of 0.94 V giving  $5 \times 10^{13}$  spins. This is an order of magnitude decrease in the number of unpaired electrons in the oxidized film as compared to its initial, reduced state.

Upon closer inspection, by averaging the cwEPR spectra in oxidized region II (between the potentials of 0.90 – 0.94 – 0.82 V), one clearly sees that the spectral shape has substantially changed from the initial region I spectrum. The region II averaged spectrum can be decomposed into two spectral components (see Fig. ??c) by simulating the spectra with the MATLAB toolbox EasySpin [107] (“garlic” function). Component 1 (“packed”) is again a broad Lorentzian derivative, similar to that of region I, but with an increased line width of 1.8 mT. Component 2 (“dilute”) is a fast-motion spectrum of tumbling nitroxides.

The presence of component 1 even at the oxidation potential of 0.94 V is at first unexpected, as at this potential the CV curve shows full TEMPO oxidation (cf. Fig. 3.9e for a representative CV in a tube for p-DiTS). We therefore suggest that component 1 corresponds to local islands of still densely packed spins, which are electrically disconnected from the rest of the film (and the electrodes) and hence not redox active. The line width of component 1 in region II at 1.8 mT is slightly broader than in region I, suggesting a change in the spin-spin couplings. Looking at the line width of component 1 at different oxidation and reduction potentials (cf. Fig. 4.12, ESI†), we clearly see a trend in that the line width increases from  $\approx$  1.3–1.4 mT in the beginning of region I to  $\approx$  1.8 mT by the end of region I, at 0.9 V. The reverse is true for region III, where the line width decreases from  $\approx$  1.8 mT at 0.9 V back to  $\approx$  1.3–1.4 mT at 0.3 V. Since the dipolar coupling between the spins should only decrease with increasing potentials (reducing spin count in the film) resulting in a decreasing line width, we expect the observed line width behavior (increasing line width when going from 0.3 V to 0.9 V) to be due to decreasing exchange coupling. As the film is oxidized, the spin density in it decreases. That reduces the exchange coupling between neighboring spins, which transforms an exchange narrowed spectrum (strong exchange coupling) into an exchange broadened spectrum (weaker exchange coupling). However, the spin concentration in the film cannot be decreased to a point where the hyperfine structure can be resolved.

Furthermore, since the component 1 spectra in region II are likely to be due to local islands of electrochemically inactive charged species, their spectral line width depends on the local spin concentration before the charges/islands become electrically inactive.

#### 4.3 p-DiTS in-operando redox series

---

It is unclear why the line width observed for component 1 is larger in region II, though possible reasons are weak cwEPR signals introduce a systematic error into the two-component spectral deconvolution, or the exchange narrowing effect is less pronounced at the decreased spin concentration, or there is a changing morphology during oxidation. The idea of electrically disconnected islands or domains will be further explored later on in this article.

The presence of component 2 (three-line feature described by an isotropic *g*-factor and hyperfine interaction) is, as discussed in Section ??, due to mobile nitroxide spins. The presence of a three-line component but no detectable five-line component suggests the nitroxide spins in electrolyte are not due to the release of monomers (as expected for this film because it underwent the cleaning procedure described in Section ?? to remove any non-polymerized DiTS). The three-line feature must therefore be due to molecular breakdown of DiTS to release mono-nitroxide fragments in the electrolyte.

We determine the spin counts for the components 1 and 2 by double integration of the simulation traces around 0.94 V. Component 1, the packed immobilized nitroxide spins, corresponds to a spin count of  $4.8 \times 10^{13}$  at 0.94 V (Fig. 5.1b, orange circles), while component 2, the dilute mobile nitroxide spins in electrolyte, corresponds to  $\approx 1 \times 10^{13}$  (Fig. 5.1b, blue triangles). The number of spins due to nitroxide groups dissolved in the electrolyte is only  $\sim 1.6\%$  of the total spins in the initial film (cf. total initial spin count of  $6.4 \times 10^{14}$ ). The number of nitroxide spins, which are still part of the film but not oxidized, is only  $\sim 7.5\%$  of the initial spin count. This shows that over 90% of the p-DiTS film is electrochemically active.

Looking at the oxidation series from 0.3 V to 0.94 V and the reduction series from 0.94 V back to 0.3 V, we see that the reduction occurs over a larger potential range as compared to the oxidation (cf. Fig. 5.1b). This suggests a changing morphology of the p-DiTS film upon oxidation, which decreases electrolyte access to the TEMPO groups in the film matrix. A similar trend is seen in thicker films, where again oxidation occurs over a narrower potential range than reduction (see Fig. 4.14, ESI†). This is a known phenomenon whereby, during oxidation, the pores and channels in the polymer film open and counter ions from the electrolyte enter the film matrix, aiding the oxidation process. During reduction, the opposite is true whereby the polymer film shrinks, and hence expulsion of counter ions slows down as a function of time. This results in a broadening of the left-hand side of the reduction branch in a CV and a slower recovery of the TEMPO spin count during the reduction series in quantitative in-operando cwEPR.

While the EPR signatures of different polymeric NiSalen complexes have been reported by Dmitrieva *et al.*,[20] we do not observe the EPR signature of the NiSalen backbone in our in-operando study of p-DiTS. Dmitrieva *et al.* noted that upon increased doping of the polymer (still one electron per monomer unit), the charges could aggregate to form diamagnetic states, and under high oxidation potentials the polymer could be doped with two electrons per monomer, thus also forming diamagnetic dications. An-

other plausible explanation for the absence of a p-NiSalen EPR signal could be related to low-intensity signals which are masked by the much more intense nitroxide signals. However, our quantitative EPR analysis of the number of spins per monomer unit in this film gave  $2.0 \pm 0.2$ , suggesting only signals corresponding to nitroxide radicals, as there are two unpaired nitroxides per DiTS monomer unit: in its charge-bearing groups. In addition, Coulomb repulsion between the positively charged TEMPO<sup>+</sup> groups in the oxidized state and the positive polarons on the backbone could lead to a depletion of mobile positive charge carriers and thus provide a credible explanation for the absence of a corresponding polaron EPR signal.

### 4.3.1 Spectral Simulations

### 4.3.2 Quantitative Analysis of Potential-Dependent EPR Spectra

The number of spins at each SoC was determined with quantitative cwEPR from the double integral of the cwEPR intensity calculated with the SpinCounting Toolbox [?] for Matlab [?]. The cwEPR spectra in Figure 4.16 were measured in a Bruker Elexsys E580 spectrometer equipped with an ER 4118 X-MD5 dielectric ring resonator with an unknown Q factor. To calibrate the intensity of the measured cwEPR signals and to determine the absolute number of spins in the film, we measured the cwEPR spectrum of the fully discharged film (SoC 0%) with a calibrated spectrometer. The calibrated spectrometer is a lab-built X-band cwEPR spectrometer equipped with a 9.4 GHz, 200 mW microwave source and a 4122-SHQE resonator. With  $Q = 6095$ , the absolute number of spins in the pDiTBuS film at SoC 0% was measured to be  $N = (6.9 \pm 0.4) \times 10^{15}$ . We used  $N$  to get the number of spins for other SoC from the spectra measured with the uncalibrated spectrometer. We assumed that the Q factor of the resonator remains the same for different SoC [?] and computed the corresponding numbers of spins from the doubly integrated spectral intensities.

The doubly integrated cwEPR spectral intensities for the pDiTBuS film in the four considered SoC relate to each other as 100:51:15:6 with the absolute number of spins of  $(6.9 \pm 0.4) \times 10^{15}$ ,  $(3.5 \pm 0.2) \times 10^{15}$ ,  $(1.1 \pm 0.1) \times 10^{15}$  and  $(3.8 \pm 0.4) \times 10^{14}$ , respectively. The respective ESOC are therefore  $(0 \pm 5)\%$ ,  $(49 \pm 3)\%$ ,  $(85 \pm 2)\%$  and  $(95 \pm 1)\%$ . Spin concentrations in the film are  $(5.3 \pm 2.7) \times 10^{20}$ ,  $(2.7 \pm 1.4) \times 10^{20}$ ,  $(0.8 \pm 0.4) \times 10^{20}$  and  $(0.3 \pm 0.2) \times 10^{20} \text{ cm}^{-3}$ , respectively. Integration of the cyclic voltammogram yields  $(2.3 \pm 0.8) \times 10^{16}$  electrons in the reduced state.

## 4.4 EPR-Detected State Of Charge

The SoC of the film determined with Coulomb counting were compared to quantitative cwEPR to directly relate the number of charges, injected into the film upon charging, to the number of paramagnetic centres in it. We refer to the fraction of spins removed from the fully discharged film to reach a given SoC as the EPR-detected state of charge, or ESOC. The fully discharged film has the maximum number of spins and its ESOC is 0%. ESOC at other SoC are determined as the fraction of the missing spins with respect to ESOC 0%. ESOC of 95% thus corresponds to the oxidation state where only 5% of the initially present spins are left in the film. The cwEPR spectra were recorded for the listed SoC, and the corresponding numbers of spins were calculated from the double integrals of the spectra. The integrated spectra and the experimental details are shown in the ESI, Section ???. The injected charges, detected spins and ESOC values are counted for each SoC in Table 4.1. The average spin concentration in the film  $\langle n \rangle$  at each ESOC was calculated from the corresponding number of spins and the estimated volume of the film of  $(1.3 \pm 0.6) \times 10^{-5} \text{ cm}^3$ .

E [mV]	SoC	ESOC	capacity drawn [\mu Ah]	charges injected	spins detected	$n_C$ [ $\text{cm}^{-3}$ ]	$\langle n \rangle$ [ $\text{cm}^{-3}$ ]	C [ $\text{cm}^{-3}$ ]
590 ± 5	98%	(95 ± 1)%	0.020 ± 0.005	$(5 \pm 1) \times 10^{14}$	$(4 \pm 1) \times 10^{14}$	$(3 \pm 2) \times 10^{19}$	$(3 \pm 2) \times 10^{19}$	$> 1 \times 10^{19}$
500 ± 5	96%	(85 ± 2)%	0.060 ± 0.005	$(1.4 \pm 0.1) \times 10^{15}$	$(1.1 \pm 0.1) \times 10^{15}$	$(1.0 \pm 0.5) \times 10^{20}$	$(8 \pm 4) \times 10^{19}$	$> 3 \times 10^{19}$
430 ± 5	65%	(49 ± 3)%	0.480 ± 0.005	$(1.07 \pm 0.01) \times 10^{16}$	$(3.5 \pm 0.2) \times 10^{15}$	$(8 \pm 4) \times 10^{20}$	$(3 \pm 2) \times 10^{20}$	—
-200 ± 5	0%	(0 ± 5)%	1.360 ± 0.005	$(3.05 \pm 0.01) \times 10^{16}$	$(6.9 \pm 0.4) \times 10^{15}$	$(2 \pm 1) \times 10^{21}$	$(5 \pm 3) \times 10^{20}$	—

Table 4.1: EPR-detected state of charge, Coulomb counting and the corresponding spin concentrations in a galvanostatically discharging pDiTBuS film with  $I = -10 \mu\text{A}$ . The electric potential of the film  $E$  was measured with respect to the Ag/AgNO<sub>3</sub> RE. The number of injected (negative) elementary charges and the corresponding concentration of charges  $n_C$  were determined from the drawn capacity. The average spin concentration  $\langle n \rangle$  is the ratio between the number of spins measured with quantitative cwEPR and the volume of the film determined by integrating the cyclic voltammogram.  $C$  is the local spin concentration in the film estimated with pEPR as described in text.

### 4.4.1 Formation of Singlet Spin States in a Reduced Cathode Film

The number of electrons left in the film were determined with the Coulomb counting from the galvanostatic discharge curves shown in Figure 3.13. The number of electron spins detected with cwEPR is close to the Coulomb counting for high SoC, that corresponds to lower spin concentrations. However, for low SoC, the difference in the number of electrons measured with the Coulomb counting and with quantitative cwEPR is dramatic: up to 70% of the electrons in the discharged film are EPR silent. The absence of cwEPR signal from the majority of the electrons indicates that their spins pair up in singlet (S=0) EPR silent states. The singlet spin pairs follow Bose statistics and

can occupy the same quantum state which is favorable for the charge transport. The formation of singlet states was detected only in low SoC.

## 4.5 Monitoring of Degradation Processes

The operando monitoring of EPR spectra in pDiTS cells has revealed that the amount of paramagnetic species reduces upon the cycling. The cwEPR spectra during one charge-discharge cycle of two different pDiTS cells are shown in Figure ?? . Both datasets show a significant amount of the three-line structure in the oxidised (fully charged) state, that corresponds to the release of dilute nitroxide radicals from the polymer film to the electrolyte. The fact that the released species exhibit a 3-line structure and not a 5-line structure excludes the release of the di-TEMPO (DiTS) monomers and suggests that individual TEMPO<sup>•</sup> fragments are being detached from the film. Therefore, it was found that it is the molecular degradation of DiTS that is responsible for the loss of cell's capacity and not the decomposition of the polymer film into the monomer fragments. The overall EPR signal intensity decreases for both samples after the charge-discharge cycle. The spectral deconvolution with quantitative analysis of the individual components has revealed that the released fragments do not explain the overall loss of the signal intensity after the cycle.

ORBs based on p-DiTS were shown to lose their capacity under repeated charge-discharge cycling,[?] but the mechanism of degradation is not yet understood on the molecular level. In order to study the processes occurring during degradation, we recorded CV curves along with cwEPR spectra during charge-discharge cycling of a tube-based p-DiTS electrochemical cell.

For this purpose, a  $400 \pm 50$  nm thick p-DiTS film (Fig. 6.2d, ESI†) was deposited onto the on-substrate WE. The cell was inserted into the microwave resonator of the cwEPR spectrometer at  $H \approx 12$  mm where it underwent a series of 36 charge-discharge cycles at a rate of  $5 \text{ mV s}^{-1}$ . The CV curves were recorded for each cycle. The cwEPR spectra were recorded after each fourth cycle for the fully reduced/discharged cell, that is at the left-most point on the corresponding CV.

Fig. 5.6 shows the cwEPR spectra (a) and the CV curves (c) measured during the repeated cycling of the electrochemical cell. During the cycling, the CV curves decrease in intensity, indicating a decrease in the number of the electrochemically active charges in the film. The number of electrochemically active charges was determined for each cycle by integrating the reduction branch of the corresponding CV. It is plotted together with the quantitative EPR results, labeled as "CV" in Fig. 5.6b. The spectra, CV and quantitative analysis for the intermediate cycles are shown in Fig. ?? (ESI†).

The cwEPR spectra in Fig. 5.6a demonstrate an initial release of the dilute component and a decrease in intensity upon further cycling. The three-line dilute component

## 4.5 Monitoring of Degradation Processes

---

corresponds to TEMPO<sup>•</sup> fragments that detach from the film in the reduced state and get released to the electrolyte. The dilute component is emerging only during the first eight cycles. Meanwhile, the amplitude of the CV (cf. Fig. 5.6c) stays as high as 100 µA during the first eight cycles. This suggests that the initial release of the reduced, EPR-active TEMPO fragments does not significantly affect the capacity of the cell and can be excluded as the main degradation pathway.

The broad, single-line packed component, on the contrary, keeps decreasing for >8 cycles, together with the CV. Therefore, the degradation of the electrical capacity of the p-DiTS film has to be associated with the decrease in the signal intensity of the packed component and is not accompanied by the release of any EPR-active products to the electrolyte.

The number of paramagnetic states in the film after each degradation step, as determined by a quantitative analysis of the respective spectral components, is shown in Fig. 5.6b along with the number of electrically active charge carriers. For the fresh film (“0 CV”), the quantitative EPR and CV results are in good agreement. In contrast, there is a significant difference after 36 cycles. This experimental observation can be rationalized as follows.

All cwEPR spectra in Fig. 5.6a were recorded when the film was brought to the reduced state, with all electrochemically active TEMPO<sup>•</sup> fragments being also EPR active. Additionally, all electrochemically inactive fragments that happen to be in the reduced, TEMPO<sup>•</sup> state also contribute to the cwEPR signal. Thus, the cwEPR signal after each charge-discharge cycle contains contributions from *electrochemically active* and *electrochemically inactive* TEMPO<sup>•</sup> fragments, and both components contribute to the overall number of spins shown in Fig. 5.6b.

The intensity of the packed spectral component substantially decreases with cycling. This indicates that some paramagnetic parts of the film (TEMPO<sup>•</sup>) become diamagnetic (TEMPO<sup>+</sup>) and stay EPR silent when the cell is brought back to the reduced state. These fragments may either stay in the film or to be released into the electrolyte. As a previous study reported no loss of mass of a p-DiTS film in a microbalance-monitored charge-discharge cycling, [?] we assume that the oxidized and electrically disconnected, EPR silent fragments do not leave the film.

Upon cycling, the number of electrochemically active charged species decreases stronger than the number of paramagnetic states (Fig. 5.6b). This indicates that some regions of the film become redox inactive upon cycling but still contribute to the EPR spectrum. These TEMPO<sup>•</sup> fragments lose the electrical connection to the rest of the film (and thus to the metal electrode) and stay in the reduced state. The possible degradation of a p-DiTS film leads to the interruption of a conductivity pathway, resulting in the formation of electrically isolated domains within the film. We suggest that these isolated domains are also responsible for the remaining packed EPR signals observed for the nominally fully-oxidized film in the in-operando redox measurement (Fig. 5.1).

The degradation of p-DiTS cells was monitored simultaneously by cwEPR and cyclic voltammetry. The number of paramagnetic species in the cells was changing during the degradation cycling. That change was quantified from both EPR and electrochemistry perspective. Quantitative analysis of the simulated components comprising the cwEPR spectra was done with the SpinCounting Toolbox[?] (developed by Christopher Engelhard) in Matlab. Cells with the electrolyte exhibit weaker signals as compared to the dry films, so an intensity scaling factor was determined and taken into account.

The CV curves during the degradation of the cells were quantitatively analyzed. The reduction branches were integrated versus time to obtain the charge transferred to the film at each degradation cycle. The integrals are shown in 4.20. The total transferred charge during the reduction of the film is a three-electron process,[?] where two electrons are transferred to the TEMPO groups and one electron is transferred to the backbone. Therefore, the number of electrons transferred to TEMPO is 2/3 of the total charge transferred to the film divided by the elementary charge. With that, the number of electro-chemically active TEMPO groups was determined at each degradation cycle.

We observed two pathways of the degradation of p-DiTS: the release of paramagnetic nitroxide fragments and the overall decrease in the cwEPR signal after a charge-discharge cycle, that is connected to the formation of diamagnetic, or oxidized, electrically isolated domains within the film. The latter may, possibly, be accompanied by a release of the diamagnetic fragments to the electrolyte.

While the cell in 4.14 a almost fully recovers its initial signal intensity, the cell in Fig. 4.14 b loses 51% of its initial spin count after being reduced back to its paramagnetic state (from 8.0E+15 spins to 3.7E+15 spins, cf. Fig. 4.14, bottom subplots for the spin count data). That indicates, some fragments have lost electrical connection to the rest of the film, and stayed in an oxidized, diamagnetic state. The dramatic decrease in spin count can be accounted for by the disappearing "dilute" component only partially, as the dilute component yields maximum 2.7E+14 spins (at 600 mV) which is only 3% of the total spin count. The remaining 48% of missing spins can not be explained by the release of paramagnetic fragments. We propose that some fragments of the film are losing connection to the film during the oxidation process. These EPR silent, oxidized nitroxide fragments may stay in the film or may leave it. That process is observed only indirectly as a change of the overall EPR signal intensity, when the cell undergoes a full charge-discharge cycle.

## 4.6 Monitoring of Self Discharge

Organic Radical Batteries have a tendency to self-discharge, as the organic electrochemically active layer partially dissolves in polar electrolytes. Particularly for the TEMPO containing ORB, the dissolved, mobile TEMPO fragments serve as redox shuttles that carry the charge between the battery electrodes and cause a self discharge. The amount of unoxidized TEMPO<sup>•</sup> shuttles can be measured with cwEPR spectroscopy as the mobile fragments have distinct spectra as compared to the fragments tightly packed in the electrode. Further in this subsection operando spectra of a TEMPO containing electrochemical cells are shown. Quantitative analysis of the released fragments during a charge-discharge cycle allows for a description of the self-discharge process in an ORB. The charge state of a battery is monitored with cwEPR and, additionally, with a potentiometric measurement to identify the self-discharge rate and to connect it with the concentration of diffusing redox shuttles. Figure 4.21 represents a gradual change in the cwEPR intensity of a self-discharging tube-based cell with a pDiTS cathode. The cell was initially discharged to  $V_{OC} = 350$  mV and then charged to  $V_{OC} = 1300$  mV, at that point the minimal cwEPR intensity was registered. The cell was left under the open circuit condition. After  $t = 500$  s, the cwEPR signal of the cell has fully recovered, that corresponds to the complete reduction of the electrochemically active nitroxide radicals in the cathode film.

## 4.7 Low Temperature Measurements

While in-operando SEC cwEPR provides information about redox systems in their natural operating environment, these measurements are limited by the time for which potentials can be applied before degradation of the active materials is observed. In contrast, in ex-situ experiments on cells without electrolyte, the desired redox states of the films can be observed for longer times without degradation effects. Additionally, ex-situ measurements can be performed at cryogenic temperatures, which drastically increases the EPR signal intensity.

### 4.7.1 p-DiTS

For the p-DiTS cells, in-operando SEC cwEPR measurements were carried out at room temperature while holding the cell at redox potentials of interest for ~200 seconds during the accumulation of the cwEPR spectra. The S/N for this setup is limited by the time available to acquire EPR spectra and by the low spin polarization at room temperature. We therefore perform ex-situ measurements on a 95 deposition cycle ( $t = 400 \pm 40$  nm) film at cryogenic temperatures, in this case at 150 K. These ex-situ measurements involved bringing the cell to the chosen redox potential using the setup shown in Fig. 3.9c,

outside the spectrometer. The potential was applied for 100–200 seconds. Then the electrodes were disconnected from the cell. Subsequently, the substrate with the on-substrate electrodes was placed in a standard 5 mm OD quartz tube filled with N<sub>2</sub> gas and sealed using a septum and Parafilm to prevent condensation of water in the tube. This method can hold the cell in different redox state regions but not necessarily the exact set redox potentials, as the charge seems to equilibrate to different overall states. This was determined by comparison of our ex-situ cwEPR results and spectral simulations to in-situ spectra shown in Ref. [20]. The aim of the ex-situ measurement was to reach representative redox states which were also seen in the in-operando measurements (Fig. 5.1), i.e. fully reduced, partially oxidized and fully oxidized states, with a higher S/N.

We therefore measure the ex-situ SEC cwEPR at different oxidation potentials, three of which are shown in Fig. 4.23a. At 0.1 V the p-DiTS film is in the reduced state and exhibits a one-line feature corresponding to densely packed spins. At 0.6 V and 0.9 V the overall signal decreases significantly and a similarly broad yet distinctly different signal appears. The signal at each of the three potentials has contributions from the nitroxides/TEMPO groups in two distinctly different environments. The broad one-line feature arising from densely packed dipole and exchange coupled nitroxide spins, and dilute immobilized nitroxide spins, described by a rhombic *g*-tensor. We can simulate the measured spectra at each oxidation potential using EasySpin [107] (“pepper” function), assuming a combination of packed and dilute contributions with changing relative weights. We find that with increasing oxidation potential the one-line packed nitroxide feature decreases, but the intensity of the dilute immobilized nitroxide does not change. The film in this ex-situ study did not contain any electrolyte, so both spectral components correspond to the nitroxide spins in the film. The spins may be situated either on mono-TEMPO fragments or di-TEMPO DiTS, but with the nitroxide groups situated far apart, resulting in a small exchange coupling and hence three instead of five lines in the spectrum. This suggests that the p-DiTS films have some nitroxide spins which are not electrochemically active yet are still a part of the film structure, again suggesting domains of electrochemically inactive spins – except this time in the paramagnetic state.

#### 4.7.2 p-NiMeOSalen

During the in-operando and ex-situ SEC cwEPR measurements of p-DiTS (cf. Fig. 5.1 and Fig. 4.23a), we observed no signals associated with polarons on the NiSalen backbone. In contrast, Dmitrieva *et al.* have shown that polymeric NiSalen films are redox active and indeed exhibit EPR signals during in-situ SEC cwEPR measurements.[20] In order to examine whether we can detect EPR signals from polarons on the backbone, we measured SEC cwEPR of p-NiMeOSalen, which closely resembles the core backbone structure of p-DiTS but does not contain any TEMPO pendant groups.

The cwEPR spectra recorded at 150 K are shown in Fig. 4.23b for a few key poten-

## **4.8 Pulsed EPR spectroscopy of TEMPO-Salens**

---

tials, while the full data set is shown in Fig. ?? (ESI†). We observe clear EPR signals that can be attributed to different paramagnetic species on the polymer backbone with the weights of the individual spectral components strongly depending on the applied potential. Simulations for three EPR-active species consistent with those reported in Ref. [20] (denoted by “Signal 1”, “Signal 2” and “Signal 2’”) are shown along with the measured spectra. Details about the change in the EPR signal as a function of the oxidation potential as well as the spectral simulations can be found in Section ?? (ESI†).

Based on the p-DiTS and p-NiMeOSalen ex-situ studies it is clear that both the TEMPO and NiSalen backbone are redox active, as expected. However, we neither see backbone-related EPR signals in the room-temperature in-operando measurement (Section ??) nor in the low-temperature ex-situ experiment (Fig. 4.23a) performed on p-DiTS films. The reason for the absence of a clear NiSalen signal in p-DiTS is possibly related to the formation of diamagnetic species or the depletion of polarons on the backbone due to Coulomb repulsion as mentioned before.

### **4.7.3 Tube Based Cells**

## **4.8 Pulsed EPR spectroscopy of TEMPO-Salens**

### **4.8.1 Pulsed EPR Spectra of TEMPOL solutions**

In a glassy, frozen solution of TEMPOL, the distance between the TEMPO radicals is controlled by the concentration of the solution. With the increasing concentration, the relaxation times shorten significantly, as the distance between the radicals decreases, which intensifies the inter-spin interactions and leads to a faster in-plane dephasing of the excited spins.

### **4.8.2 Pulsed EPR Spectroscopy of a charged pDiTBuS Cathode film**

While it is highly desirable to perform in-situ cwEPR experiments on electrochemical cells and fully processed batteries under ambient conditions at room temperature, most pulse EPR measurements performed on battery-relevant materials require low temperatures, primarily to increase spin-relaxation times. The necessity for low-temperature measurements already precludes the use of conventional flat cells in combination with cylindrical resonators.[?, ?]

Recently, successful pEPR measurements performed on batteries based on inorganic, lithium-containing electrode materials in an X-band dielectric ring resonator were reported,[?] clearly showing that pEPR experiments are indeed feasible and can provide insights into the kinetics of processes occurring on the electrodes upon fast charg-

ing. However, the cell geometry used in Ref. [?] only allows for room-temperature measurements. We believe that the possibility of performing low-temperature pEPR measurements is the key to a widespread use of pEPR techniques for polymer battery research, providing access to the full arsenal of advanced echo-detected pEPR experiments. Our versatile on-substrate electrode setup (see Section 3.5.1) readily allows for low-temperature pEPR experiments.

As a first step, we sought to perform pEPR measurements on an oxidized p-DiTS film in order to detect electrochemically inactive nitroxide radicals. For this purpose, a p-DiTS cell was brought into its fully charged state at 900 mV vs. Ag/AgNO<sub>3</sub> and kept at this potential while the electrolyte was removed and the sample was thoroughly dried. The substrate was subsequently flame-sealed in a helium-filled quartz tube. The cwEPR spectrum measured at  $T = 80$  K (Fig. 4.27a) is indicative of immobilized, isolated nitroxides[?] and clearly deviates from the broad and unstructured single-line spectrum observed for a reduced p-DiTS film at room temperature (Fig. 5.1c) and at  $T = 150$  K (Fig. 4.23a). This confirms that the charge state of the of the p-DiTS film is indeed preserved in the electrically disconnected sample without electrolyte.

Next, we performed low-temperature pEPR measurements using the standard Hahn Echo sequence ( $\frac{\pi}{2} - \tau - \pi - \tau - \text{echo}$ ). The resulting echo-detected field-sweep spectrum is shown in Fig. 4.27a along with the cwEPR spectrum measured under identical conditions. Based on the overall shape and width of the spectrum, which is given by  $2A_{zz}$  with  $A_{zz}$  being the  $z$  component of the hyperfine tensor, we can unambiguously attribute the resonant signal to immobilized nitroxides. However, the pEPR spectrum differs from the usual TEMPO powder spectrum. Most notably, the relative intensity of the central ( $m_I = 0$ ) peak is significantly lower than expected. Echo-decay measurements reveal that the spin-spin relaxation times  $T_2$  (Fig. 4.27b) are comparable for all three  $m_I$  components, suggesting that anisotropic relaxation is not the main reason for the reduced intensity of the central peak. On the other hand,  $T_2$  is at least one order of magnitude shorter than for isolated nitroxides, indicating that spin-spin coupling significantly influences  $T_2$  for the paramagnetic centers in the oxidized p-DiTS film.

Further measurements will help identifying the main factors responsible for the peculiar shape of the pEPR spectrum, among them possible partial ordering of the TEMPO groups in the p-DiTS film, (restricted) motion of the nitroxides even at low temperatures and/or the existence of redox-inactive sites in different microscopic environments associated with dissimilar relaxation properties.

The pEPR spectrum in Fig. 4.27a is likely a result of the same electrochemically inactive dilute spins observed in the ex-situ p-DiTS redox series (Fig. 4.23). Potential dependent SEC pEPR measurements are ongoing to confirm this hypothesis, and ELDOR and hyperfine spectroscopy could lead to critical information about the local environment which causes these spins to be electrochemically inactive. These advanced pEPR methods could further give insight into degradation mechanisms in p-DiTS and

## 4.8 Pulsed EPR spectroscopy of TEMPO-Salens

---

other ORB materials. Realization of SEC pEPR, particularly on film electrodes, makes these techniques available for other research field such as the study of hydrogenases and enzymes or metal catalysis.

### **4.8.3 Field Swept Echo of a charged pDiTBuS Cathode film**

### **4.8.4 Instantaneous Diffusion in Charged pDiTBuS**

We have seen that the ESOC has a strong influence on the shape of the EDFS spectra. Furthermore, the EDFS spectra of pDiTBuS are quite different from the reference spectrum of TEMPOL in a dilute frozen solution.

In Section /// it is shown that in a densely packed radical system, as in a TEMPO-Salen cathode film, the phase memory time can be shorter than  $T_m \leq 100$  ns. That is, the spin echo is decaying by  $e \approx 3$  times at  $t = 100$  ns. The short phase memory time limits the duration of the pulse sequence at which the echo is detectable. For a  $\pi/2 - \tau - \pi - \tau - \text{echo}$  sequence, with a hardware limitation on  $\tau \geq t_d \approx 100$  ns, the shortest realizable pulse sequence becomes longer than  $t > 200$  ns. By this time, the spin echo decreases by  $e^2 \approx 7$  times and may be comparable to noise. The limitations imposed by the finite  $T_m$  and  $t_d$  force one to use shorter microwave pulses.

A short microwave pulse may have a spectral width comparable to the width of the observed spectrum. According to the Fourier theorem, the spectral width of a pulse is inversely proportional to the pulse length:  $\Delta\omega \sim 1/t_p$ . A spectrum of a 100 ns long rectangular pulse shown in Figure /// is //MHz wide (FWHM).

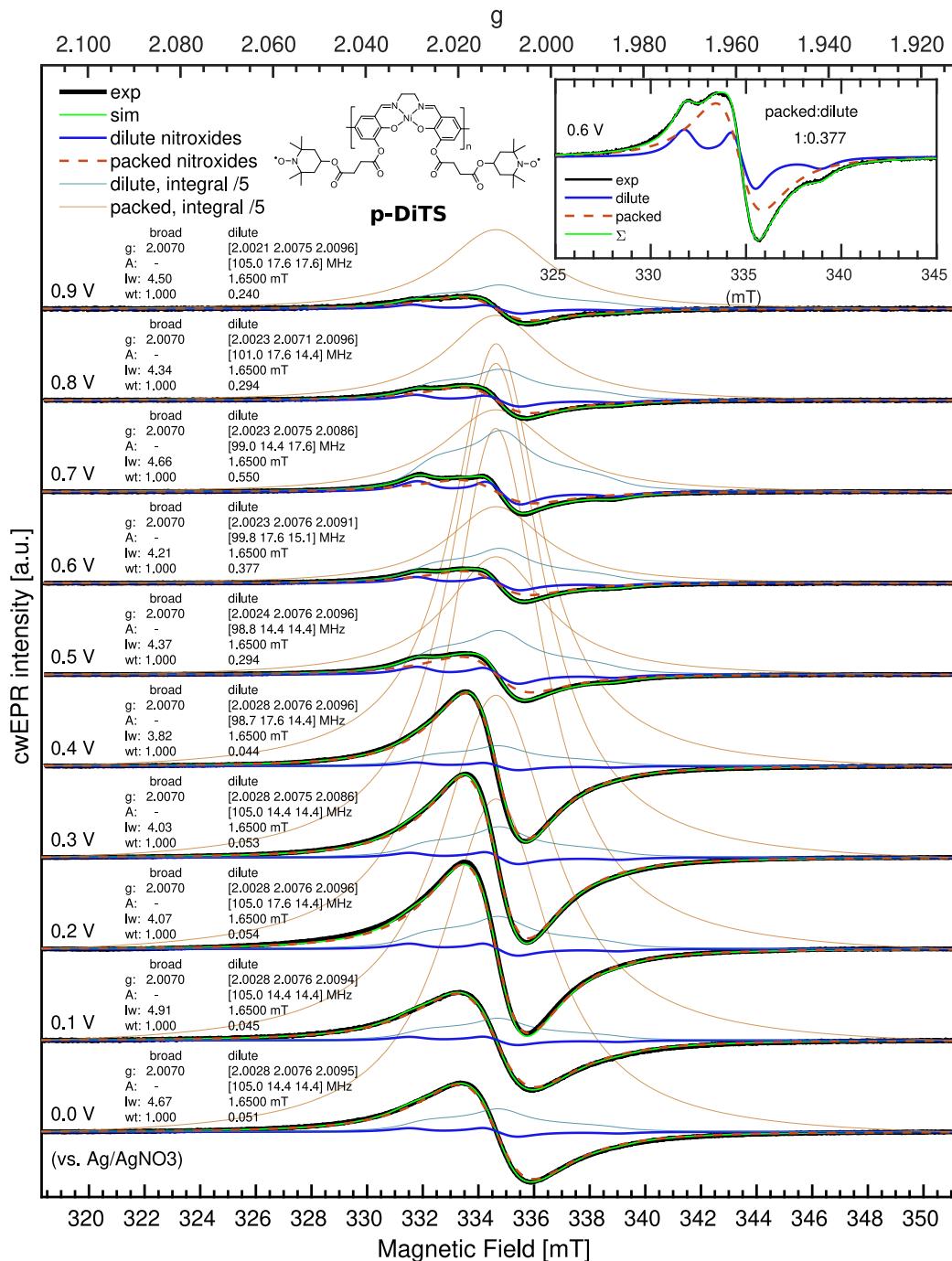


Figure 4.8: Ex-situ SEC cwEPR measurements ( $\nu = 9.4$  GHz) on a dry p-DiTS film at 150 K. Decomposition of spectra into two components with numeric simulations using EasySpin [?]: a broad Lorentzian line ( $g = 2.0070$ ,  $Iw = 4.63 \pm 1.00$  mT) and a dilute component with a hyperfine coupling to  $^{14}\text{N}$  ( $I = 1$ ,  $g = [2.00231 2.00711 2.00912]$ ,  $A = [100 15 15] \pm 5 2 2$  MHz, Lorentzian broadening with  $Iw = 1.65$  mT). The absorption profiles are shown with the integrals of the EPR signals. The ratio between the simulated components for each potential is shown by the double integrals of the components. Inset: sum of the broad and dilute components that reproduce the line shape at 0.6 V.

#### 4.8 Pulsed EPR spectroscopy of TEMPO-Salens

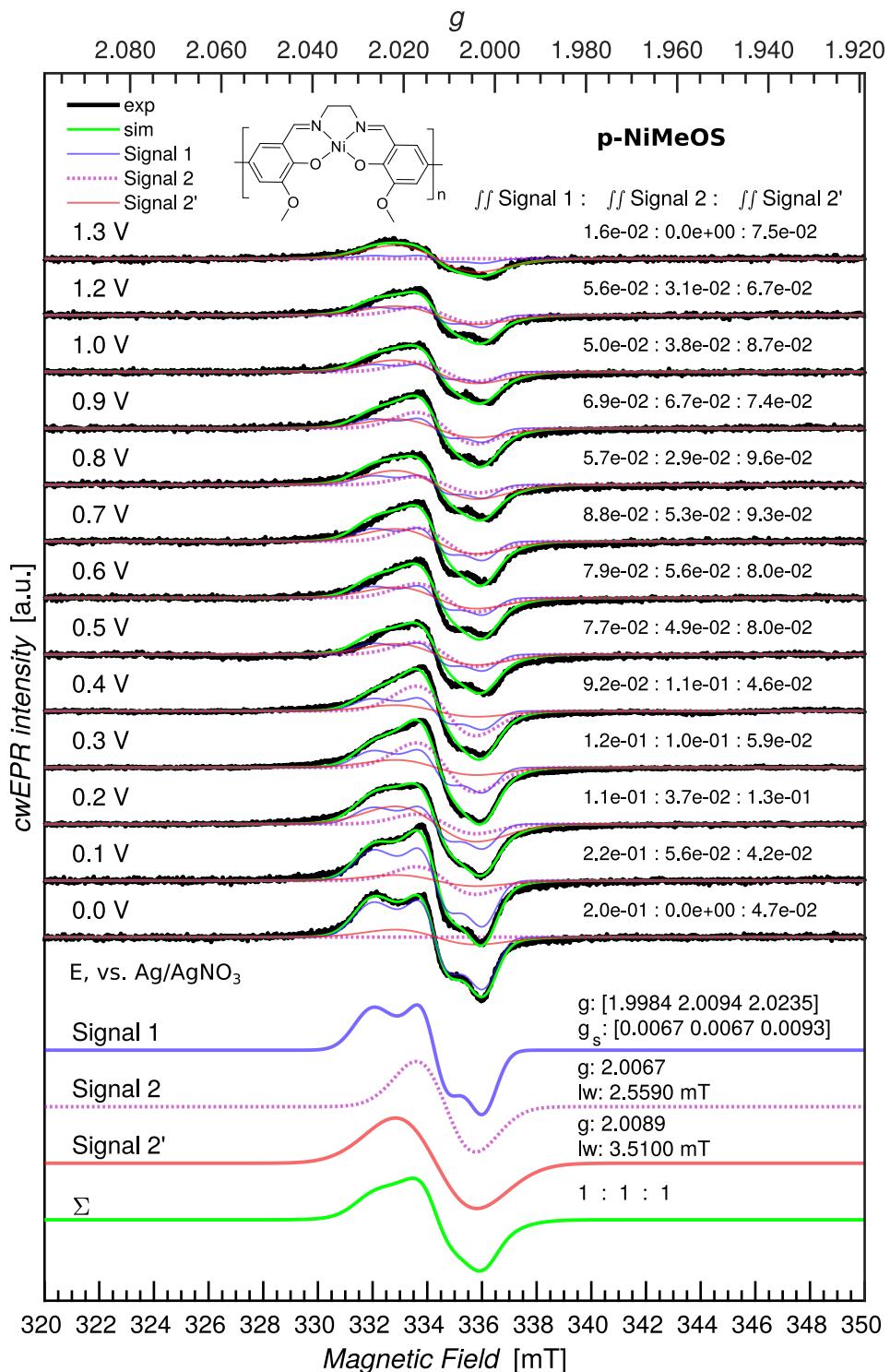


Figure 4.9: Potential-dependent cwEPR spectra of a NiMeOSalen film measured at 150 K. Simulation of the spectra with three components reported by the Timonov group.

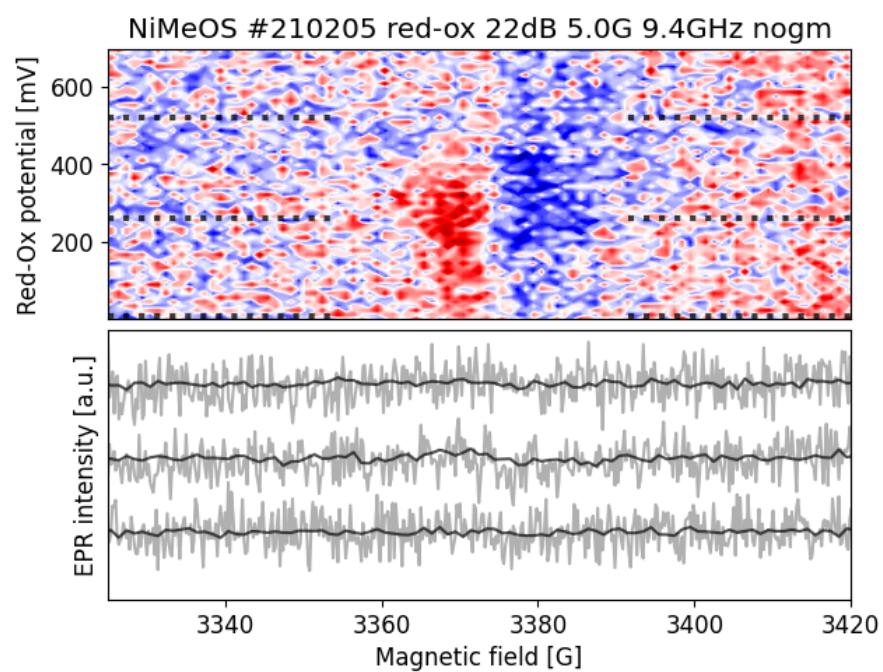


Figure 4.10: Potential-dependent operando cwEPR spectra of a NiMeOSalen cathode film measured at room temperature.

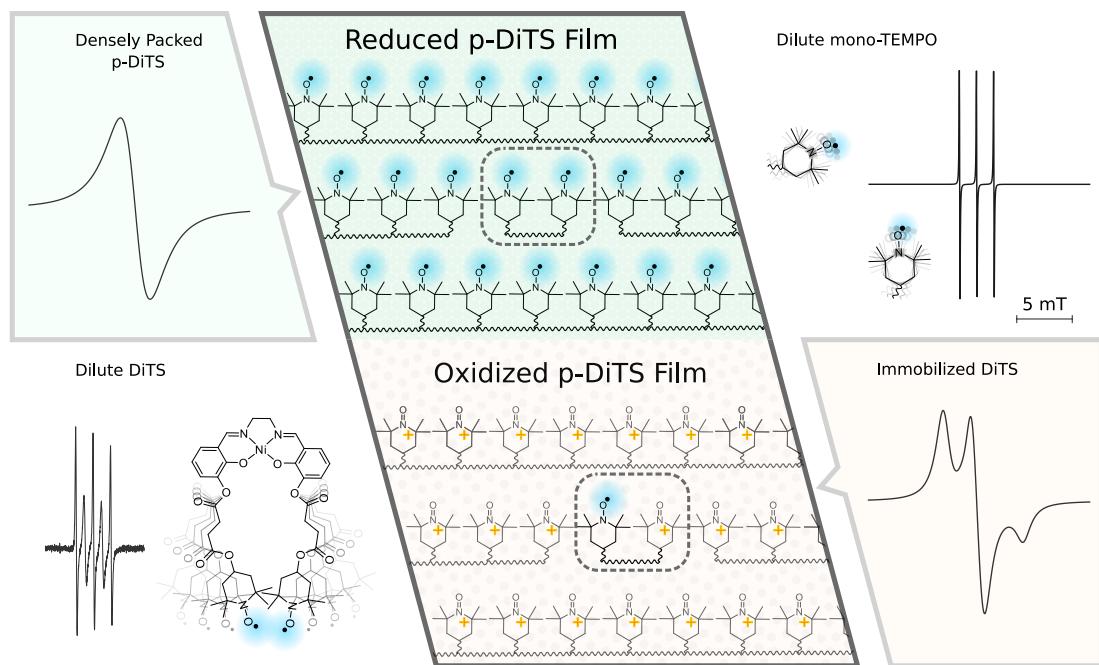


Figure 4.11: Classification of the nitroxide cwEPR spectra observed for p-DiTS under different conditions and in different environments. a): Densely packed nitroxide film with dipolar broadening and exchange narrowing or broadening giving a single derivative line. b): Typical spectrum of dilute mono-nitroxide in solution, three-lines due to  $S = 1/2, I = 1$   $^{14}\text{N}$  hyperfine interaction (described by isotropic  $g$ -factor and isotropic hyperfine ( $A$ ) interaction). c): Typical spectrum of tumbling di-nitroxide in solution where dynamic changes in the nitroxide – nitroxide distance modulate the exchange interaction yielding a five-line structure with alternating line width (measured cwEPR of DiTS monomers in solution at room temperature). d): Immobilized nitroxide spectrum with both  $g$  and  $A$  anisotropy.

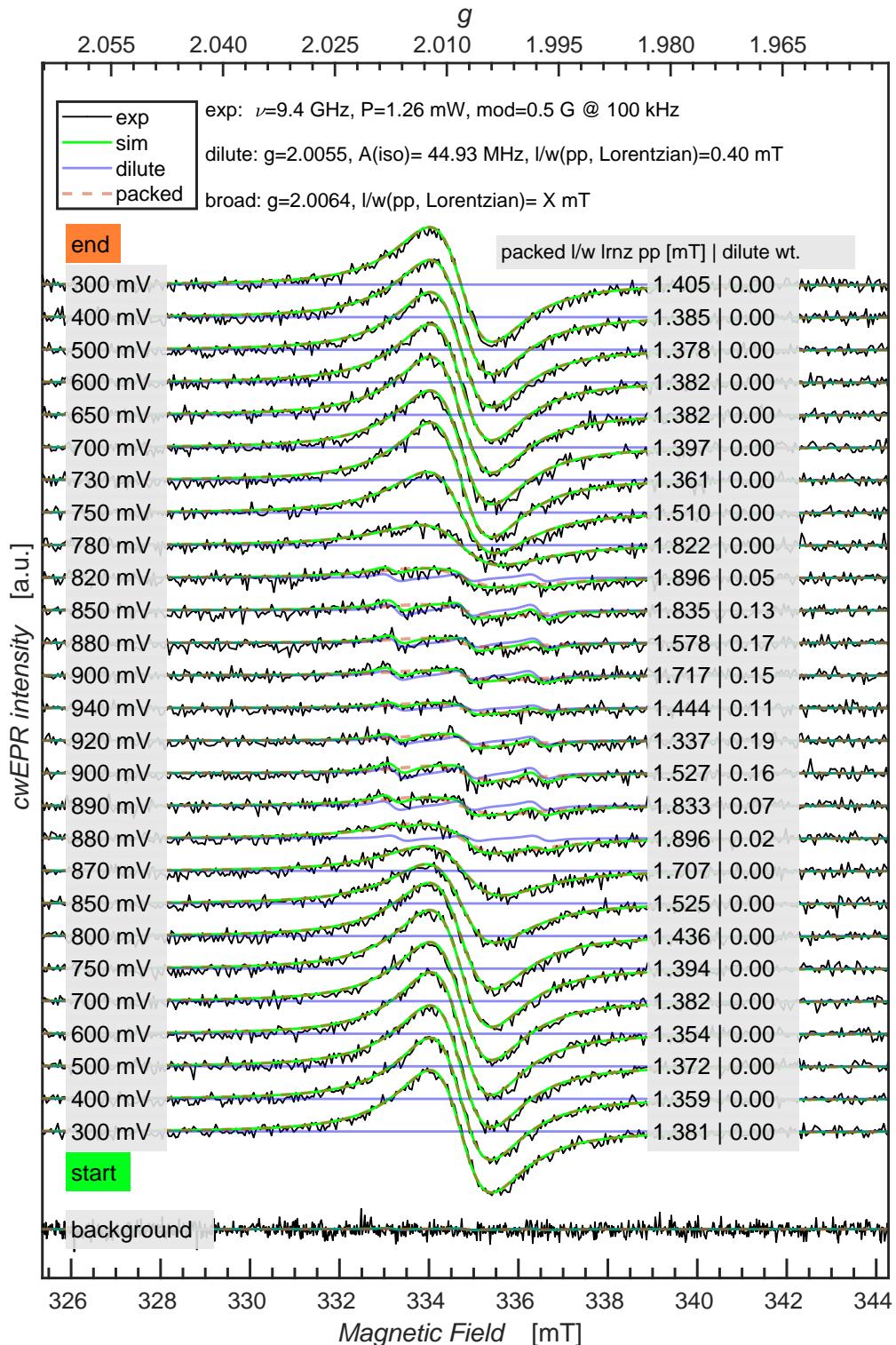


Figure 4.12: Room temperature in-operando SEC cwEPR on a 8-CV p-DiTS film.  $\nu = 9.4$  GHz. black - experimental spectra, green - simulation consisting of two components with relative weight as shown in the plot, dashed-red - component 1 the coupled spins in the film, blue - component 2 the dilute mobile spins in electrolyte. All simulation done using Easyspin.[107]

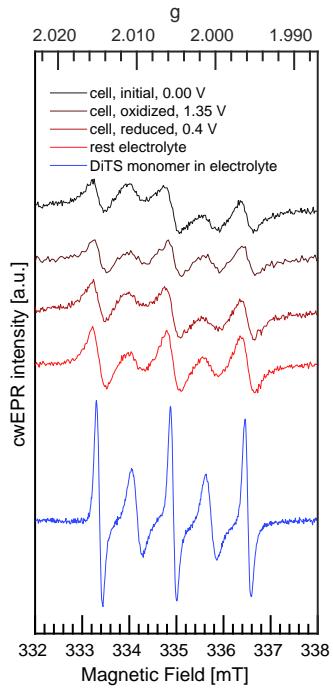


Figure 4.13: Top: Room temperature SEC cwEPR on 150-CV p-DiTS film.  $\nu = 9.4$  GHz. This film has not undergone the cleaning/rinsing procedure and therefore as expected we see spectral signatures of the DiTS monomer which is released into the electrolyte and exhibits a five-line structure characteristic of di-tempo systems with changes in the exchange coupling associated with changes in the nitroxide – nitroxide distance. This figure shows the primary release of monomeric DiTS from a raw p-DiTS film into electrolyte (Modulation amplitude 0.1 mT – overmodulated). Bottom: cwEPR of DiTS monomer in electrolyte 100  $\mu\text{M}$  concentration at room temperature for comparison (Modulation amplitude 0.02 mT).

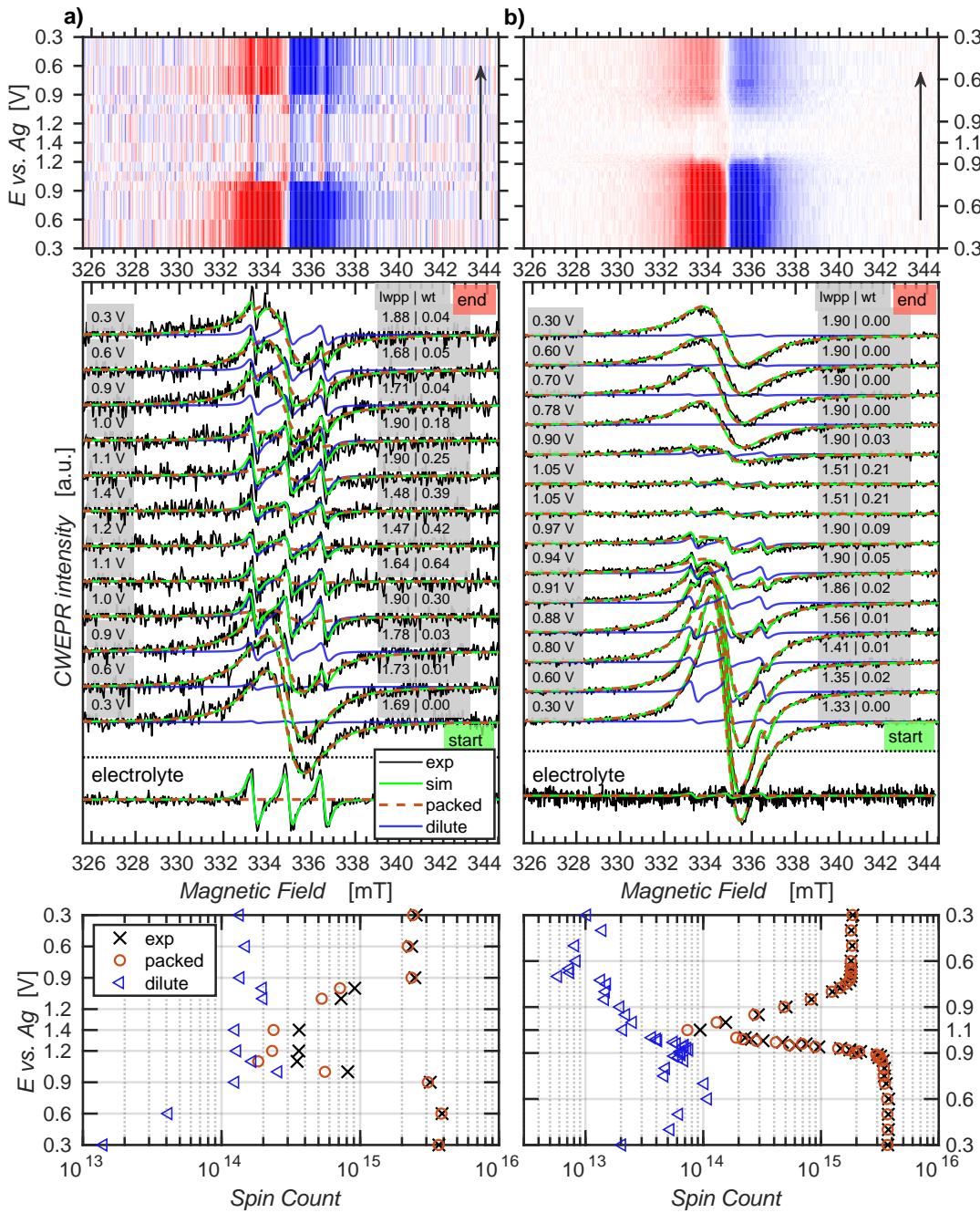


Figure 4.14: Room-temperature in-operando cwEPR measurements for two p-DiTS electrochemical cells.  $\nu = 9.4$  GHz. Two-component spectral deconvolution to identify dilute and packed nitroxide fragments. Spectrum of the rest electrolyte. a): Cell with a p-DiTS film grown by 150 deposition cycles ( $t \approx 400$  nm) that was left untreated and underwent one charge-discharge cycle before the measurement. The dilute component is released during the oxidation and remains detectable in the rest electrolyte. b): Cell with a p-DiTS film grown by 200 deposition cycles ( $t \approx 500$  nm) that was rinsed in solvents and cycled in the electrolyte to remove the not polymerized nitroxide fragments. The initially released dilute component is electrochemically active and does not appear in the rest electrolyte.

#### 4.8 Pulsed EPR spectroscopy of TEMPO-Salens

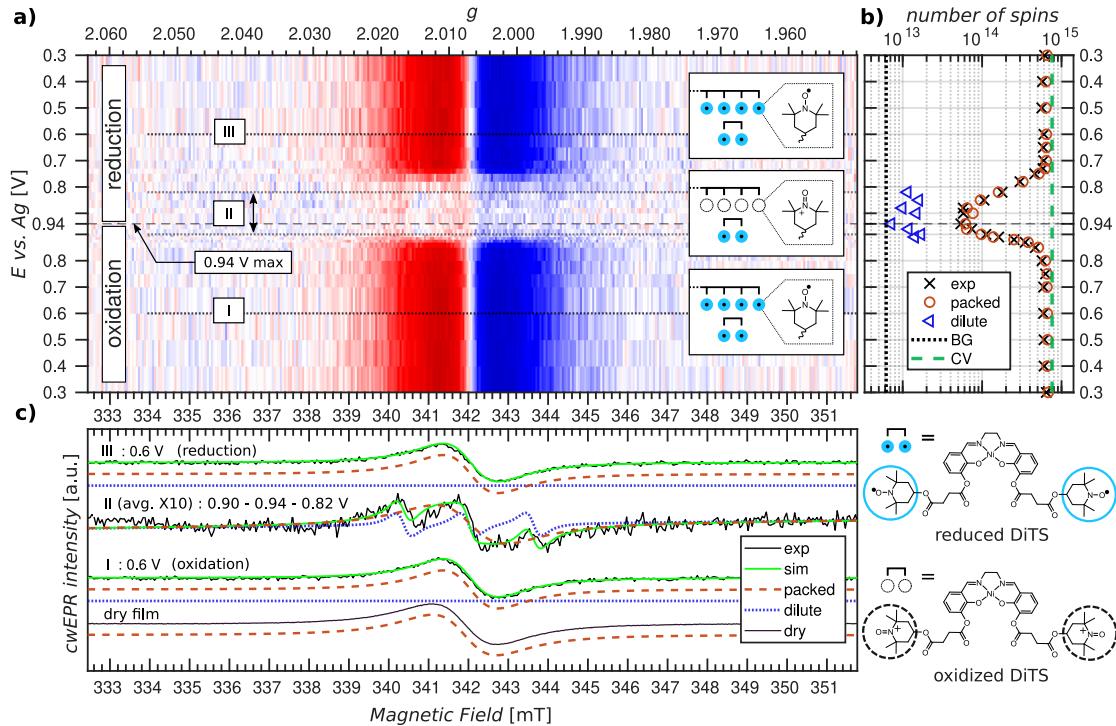


Figure 4.15: Room-temperature in-operando cwEPR for a p-DiTS electrochemical cell ( $\nu = 9.6$  GHz). a): CwEPR spectra during charging (oxidation) and discharging (reduction) of the cell. b): Number of unpaired electron spins determined from a quantitative analysis of the spectra (exp). Deconvolution of the total spin count into packed and dilute spectral components. Number of electrochemically active electrons in the p-DiTS film determined from its cyclic voltammogram. Background spin count on a cell without the p-DiTS film (BG). c): Slices of subplot a) for the initially discharged state (I, 0.6 V), charged state (II, 0.90–0.94–0.82 V, averaged within the region denoted by  $\uparrow$ , scaled up  $\times 10$ ), and the final discharged state (III, 0.6 V). Two-component spectral simulations to identify the contributions of dilute and packed nitroxide fragments at each potential. Potentials were recorded vs. Ag RE.

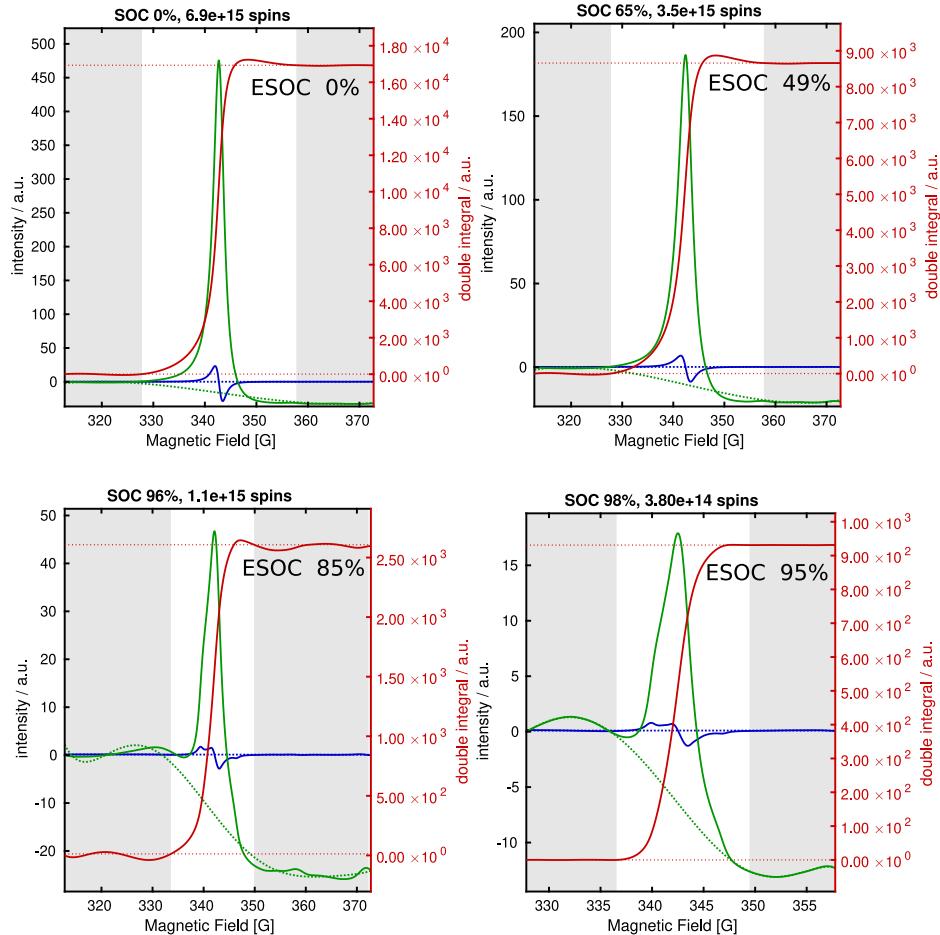


Figure 4.16: cwEPR spectra for a pDiTBuS film in four charge states. Single and double integrals of the signal. Spin count is proportional to the end value of the double integral. Temperature: 80 K,  $\nu \approx 9.6$  GHz, field modulation: 5 G at 100 kHz. ER 4118 X-MD5 dielectric ring resonator.

#### 4.8 Pulsed EPR spectroscopy of TEMPO-Salens

---

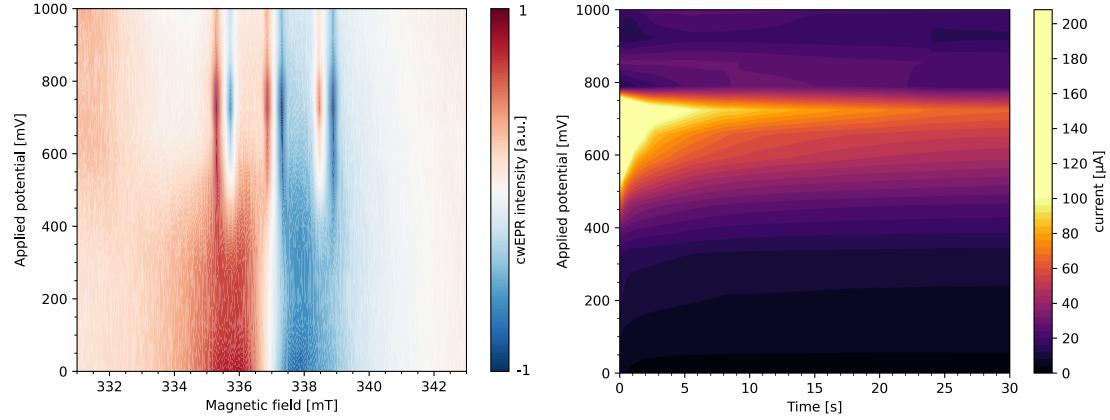


Figure 4.17: Operando cwEPR spectra of a pDiTS electrochemical cell showing irreversible release of charge-bearing fragments and decomposition of the device upon potentiostatic charging with currents up to  $I < 0.2 \text{ mA} \approx 125 \text{ C}$ .

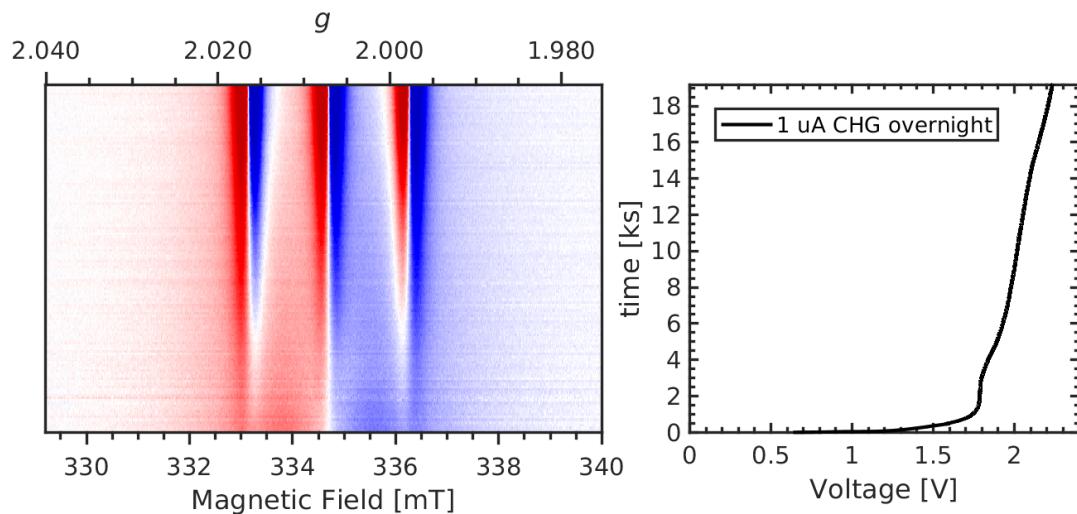


Figure 4.18: Operando cwEPR spectra of a pDiTS electrochemical cell showing irreversible release of charge-bearing fragments upon moderate charging currents.

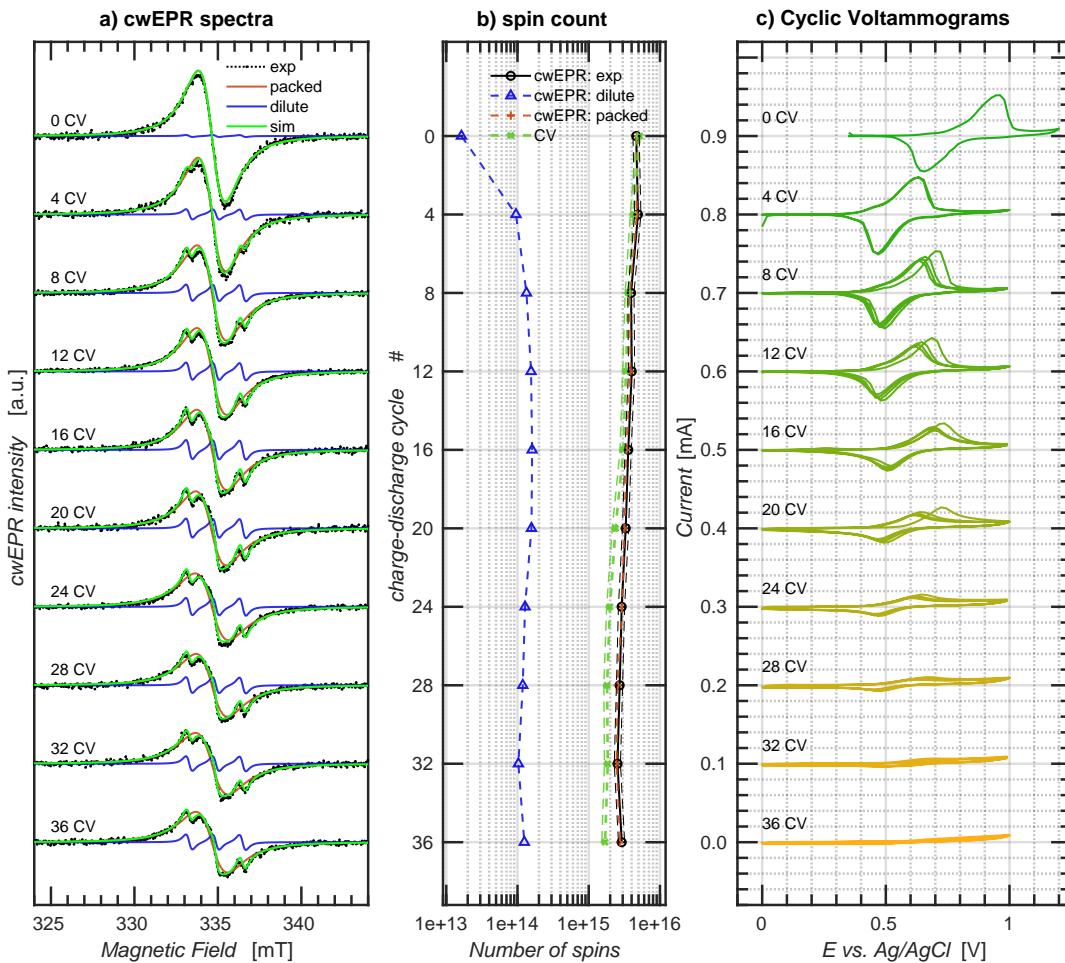


Figure 4.19: a): Evolution and component decomposition of cwEPR spectra for a tube-based, 150 CV p-DiTS ORB upon 36 charge-discharge cycles. b): Quantitative analysis of the separated spectral components.  $\nu = 9.4$  GHz, Mod. Amp: 0.5 mT. Quantitative analysis of the CV curves. c): Cyclic voltammograms of the cell, recorded with respect to Ag/AgCl RE at a rate of  $5 \text{ mV s}^{-1}$  in between the EPR scans, in the modified tube inside the microwave resonator. The CV were taken at  $5 \text{ mV s}^{-1}$ , which is 10 times slower than the CV curves taken in the larger beaker, because limited amount of the electrolyte in the modified tube was found to strongly affect the shape and positions of the CV peaks at higher speeds of cycling.

## 4.8 Pulsed EPR spectroscopy of TEMPO-Salens

---

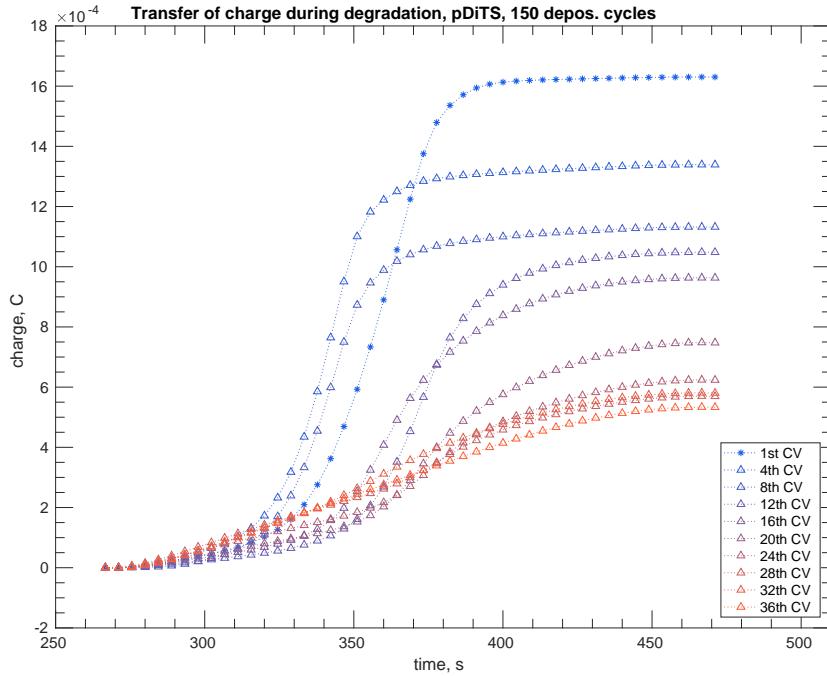


Figure 4.20: Degradation of capacity of a p-DiTS film upon 36 charge-discharge cycles. Transferred charge calculated as integrals of the reduction branches of the CV curves. By the last charge-discharge cycle the film can accept 10 times less the charge as in the beginning of the cycling.

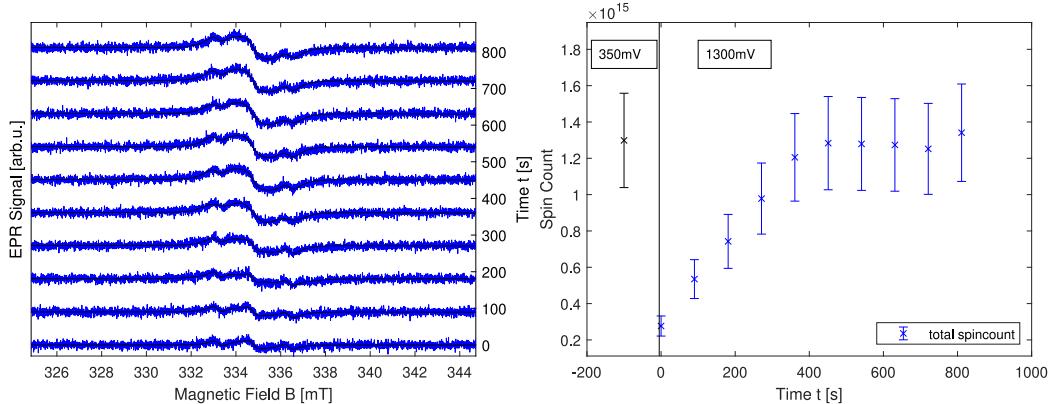


Figure 4.21: cwEPR monitored self-discharge of a tube-based cell containing a pDiTS film made with 50 deposition cycles. Left: Development of the EPR spectra of the oxidised sample over time from bottom to top; Right: Development of the spincount of the oxidised sample over time and comparison to the reduced state. [105]

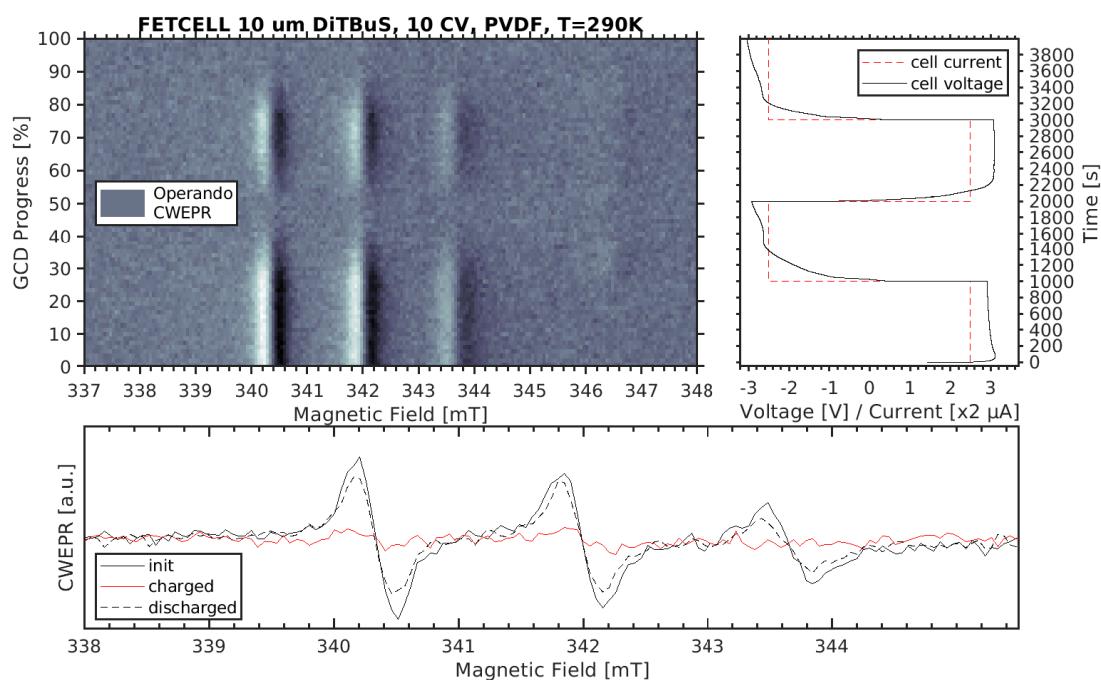


Figure 4.22: Operando cwEPR on an all-polymer organic radical battery made on a  $5 \mu\text{m}$  grid with a PVDF/TFSI gel electrolyte.

#### 4.8 Pulsed EPR spectroscopy of TEMPO-Salens

---

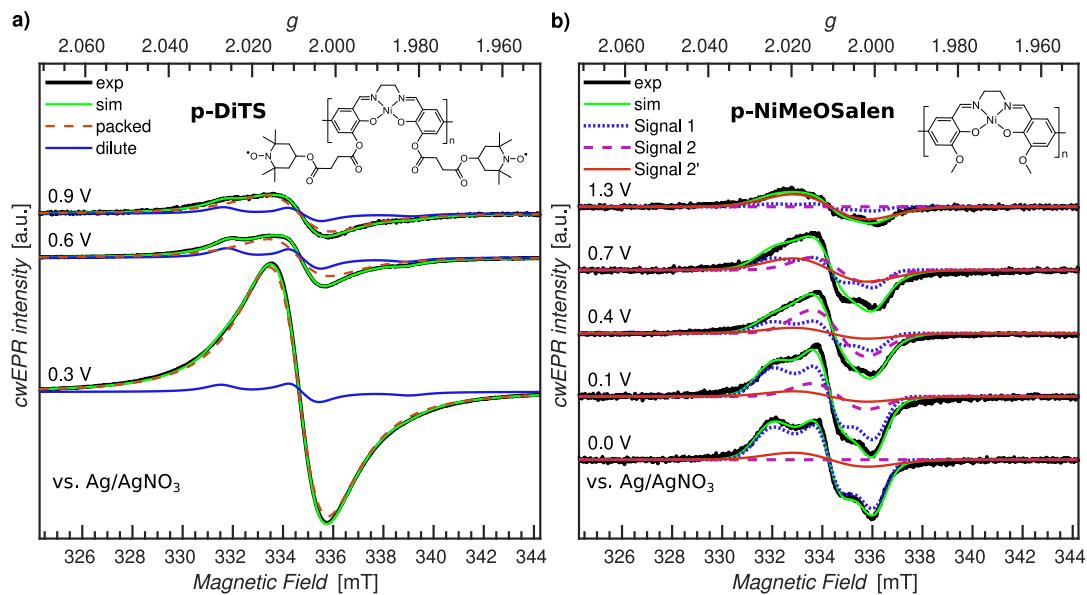


Figure 4.23: Cryogenic (150 K) ex-situ cwEPR in a range of redox potentials for p-DiTS and its molecular backbone, p-NiMeOSalen ( $\nu = 9.4$  GHz). a): p-DiTS film ( $t \approx 400$  nm). Two-component spectral deconvolution to identify the densely packed (dashed-red curve) and dilute (solid-blue curve), immobilized nitroxide fragments. b): p-NiMeOSalen film ( $t \approx 900$  nm). Three-component spectral deconvolution into the components observed earlier.[20]

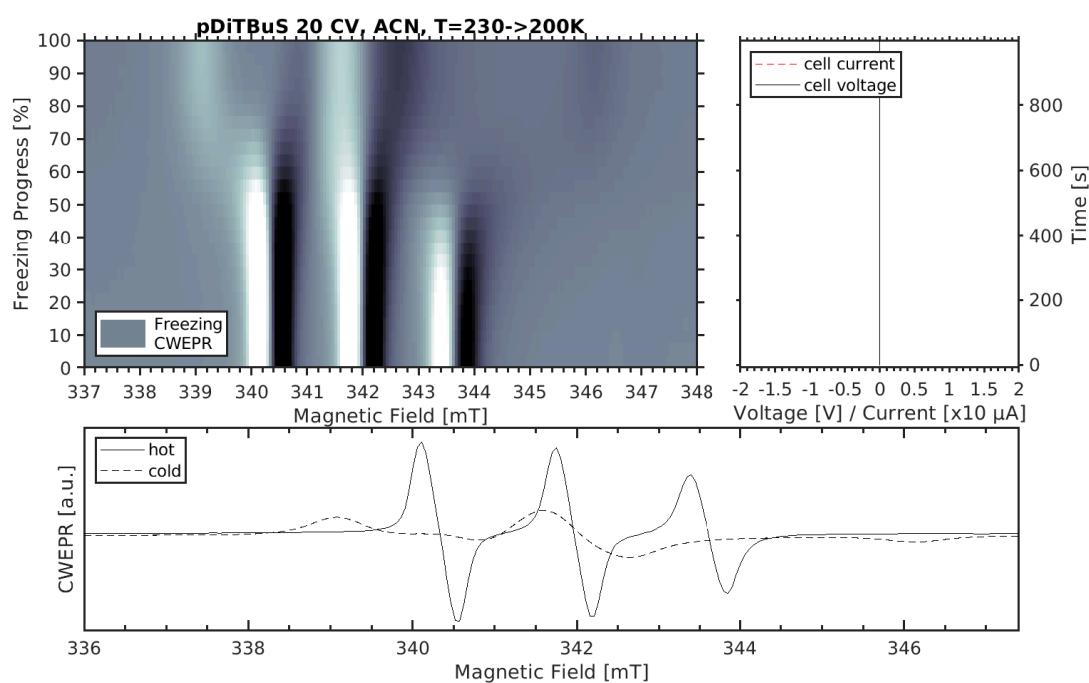


Figure 4.24: Freezing a pDiTBuS cell

#### 4.8 Pulsed EPR spectroscopy of TEMPO-Salens

---

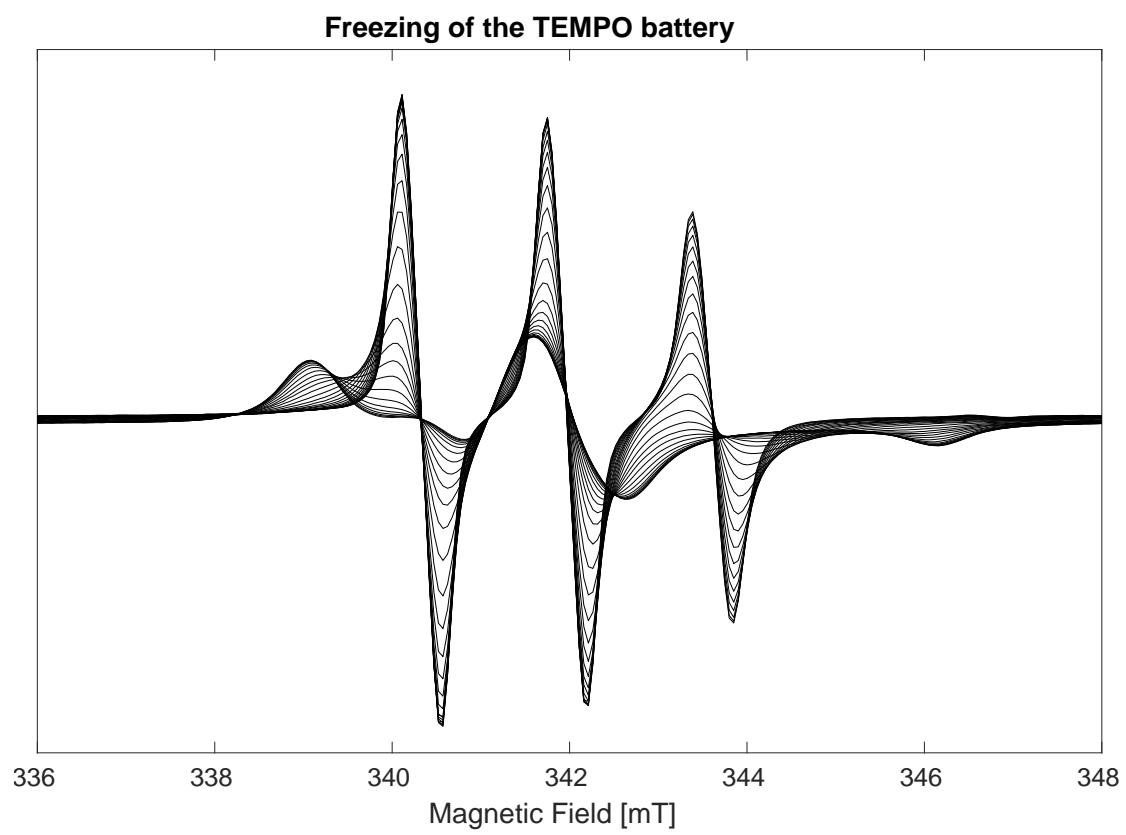


Figure 4.25: Freezing a pDiTBuS cell

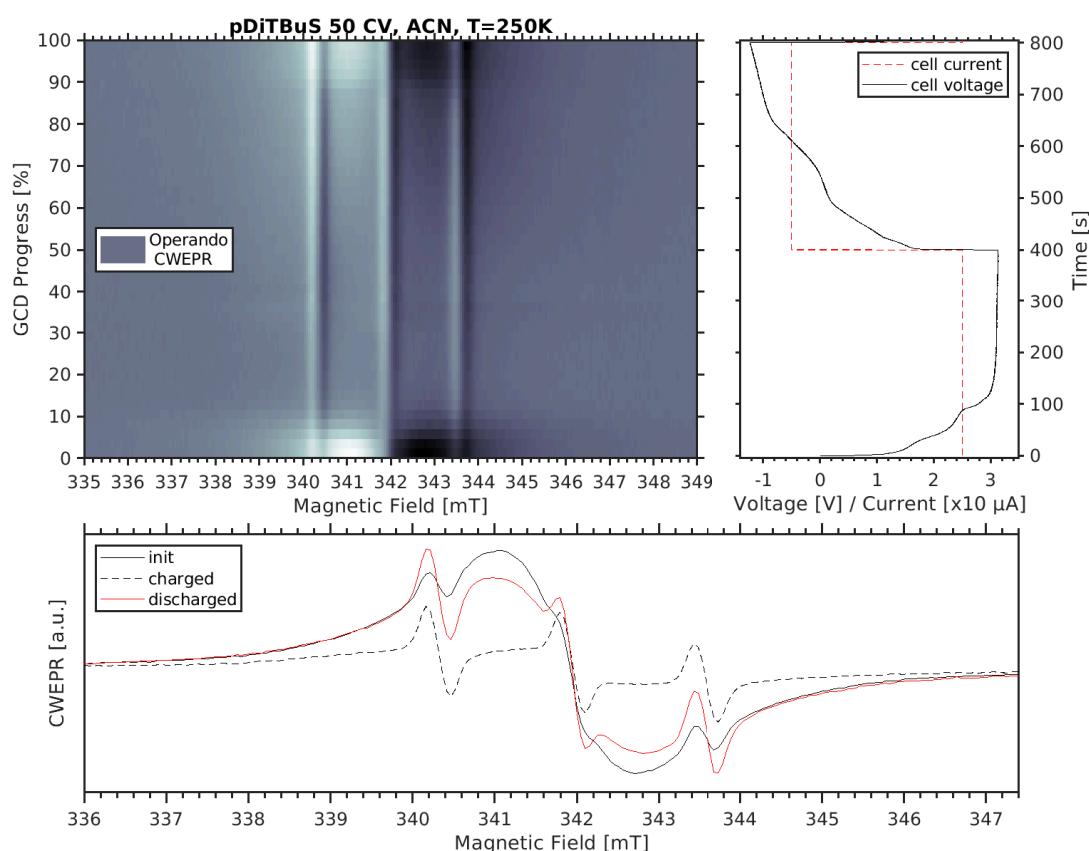


Figure 4.26: XXX

## 4.8 Pulsed EPR spectroscopy of TEMPO-Salens

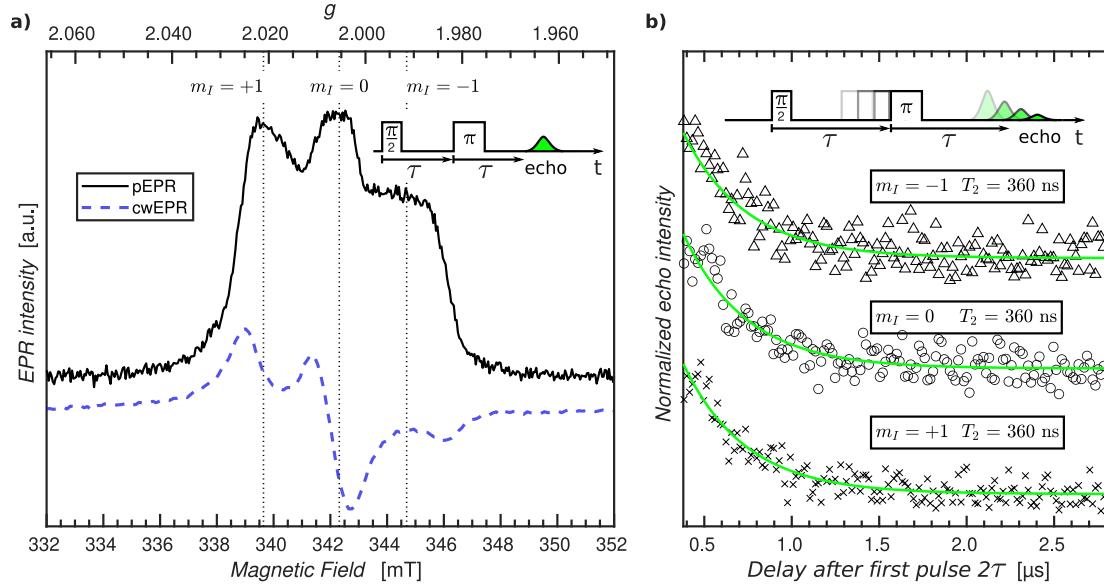


Figure 4.27: a): Pulse EPR echo-detected field-sweep spectrum (solid line) and cwEPR spectrum (dashed line) of a  $\approx 500$  nm thick p-DiTS film charged to +900 mV vs. Ag/AgNO<sub>3</sub> measured at  $T = 80$  K ( $\nu = 9.6$  GHz). b): Results of echo-decay measurements performed at the peak positions indicated by the dotted vertical lines in a) along with single exponential fits to determine the spin-spin relaxation times  $T_2$ .

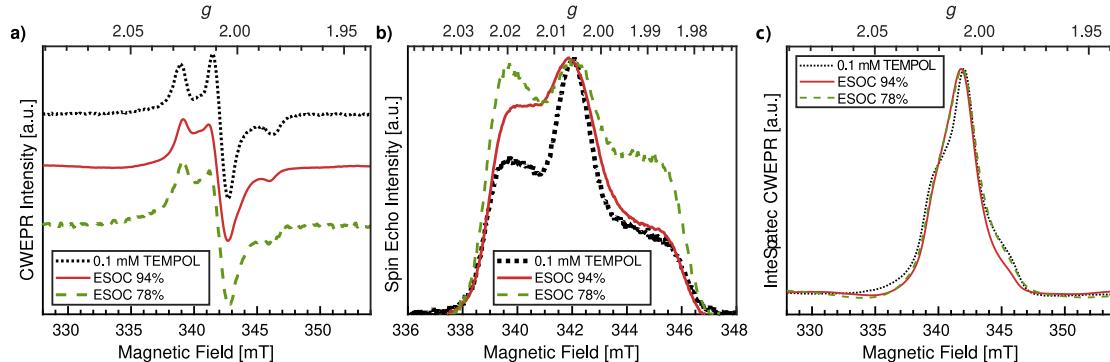


Figure 4.28: a): cwEPR spectra for pDiTBuS charged to 95% and 85%, and for a frozen 0.1 mM solution of TEMPOL. Normalized intensities. Temperature 80 K. b): Corresponding pEPR spectra measured at 5 K. Intensities scaled by the  $m_I = 0$  central peak. c): Integrated cwEPR intensities show similar spectral shapes. Temperature: 80 K, microwave frequency: 9.6 GHz, field modulation: 5 G at 100 kHz. ER 4118 X-MD5 dielectric ring resonator.

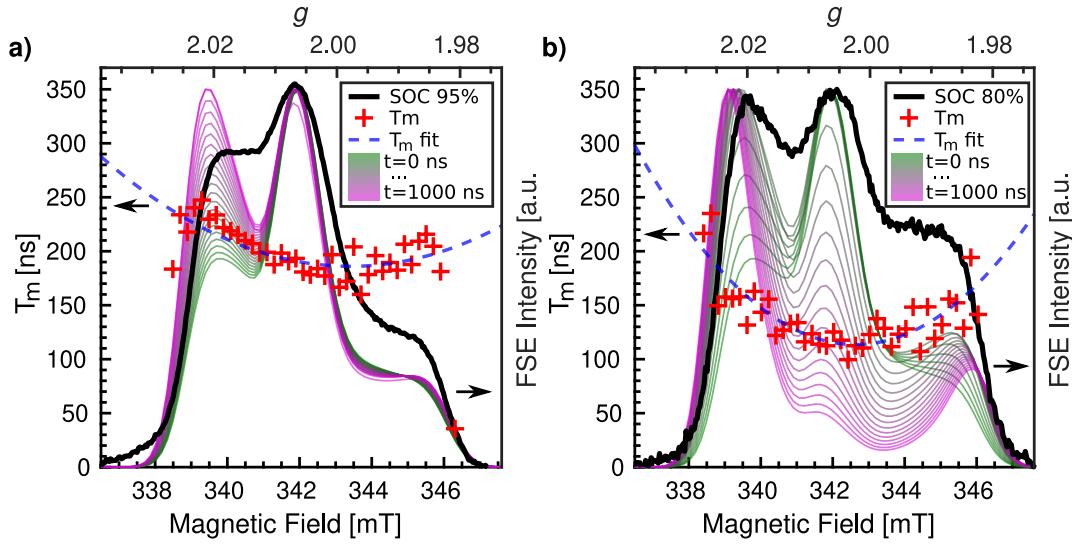


Figure 4.29: X

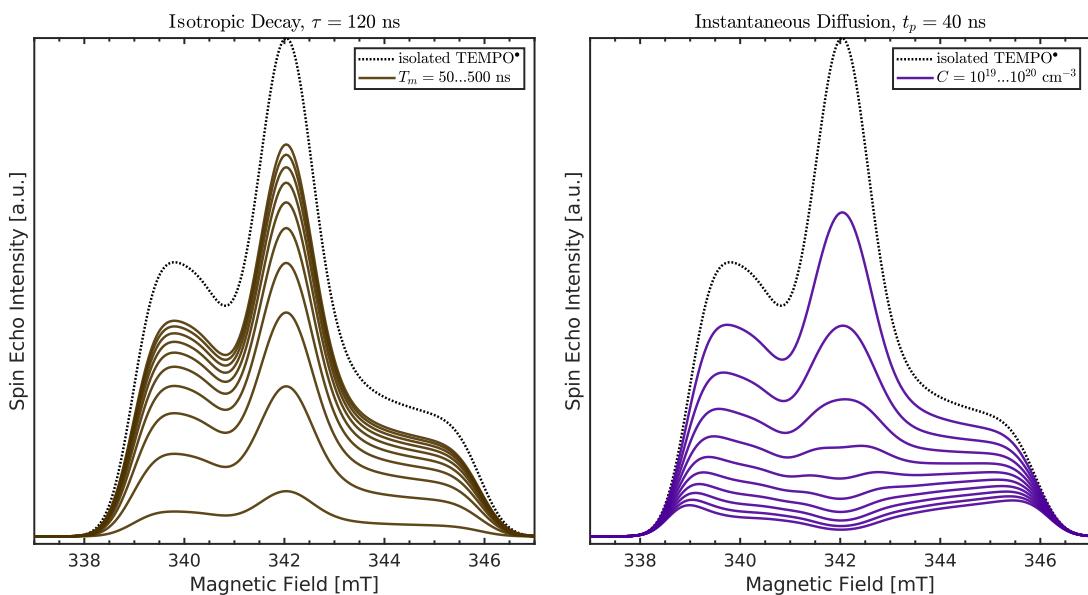


Figure 4.30: Distortions of a nitroxide FSE spectrum caused by isotropic spin relaxation (left) and instantaneous diffusion (right).

# Chapter 5

## Results and Discussion

### 5.1 Instantaneous Diffusion in pDiTS

High spin concentration in a pDiTBuS electrode suggests strong inter-spin dipolar couplings which cause instantaneous diffusion when probed with short (broad-band) microwave pulses [112], as it was observed in a PTMA/carbon mixture [16]. Instantaneous diffusion caused by a broad-band microwave pulse shown in Figure 5.1, dashed-red, manifests itself in an additional field-dependent spin relaxation factor  $V(B_0)$ , that alters the relative peak intensities in the echo-detected spectrum. For spins uniformly distributed in space,  $V(B_0)$  is described [112] by Equation 5.1:

$$V(B_0, 2\tau, C) = V_0(2\tau) \exp\left(-2\tau \frac{4\pi^2}{9\sqrt{3}} \gamma^2 \hbar C \langle \sin^2(\theta/2) \rangle\right) \quad (5.1)$$

with

$$\langle \sin^2(\theta/2) \rangle = \frac{\int \frac{B_1^2}{(B-B_0)^2+B_1^2} \sin^2\left(\frac{\gamma t_p}{2} \sqrt{(B-B_0)^2 + B_1^2}\right) g(B) dB}{\int g(B) dB} \quad (5.2)$$

where  $B_0$  is the static magnetic field,  $C$  is the concentration of spins,  $\tau$  is the time between the first and second pulses in the microwave pulse sequence,  $\gamma$  is the gyromagnetic ratio of the electrons at resonance,  $t_p$  is the duration of the second microwave pulse,  $B_1$  is the amplitude of the second microwave pulse,  $g(B)$  is the EDFS spectrum at  $\tau = 0$  that is not affected by the instantaneous diffusion. As the resulting spectral shape depends on the spin concentration, comparing spectra simulated according to Equation 5.1

and measured spectra thus allows us to provide information about the local spin concentrations. Since the spin echo of the most densely packed and thus quickly relaxing spins is not detectable with the given  $t_d$ , the regions of the highest spin concentration do not contribute to the EDFS spectrum. Thus,  $C$  is lower than the true concentration of spins in the densely packed domains and can also be lower than the average spin concentration  $\langle n \rangle$  measured with cwEPR that is most sensitive to the quickly relaxing spins.

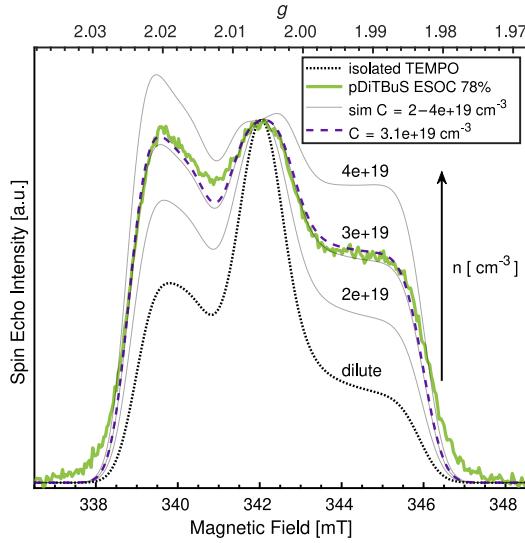


Figure 5.1: EDFS spectrum of p-DiTBuS at ESOC 85% (solid-green) affected by instantaneous diffusion with  $t_p = 40$  ns. Simulation of the spectrum with spin concentration  $C = 3.1 \times 10^{19} \text{ cm}^{-3} = 52 \text{ mM}$  as a fit parameter (dashed-purple). Simulated spectrum of non-interacting TEMPO with  $g=[2.0099, 2.0055, 2.0026]$ ,  $A=[21.99, 21.43, 96.27]$  MHz and 0.812 mT (lwpp) Gaussian line shape as the starting values for the simulation (dashed-black). Excitation profile of the 40 ns pulse at  $B_0 = 340$  mT is shown in dashed red.

We have used a 50 mM solution of TEMPOL as a model system to explore how the excitation bandwidth affects instantaneous diffusion for nitroxides (see Section 5.2.1, ESI). The EDFS spectrum recorded with  $t_p = 40$  ns and  $\tau = 120$  ns shows a distortion that corresponds to  $C = 9 \text{ mM}$ , while for  $t_p = 1000$  ns no effect of instantaneous diffusion is observed. We simulated the undistorted EDFS spectrum of TEMPOL using the Easyspin toolbox [107] for Matlab and obtained the  $g$  matrix and the hyperfine coupling tensor  $A$  (for simulation details see Section ??, ESI). Then we simulated the EDFS spectrum for pDiTBU, ESOC 85%, using the obtained parameters and Equation 5.1 with  $t_p = 40$  ns and the concentration  $C$  as a fit parameter. The result of the simulation with  $C = 3.1 \times 10^{19} \text{ cm}^{-3} = 50 \text{ mM}$  is shown in Figure 5.1. At the same time, quantitative cwEPR yields a higher spin concentration for ESOC 85%:  $\langle n \rangle = (8 \pm 4) \times 10^{19} \text{ cm}^{-3}$

## 5.2 Simulations of the EDFS Spectra Considering Instantaneous Diffusion

---

= 130±70 mM.

The ESOC 95% spectrum cannot be simulated with Equation 5.1 because of the increased intensity of the low-field peak. The ratio of the two remaining peaks at ESOC 95% corresponds to  $C = 1.2 \times 10^{19} \text{ cm}^{-3} = 20 \text{ mM}$  (see ESI, Section 5.2.4), while cwEPR again yields a higher  $\langle n \rangle = 3 \pm 2 \times 10^{19} \text{ cm}^{-3} = 50 \pm 30 \text{ mM}$ .

## 5.2 Simulations of the EDFS Spectra Considering Instantaneous Diffusion

We used Equation 5.1 from the main text with varying  $C$  to fit the EDFS spectra affected by ID.

### 5.2.1 EDFS in 50 mM TEMPOL Measured with Narrow-Band Pulses

The EDFS spectrum of a 50 mM frozen solution of TEMPOL measured with long (selective, narrow band) microwave pulses shows no asymmetry with  $t_P = 1000 \text{ ns}$  and  $\tau = 1000 \text{ ns}$ . The spectrum was deconvoluted into the broad ('packed') and the narrow ('dilute') components. The narrow component is an Easyspin simulation with the typical g and A tensors for a nitroxide radical (see Figure caption for parameters). The broad spectral component might correspond to densely packed agglomerates in the not perfect glass. The fit is shown in Figure 5.2 a.

### 5.2.2 EDFS in 50 mM TEMPOL Measured with Broad-Band Pulses

The EDFS spectrum of a 50 mM solution of TEMPOL in Figure 5.2 b shows asymmetry when measured with shorter,  $t_P = 40$  and  $\tau = 120 \text{ ns}$  pulses with a microwave power attenuation 11 dB. The spectrum has a stronger contribution of the broad component which in this case was calculated as the weighted integral of the cwEPR spectrum. The asymmetric dilute component was simulated considering the anisotropic relaxation of the 'standard' TEMPOL spectrum which was caused by instantaneous diffusion using Equation 5.1 in the main text. The fit of the EDFS spectrum of 50 mM TEMPOL was done with a concentration  $C = 5.6 \times 10^{18} \text{ cm}^{-3}$  or 9.3 mM as a fit parameter,  $t_P = 40 \text{ ns}$ ,  $\tau = 120 \text{ ns}$  and  $\gamma = -1.76 \times 10^{11} \text{ rad/T}$  (for  $g = g_e$ ). The spin concentration determined from the instantaneous diffusion simulation is only 19% of the molecular concentration that was used to prepare the TEMPOL solution. The presence of the broad component in the EDFS spectrum suggests that the concentration of TEMPOL was not homogeneous within the sample.

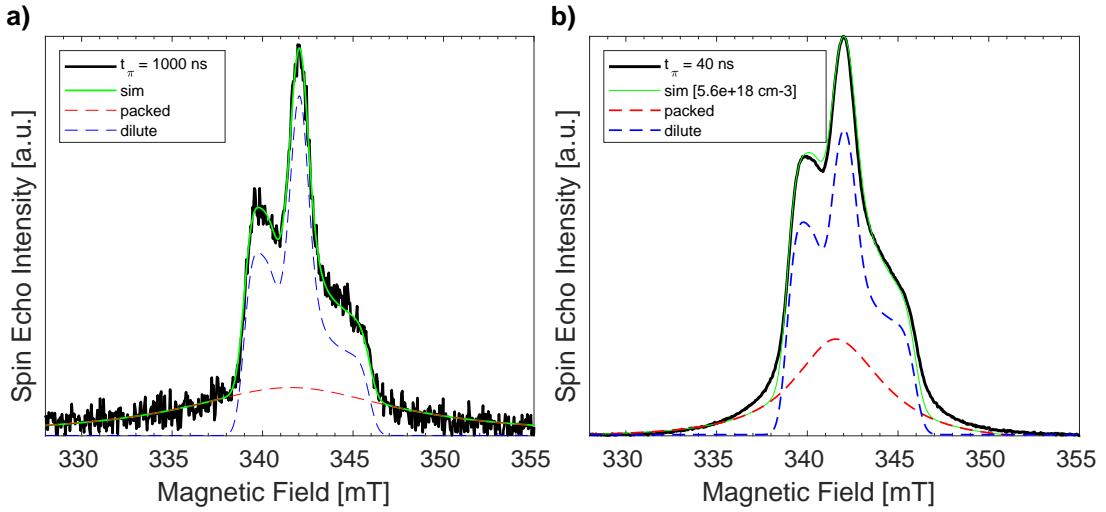


Figure 5.2: a): EDFS of 50 mM TEMPOL in Acetonitrile/Dichloromethane glass measured with long (selective, narrow-band) microwave pulses.  $t_P = 1000$  ns,  $\tau = 1000$  ns, microwave frequency: 9.6 GHz, microwave power attenuation: 36 dB. Temperature: 5 K. 2-component spectral simulation. Dilute component:  $\mathbf{g}=[2.0099 \ 2.0055 \ 2.0026]$  and  $\mathbf{A}=[21.9850 \ 21.4260 \ 96.2707]$  MHz. Broad component:  $\mathbf{g}=2.0082$ ,  $lwpp=8.08$  mT (Lorentzian). No effect of instantaneous diffusion is detectable with the long pulses. b): Same, measured with short (non-selective, broad-band) microwave pulses.  $t_P = 40$  ns,  $\tau = 120$  ns, microwave frequency: 9.6 GHz, microwave power attenuation: 11 dB. Temperature: 5 K. 2-component spectral simulation. Dilute component: same as in (a), but affected by the instantaneous diffusion with  $C = 5.6 \times 10^{18} \text{ cm}^{-3}$ . Broad component: integrated cwEPR spectrum.

### 5.2.3 EDFS in PDiTBuS at ESOC 85% Affected by Instantaneous Diffusion

The quick echo decay in pDiTBuS necessitates the usage of short microwave pulses that lead to ID. The asymmetric EDFS spectrum of pDiTBuS at 85% ESOC was simulated considering the distortion of the standard TEMPO spectrum caused by the ID. The anisotropic relaxation of the spectral components is given by the equation 5.1 in the main text. The fit of the EDFS spectrum of pDiTBuS at 85% ESOC was done with a concentration  $C=3.1 \times 10^{19} \text{ cm}^{-3} = 50 \text{ mM}$  as a fit parameter,  $t_P = 40$  ns,  $\tau = 120$  ns and  $\gamma = -1.76 \times 10^{11} \text{ rad/T}$ . The fit was done with  $\mathbf{g}=[2.00987, 2.0055, 2.0026]$ ,  $\mathbf{A}=[22.0 \ 21.5 \ 96.3]$  MHz, 0.81 mT ( $lwpp$ ) Gaussian line shape, Figure 5.3.

## 5.2 Simulations of the EDFS Spectra Considering Instantaneous Diffusion

---

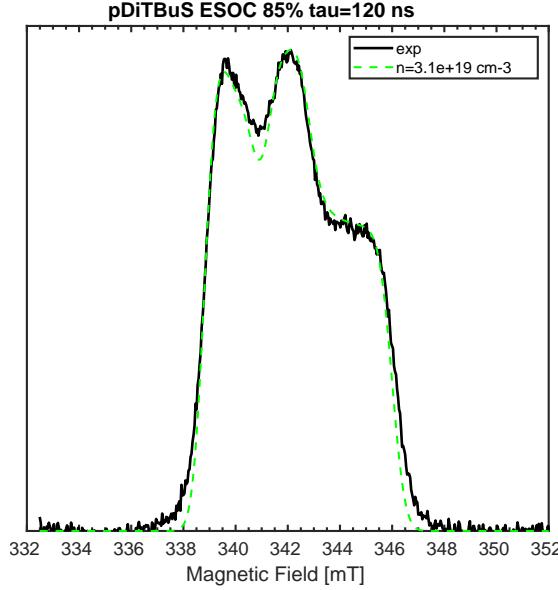


Figure 5.3: EDFS spectrum of pDiTBuS at 85% ESOC (solid-black). Spectral simulation with  $\mathbf{g}=[2.00987, 2.0055, 2.0026], \mathbf{A}=[22.0 \ 21.5 \ 96.3]$ , 0.81 mT (lwpp) Gaussian line shape and anisotropic relaxation caused by instantaneous diffusion (dashed-green). Relative peak intensities correspond to  $C=3.1e19 \text{ cm}^{-3}$  or 52 mM. Microwave frequency: 9.6 GHz,  $\pi/2 = 20 \text{ ns}$ ,  $\tau=120 \text{ ns}$ . Temperature: 5 K.

### 5.2.4 EDFS in PDiTBuS at ESOC 95% Affected by Instantaneous Diffusion

The asymmetric EDFS spectrum of pDiTBuS at 95% ESOC could not be simulated considering the distortion of the standard TEMPO spectrum caused by the ID given by Eq. 5.1 in the main text. The spectrum and the attempted fit are shown in Figure 5.4. The low-field peak has a much higher relative intensitiy than expected from the ID model. The observed spectrum may be a superposition of a dilute species that do not experience instantaneous diffusion and the densely packed species that is affected by ID.

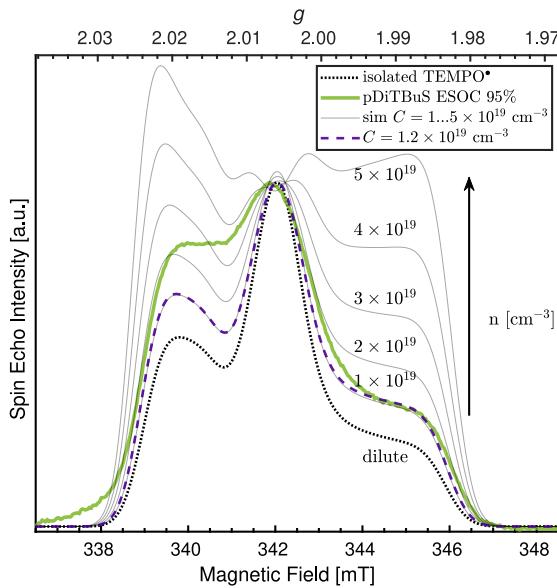


Figure 5.4: EDFS spectrum of pDiTBuS at ESOC 95% (solid-green). Spectral simulation with  $\mathbf{g}=[2.0099, 2.0055, 2.0026]$ ,  $\mathbf{A}=[21.9850 \ 21.4260 \ 96.2707]$  MHz, 0.24 mT (lwpp) Lorentzian line shape and anisotropic relaxation caused by instantaneous diffusion (dashed-blue). Relative peak intensities correspond to  $C= 1.2 \times 10^{19} \text{ cm}^{-3}$  or 22 mM. Microwave frequency: 9.6 GHz,  $\pi/2 = 20$  ns,  $\tau=120$  ns. Temperature: 5 K.

### 5.2.5 Estimation of Local Spin Concentrations with Instantaneous Diffusion

## 5.3 Spin Relaxation in a charged pDiTBuS Cathode Film

As we have shown in Section 4.8.4, the reason for the distorted spectral shape in pDiTBuS at ESOC 85% is instantaneous diffusion that manifests itself in anisotropic spin relaxation which alters the relative peak intensities. However, the spectrum for ESOC 95% cannot be simulated assuming just instantaneous diffusion (cf. Figure 5.4, ESI). In order to gain additional information about the processes that may influence the shape of the EDFS spectra, we performed field-dependent measurements of the spin relaxation times.

Figure 5.5a shows the EDFS spectra of pDiTBuS for 85% and 95% ESOC as well as a reference sample (50 mM solution of TEMPOL in Dichloromethane:Acetonitrile (3:1) glass) measured at  $T = 5$  K. The spectra reveal markedly different intensities of the three hyperfine components.

The changed relative peak intensities in pDiTBuS may be the result of a magnetic field-dependent spin relaxation mechanism that manifests itself in a field-dependent

### 5.3 Spin Relaxation in a charged pDiTBuS Cathode Film

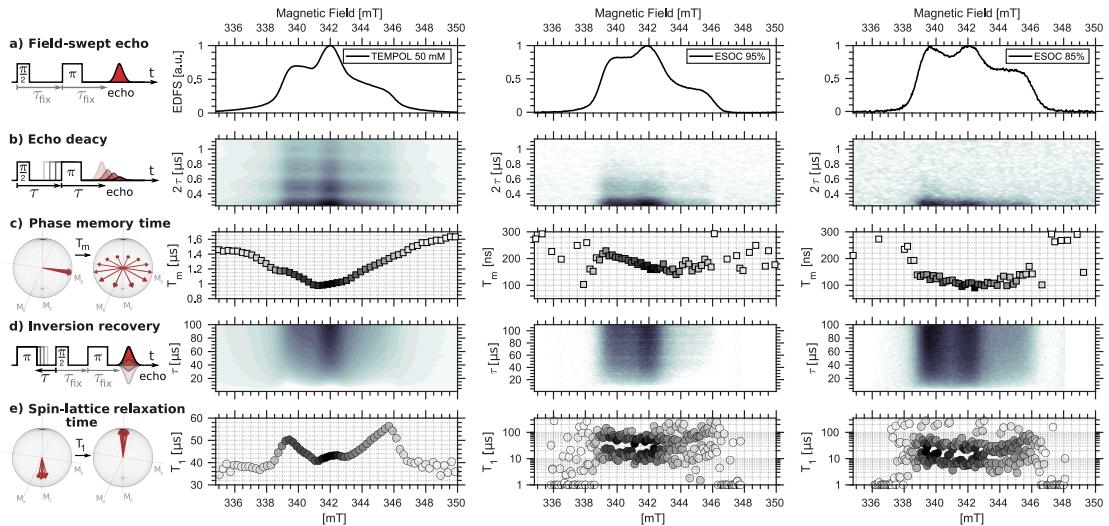


Figure 5.5: Field-swept echo (a), echo decay transients (b), phase memory times  $T_m$  (c), inversion recovery (d) and spin-lattice relaxation times  $T_1$  (e) measured in 50 mM frozen electrolyte solution of TEMPOL (left) and in dry pDiTBuS film charged to ESOC 95% (center) and to ESOC 85% (right). Temperature 5 K. Grayscale represents the intensity in b)–e).

phase memory time  $T_m$  [101]. The  $T_m$  for pDiTBuS and for TEMPOL was probed in a field-swept echo decay experiment. The echo decay transients for the three samples are shown in Figure 5.5b. A Hahn echo pulse sequence was used with a  $\pi/2$  pulse length of 20 ns and variable pulse separation time  $\tau \geq 120$  ns. Spin echo was detected at  $2\tau$  after the  $\pi/2$  pulse. Periodic oscillations in the echo decay transients correspond to the ESEEM effect from protons [101] with  $\Delta\omega_L \approx 15$  MHz, which are particularly pronounced for TEMPOL.

If the sample contains several different species (i.e. nitroxide radicals in different environments and/or different local concentration) with distinct spin-spin relaxation times, the echo decay transients may contain multiple decay components, so more than one  $T_m$  can correspond to each field point. This effect is not considered when simulating the effect of instantaneous diffusion using Equation 5.1. To determine the number of decay components in the echo decay transients, we studied the poles of the Padé approximation of the Taylor expansion of the Laplace transforms of the transients that is known as the Padé-Laplace method [40] (see ESI, Section 5.4.1 for details). This analysis revealed only monoexponential spin echo decays for both 95% ESOC and 85% ESOC. We therefore assumed a monoexponential spin echo decay for pDiTBuS, though some faster relaxing components with  $T_m < t_d$  might have decayed by the earliest achievable  $\tau$ , as shown in Section 5.3.2, ESI. The detected decay times  $T_m(B_0)$ , extracted from

fits of the background-corrected echo-decay curves, are shown in Figure 5.5c as filled squares with the grayscale representing the amplitude of the corresponding fit component. As expected,  $T_m$  is significantly larger for 95% than for 85% ESOC, consistent with the weaker spin-spin couplings in the fully charged film. Further, we note that the field-dependence of  $T_m$  is more pronounced for 95% ESOC, with  $T_m \geq 200$  ns for the  $m_I = +1$  hyperfine component. This anisotropy in  $T_m$  results in an increased intensity of the low-field peak, which is in line with the observation that we cannot describe the 95% ESOC spectrum assuming only instantaneous diffusion (see Section 4.8.4). The transient fits and the residuals are shown in Section 5.4.1, ESI.

We attempted to reproduce the pDiTBuS spectra from a standard nitroxide spectrum by considering anisotropic transient decay of the spectral intensity at  $t = \tau = 120$  ns for each  $B_0$  with the measured  $T_m(B_0)$ . However, this approach did not allow us to reconstruct the pDiTBuS spectra for neither 85%, nor 95% ESOC.

It was recently shown, that densely packed TEMPO radicals in a TEMPO-containing, non-conductive polymer PTMA, intermixed into an amorphous carbon mesh, show multiple spin-lattice relaxation times  $T_1$  because of different types of contact between the TEMPO radicals and the conductive additive in the TEMPO/carbon composite [16]. In order to find out whether such behavior can also be observed for the porous pDiTBuS film, we measured spin-lattice relaxation times  $T_1$  with an inversion-recovery pulse sequence ( $\pi - \tau - \pi/2 - \tau_{fix} - \pi - \tau_{fix} - echo$ ) with variable  $\tau$  (Figure 5.5d). The Padé-Laplace analysis yielded one decay component for TEMPOL and two decay components for pDiTBuS both at 85% ESOC and 95% ESOC (see ESI, Section 5.4.1 for details). The  $T_1$  for charged pDiTBuS is on the same order as for TEMPOL and splits in two rather broad distributions with similar intensities (Figure 5.5e). Similar as in the case of  $T_m$ , also  $T_1$  is larger for 95% than for 85% ESOC. Irrespective of the ESOC there is no significant field dependence of  $T_1$ , in contrast to what is observed for the TEMPOL reference sample.

Daniel et al. [16] concluded that separate distributions of  $T_1$  correspond to different binding between TEMPO and the carbon mesh, representing the quality of electrical contact between TEMPO and the conductive additive. With the observed distribution of  $T_1$  and considering the two-component cwEPR spectral contributions for charged pDiTBuS (“broad” and “dilute” components, cf. Section ??, ESI), we suggest that two types of domains could exist in a partially charged pDiTBuS film as well. These two morphologies may correspond to “conductive” domains with shorter  $T_1$ , where TEMPO<sup>•</sup> are close to the conductive pNiSalen backbone, and “non-conductive” domains with longer  $T_1$ , where TEMPO<sup>•</sup> are separated from pNiSalen. We note, however, that based on the experimental data presented here, this interpretation is rather speculative. The

## 5.3 Spin Relaxation in a charged pDiTBuS Cathode Film

---

detected  $T_1$  values for pDiTBuS may also correspond to one distribution, as the separation between the  $T_1$  values is comparable to the widths of their distributions.

### 5.3.1 Temperature Dependence of Pulse Spectra of Charged pDiTBuS

Spin relaxation times usually depend on temperature[101]. We measured EDFS of charged pDiTBuS at 5 K and at 80 K to see how faster spin relaxation affects the spectral shape. Figure 5.6 shows EDFS spectra for pDiTBuS charged to ESOC 95% (a) and to ESOC 85% (b) at 80 K (solid) and at 5 K (dashed). At 80 K an overnight scan was required to obtain a satisfactory signal-to-noise ratio, whereas at 5 K the spectrum was recorded in a few minutes. The spectral intensities at different temperatures were scaled such that the high-field  $m_l = -1$  peak has the same intensity. Figure 5.6 clearly shows that the relative intensities of the peaks change with temperature for both ESOC. At higher temperatures the EDFS spectrum of pDiTBuS has a peak ratio closer to that of dilute TEMPOL that corresponds to a lower spin concentration, according to Equation 5.1. The influence of the temperature increase on the spectral shape is stronger for the lower, 85% ESOC.

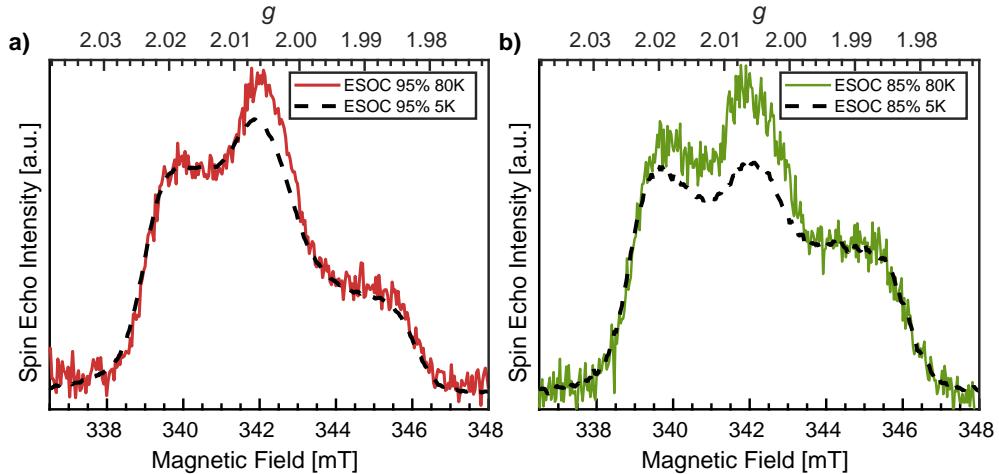


Figure 5.6: EDFS spectra for pDiTBuS charged to 95% ESOC (a) and to 85% ESOC (b) measured at 5K and at 80K.

The overall relaxation times in the film decrease with increasing temperature, but the dead time of the spectrometer ( $t_d = 120$  ns) does not change. Therefore, at a given temperature, only spins with  $T_m > t_d$  contribute to the signal. At higher temperature only the weakly coupled spins (with the longest  $T_m$ ) are detectable, which results in a spectral shape that is less affected by instantaneous diffusion and thus closer to a dilute

nitroxide solution.

### 5.3.2 Limitation on Shortest Detectable $T_m$ by the Spectrometer Dead Time

If a system exhibits multiple phase memory times  $T_m$ , the spin echo from the species with short memory times may decay below the noise level at a given pulse separation  $\tau$ . Figure 5.7 illustrates the spin echo intensity in a two-component system with  $T_m^1 = 100$  ns and  $T_m^2 = 25$  ns in dependence on the pulse separation  $\tau$ . The fast relaxing component with  $T_m^2 = 25$  ns decays below the noise level after the dead time of  $t_d = 100$  ns.

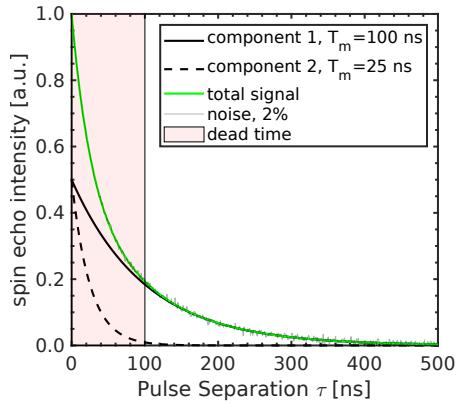


Figure 5.7: Simulated echo decay transient of a spin ensemble exhibiting two distinct phase memory times  $T_m^1 = 100$  ns and  $T_m^2 = 25$  ns. The 100 ns dead time, during which the spin echo detection is not possible, is marked in red. After the dead time, the sum of the two components is indistinguishable from the slowly relaxing component within the 2% noise.

## 5.4 Padé-Laplace Deconvolution of Polyexponential Decay Signals

The echo decay and inversion recovery transients measured in the corresponding experiments may contain multiple exponential decay components. The conventional method of determining the distribution of the decay components in a transient decay is the Laplace inversion, where the signal in the time domain  $s(t)$  is converted into its Laplace image  $L(p) = \int_0^{+\infty} s(t)e^{-pt}dt$  in the time-constant domain  $p = 1/t$ , where the peaks of

## 5.4 Padé-Laplace Deconvolution of Polyexponential Decay Signals

---

$L(p)$  give the decay constants that make up the signal. However, for the noisy signal, the direct calculation of the Laplace transform brings in artifacts that drastically vary with the noise. The signal-to-noise ratio (SNR) of the recorded data makes it difficult to apply the Laplace inversion to determine the number of the decay components, as the Laplace transform is unstable at that SNR.

The Padé-Laplace method comes useful for analyzing noisy polyexponential decays as it was demonstrated in Ref. [41]. The idea of the Padé-Laplace method is to analyze the Padé approximation of the Taylor expansion of the  $L(p)$  in the vicinity of one of the expected decay constants  $p_0$ , rather than considering the  $L(p)$  fully. This way of signal decomposition is stable against the noise for SNR<10 (see Figure 5.8). The number of exponents detected by the Padé-Laplace method as well as their locations in the  $p$  space may vary depending on the expansion point  $p_0$ . We considered  $p_0 = 1/t_{1/2}$  where  $t_{1/2}$  is the time at which the signal amplitude halves.

We implemented the following algorithm to detect the number of exponents in the decaying transient  $s(t)$ :

First, a point  $p_0 = 1/t_{1/2}$  was chosen, at which  $s(t)$  halves.

Then, 11 coefficients of the Taylor expansion of the Laplace transform  $L(p)$  were calculated in the vicinity of  $p \rightarrow p_0$

$$L(p)|_{p \rightarrow p_0} = \sum_{n=0}^{11} d_i(p - p_0)^i \quad (5.3)$$

with

$$d_i = \frac{1}{i!} \left( \frac{d^{(i)} L}{dp^{(i)}} \right)_{p=p_0} \quad (5.4)$$

where the derivatives  $\frac{d^{(i)} L}{dp^{(i)}}$  are computed numerically at the point  $p = p_0$  from the discrete signal  $s(t) = (t_j, f_j)$ ,  $j = 1 \dots M$ :

$$\frac{d^{(i)} L}{dp^{(i)}} = \sum_{j=2}^{M-1} (-t_j)^i e^{(-p_0 t_j)} f_j + \frac{1}{2} \left( (-t_1)^i e^{(-p_0 t_1)} f_1 + (-t_M)^i e^{(-p_0 t_M)} f_M \right) \quad (5.5)$$

Then the Taylor expansion for  $L(p)$  was approximated in the vicinity of  $p_0$  with the Padé polynomials  $a(p)$  and  $b(p)$  of orders  $n = 5$  and  $n = 6$  respectively:

$$L(p)|_{p \rightarrow p_0} = d_0 + d_1(p - p_0) + \cdots + d_{11}(p - p_0)^{11} = \frac{a_0 + a_1(p - p_0) + \cdots + a_5(p - p_0)^5}{1 + b_1(p - p_0) + \cdots + b_6(p - p_0)^6} \quad (5.6)$$

The equation 5.6 is multiplied by the denominator and the prefactors at  $(p - p_0)^n$  for  $n = 6 \dots 11$  are compared. This defines a system of linear equations on coefficients  $b_i$ :

$$\begin{pmatrix} d_5 & d_4 & d_3 & d_2 & d_1 & d_0 \\ d_6 & d_5 & d_4 & d_3 & d_2 & d_1 \\ d_7 & d_6 & d_5 & d_4 & d_3 & d_2 \\ d_8 & d_7 & d_6 & d_5 & d_4 & d_3 \\ d_9 & d_8 & d_7 & d_6 & d_5 & d_4 \\ d_{10} & d_9 & d_8 & d_7 & d_6 & d_5 \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6 \end{pmatrix} = \begin{pmatrix} -d_6 \\ -d_7 \\ -d_8 \\ -d_9 \\ -d_{10} \\ -d_{11} \end{pmatrix} \quad (5.7)$$

From 5.7,  $b_i$  are found. The coefficients  $a_i$  are found from  $d$  and  $b$ .

Finally, the Padé approximation  $P = \frac{a}{b}$  is constructed and its poles are analyzed. The position of the poles reveal the decay constants. The residues at the poles may give the amplitudes of the decay components, but this was not used in the present study.

## 5.4 Padé-Laplace Deconvolution of Polyexponential Decay Signals

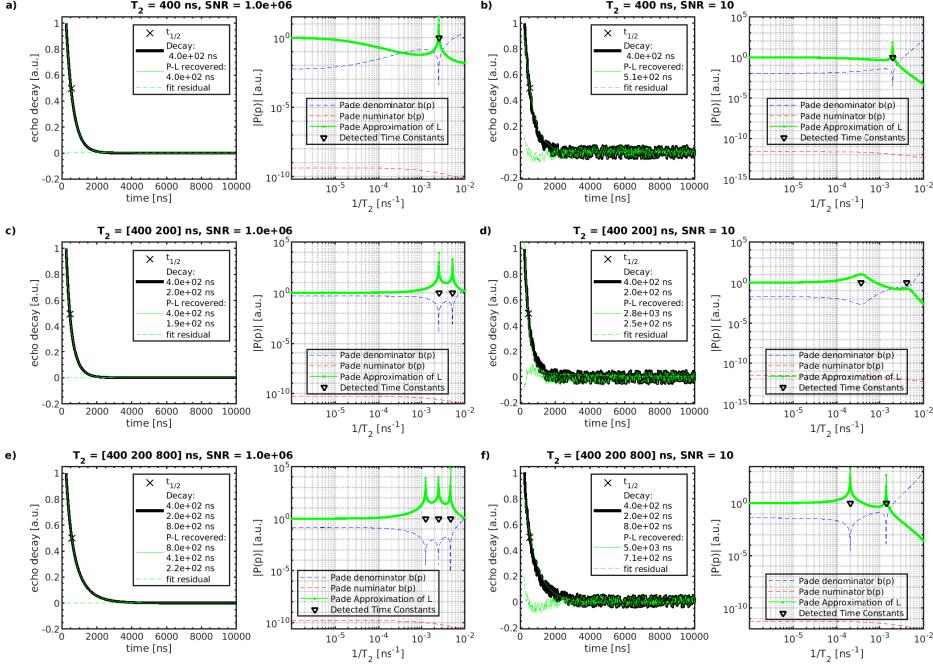


Figure 5.8: Padé-Laplace deconvolution of the mock data containing two decay constants with various signal-to-noise (SNR) ratios.

### 5.4.1 Padé-Laplace Deconvolution of the Echo-Decay and Inversion-Recovery Transients

We used the Padé-Laplace method to determine the number of the decay constants in the signals and used multiexponential fits to adjust the decay constants and their amplitudes. For the echo decay transients the best fits were monoexponential fits, even though the Padé-Laplace analysis initially showed biexponential behavior for pDiTBuS with major contribution from the fast decay constants in the order of the detector's dead time. All recorded echo decay transients contain oscillations due to the ESEEM effect. The oscillations were excluded from the analysis as shown in the 'fit area' on the plots in Figure 5.10, Figure 5.12 and Figure 5.14.

### Echo Decay in 50 mM TEMPOL

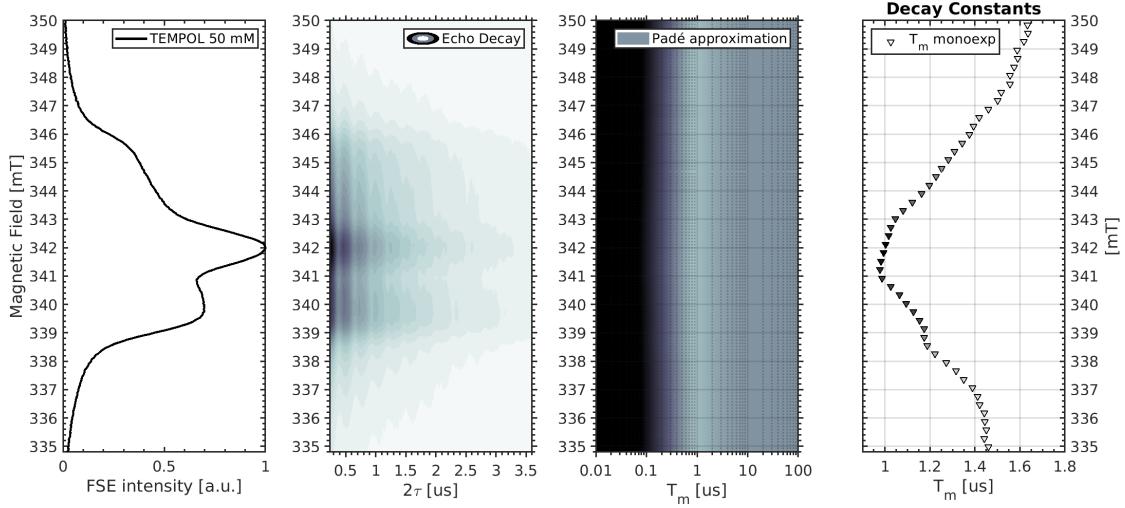


Figure 5.9: Padé-Laplace deconvolution of the field-swept spin echo decay in a frozen 50 mM solution of TEMPOL in Dichloromethane:Acetonitrile glass (3:1). One decay component detected with Padé-Laplace (triangles, right panel). Monoexponential fit (squares for faster component, circles for slower component, right panel). Temperature 5K.

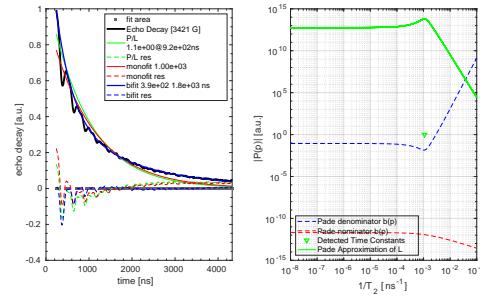


Figure 5.10: Fits of the echo decay transient in the frozen 50 mM TEMPOL solution at the central spectral peak ( $m_I = 0$ , 342 mT). Padé-Laplace deconvolution the transient vs. free monoexponential fit vs biexponential fit. Temperature 5K. Data was fit in the 'fit area' region. ESEEM oscillations were excluded from the data for fit and Padé-Laplace analysis.

## 5.4 Padé-Laplace Deconvolution of Polyexponential Decay Signals

---

### Echo Decay in DiTBuS 95% ESOC

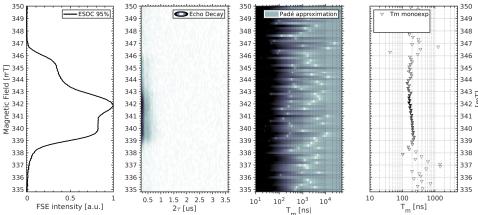


Figure 5.11: Padé-Laplace deconvolution of the field-swept spin echo decay in the pDiTBuS film at 95% ESOC. Temperature 5K.

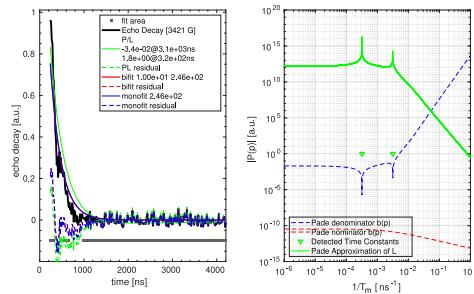


Figure 5.12: Fits of the echo decay transient in the pDiTBuS film at 95% SoC at the central spectral peak ( $m_I = 0$ , 342 mT). Padé-Laplace deconvolution the transient vs. free monoexponential fit vs biexponential fit. Temperature 5K. Data was fit in the 'fit area' region. ESEEM oscillations were excluded from the data for fit and Padé-Laplace analysis.

### Echo Decay in DiTBuS 85% ESOC

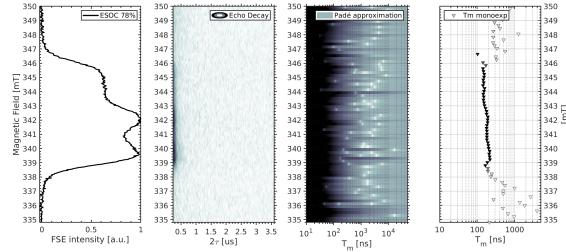


Figure 5.13: Padé-Laplace deconvolution of the field-swept spin echo decay in a pDiTBuS film at 85% ESOC. Temperature 5K.

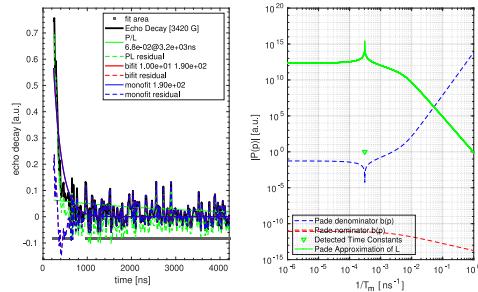


Figure 5.14: Padé-Laplace deconvolution, biexponential and monoexponential fits of the spin echo decay in a pDiTBuS film at 85% SoC at the  $m_I = 0$  spectral position. Temperature 5K. Data was fit in the 'fit area' region. ESEEM oscillations were excluded from the data for fit and Padé-Laplace analysis.

### Inversion Recovery in 50 mM TEMPOL

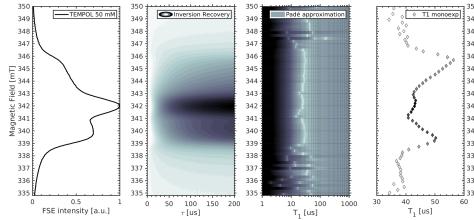


Figure 5.15: Padé-Laplace deconvolution of the field-swept inversion recovery in a frozen 50 mM solution of TEMPOL in the Dichloromethane:Acetonitrile glass (3:1). Two decay components detected with Padé-Laplace (separated poles in the Padé-Laplace approximation, third panel). Biexponential fit (circles for faster component, squares for slower component, right panel). Temperature 5K.

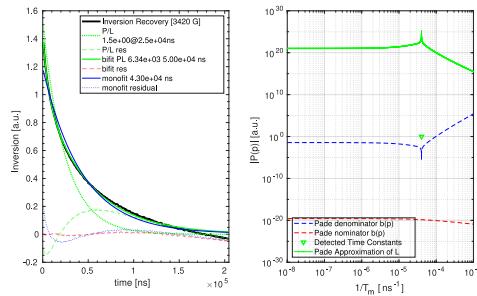


Figure 5.16: Fits of the inversion recovery transient in the frozen 50 mM TEMPOL solution at the central spectral peak ( $m_I = 0$ , 342 mT). Padé-Laplace deconvolution the transient and a biexponential fit. Temperature 5K.

### Inversion Recovery in DiTBuS 95% ESOC

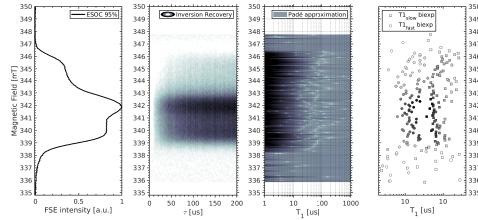


Figure 5.17: Pade-Laplace deconvolution of the field-swept inversion recovery in a pDiTBuS film at 95% ESOC. Temperature 5K.

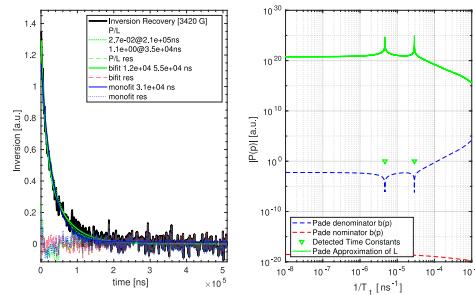


Figure 5.18: Fits of the inversion recovery transient in the 95% ESOC pDiTBuS film at the central spectral peak ( $m_I = 0$ , 342 mT). Padé-Laplace deconvolution the transient and a biexponential fit. Temperature 5K.

### Inversion Recovery in DiTBuS 85% ESOC

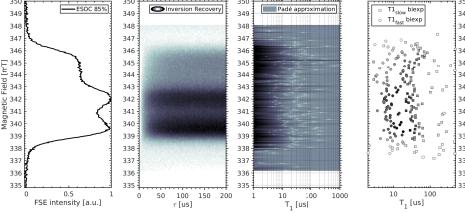


Figure 5.19: Pade-Laplace deconvolution of the field-swept inversion recovery in a pDiTBuS film at 85% ESOC. Temperature 5K.

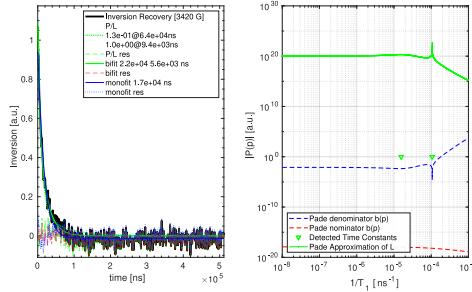


Figure 5.20: Pade-Laplace deconvolution and biexponential fit of the inversion recovery in a pDiTBuS film at 85% ESOC at the  $m_I = 0$  spectral position. Temperature 5K. Data is inverted and scaled before fitting.

#### 5.4.2 Detection of Domains with Poor Conductivity

#### 5.4.3 Towards Electron Resonance Imaging of Spin Concentrations in Battery Electrodes

The local spin concentrations that are present in an electrode film can be obtained by the time-constant-domain analysis of the echo decay transients, as it was described in 5.4.2. One can extend this characterization technique and obtain a spatially resolved image of the spin concentrations inside the battery electrode by encoding the position at which the sample is excited with a gradient of the magnetic field. A strongly asymmetric ferromagnetic wedge [32] can be used to superimpose a gradient of  $B_0$  in a chosen direction so one can not only measure the spin concentrations that are present in the electrode, but also to locate the electrochemically inactive domains and to visualize the conductive paths throughout the electrode, analogously to the NMR imaging. The

difficulty on the way to apply this visualization technique lies in the large excitation bandwidth of the pulse sequence.

Let the cathode film of width  $l$  be oriented along the static magnetic field so that  $B_0$  lies in the film plane. Let the  $B_0$  be fixed at the maximum intensity of the FSE spectrum, say,  $B_0 = B_0^{res} = 342$  mT. Let  $B_0$  be homogeneous within the film length, which is normally the case for the EPR resonator. Let the film contain a distribution of spin concentrations within its length  $C_{min} < C(z) < C_{max}$ . With the homogeneous  $B_0$ , the microwave pulse will excite the entire film length and the spin echo signal will contain spin echoes from all length elements of the film, that correspond to all  $C(z)$ . The inversion recovery transient will contain the time constants from all length elements of the film  $T_1(z)$ . With the Padé-Laplace analysis one recovers the distribution of the concentrations within the film  $C_i$ , but since the  $B_0$  is homogeneous, the information on the position  $z_i$  at which the domains are located, is lost.

Let now the  $B_0$  to be linearly increasing from  $B_0(z = -l/2) = B_0^{res} - \Delta B_0$  at one side of the film to  $B_0(z = l/2) = B_0^{res} + \Delta B_0$  by the other side of the film, so that for a given length element  $dl$  the inhomogeneity of  $B_0$  is  $dB/dl = \frac{B(z=l/2)-B(z=-l/2)}{l}$ . In the center of the film (at  $z = 0$ ) the  $B_0$  is resonant and the spin echo signal will be generated, while from the other positions of the film the magnetic field will be non-resonant and no spin echo signal will be generated. Let the width of the EPR spectrum be  $\Delta B_{FWHM} = 8$  mT and that to define the probed length element  $\Delta l$  with the given  $B_0$  gradient.  $\frac{\Delta B_{FWHM}}{\Delta l} = \frac{B(z=l/2)-B(z=-l/2)}{l}$ , so the spatial resolution is

$$\frac{\Delta l}{l} = \frac{\Delta B_{FWHM}}{B(z = l/2) - B(z = -l/2)} \quad (5.8)$$

With the spectral width of  $\Delta B_{FWHM} \leq 8$  mT and the film width of  $l \leq 3 \times 10^{-1}$  cm to get 256 points per film length one needs a  $B_0$  gradient of  $dB/dl \geq 256 * 8/0.3 \geq 6.8$  [T/cm] which is a realistic value for a typical Stern-Gerlach apparatus [32, 66].

# Chapter 6

## Conclusions and Outlook

**EES** Our results show that electron spins can be used as unique local probes for elucidating redox reactions associated with charging and discharging of ORBs with active electrode materials prepared by electropolymerization. EPR spectroscopy can thus be employed to analyze these processes, identify performance-limiting loss mechanisms, and eventually help developing strategies for making polymer batteries powerful contenders on the path towards sustainable electrochemical power sources.

The fact that we can observe a strong influence of the electrical potential on the in-situ EPR spectrum at ambient conditions provides the basis for systematically studying the redox-active sites in different states of the active electrode materials. For instance, changes in the film structure, e.g. caused by degradation, can be detected in in-situ cwEPR experiments (cf. Fig. 5.5) as nitroxides in different environments are associated with unique and characteristic EPR signatures (cf. Fig. ??). Much more detailed and specific information about degradation processes can, however, be extracted from advanced (pulse) EPR experiments which usually require low temperatures, mostly to increase spin-relaxation times. We believe that the possibility of performing low-temperature pEPR measurements is the key factor that is mandatory for a widespread use of advanced EPR techniques for ORB research.

The electrochemical cells for in-situ studies, as described in this article, were designed in such a way that they fit into a standard EPR tube. They are thus compatible with (low-temperature) experiments using conventional pEPR instrumentation. This opens up the intriguing perspective of exploiting the coupling between neighboring electron spins as well as the hyperfine coupling between electron and nuclear spins in close vicinity to determine the coupling (and thus the distance) between redox-active centers and the degree of delocalization for charge carriers on the conjugated polymer backbone. In particular, it is conceivable to find out whether inactive redox centers, which are not changing their redox state upon charging and discharging, can be found in clusters or are rather isotropically distributed in the cathode films. This provides the possibility to identify inactive redox sites that reduce the maximum attainable cell ca-

pacity. The pEPR measurements can either be performed ex situ (without electrolyte, cf. Fig. 4.23 and Fig. 4.27) or on samples that are flash-frozen while the desired electrical potential is applied to the cell.

The experiments presented here are by no means limited to the electrochemical cells used in this study. Specifically, they could also be used for investigating all-organic solid-state batteries such as the recently reported and very promising cells comprising polymeric anode and cathode materials as well as gel electrolytes based on ionic liquids.[?] In particular, low-temperature spin-echo experiments also hold promise for elucidating electron transfer processes in redox flow batteries.[132]

A strategy for overcoming sensitivity limitations of advanced EPR experiments is to combine them with electrical readout schemes and make Electrically Detected Magnetic Resonance (EDMR) applicable to study redox and transport processes in polymer batteries. EDMR possesses a sensitivity many orders of magnitude higher than conventional EPR measurements.[?] The possibility of using EDMR techniques for battery characterization at ambient conditions would also open up entirely new opportunities for imaging techniques. EDMR imaging could provide a detailed picture of the spatial distribution of active and inactive redox centres and, in general, usefully complement information obtained through imaging techniques based on conventional EPR [?, ?, ?] or nuclear magnetic resonance.[?]

**JMRO** We connected the Coulomb-counting state of charge of a pDiTBuS film to the number of reduced and thus paramagnetic TEMPO moieties by measuring the number of spins at various SoC with cwEPR. The spin counting performed with cwEPR allowed us to determine the average spin concentration in a film at a given ESOC. The average spin concentration in the film changes upon oxidation between  $(5 \pm 3) \times 10^{20}$  and  $(3 \pm 2) \times 10^{19} \text{ cm}^{-3}$ . At high SoC, the number of injected charges fits well to the number of EPR-detected charges. However, the lower the SoC, the larger fraction of the injected charges becomes EPR silent. At SoC 0%, the fraction of EPR silent charges is 78 %. The concentration of injected charges at SoC 0% corresponds to the average distance between the charges of  $d = 0.8 \text{ nm}$ , which may allow for a formation of singlet spin states (with  $S = 0$ ) [?]. While all ESOC yield a measurable cwEPR signal, at ESOC  $\leq 49\%$  no spin echo can be observed.

The strong inter-spin interactions in the discharged battery cathode drastically reduce the phase memory time  $T_m$  of the spin packets probed by pEPR, especially for the domains with the highest concentration of spins. For  $\text{ESOC} < (49 \pm 3)\%$  with the average spin concentration  $\langle n \rangle > (3 \pm 2) \times 10^{20} \text{ cm}^{-3}$ , the  $T_m$  becomes shorter than the spectrometer dead time  $t_d = 120 \text{ ns}$ , thus by the time of detection, the spin echo becomes indistinguishable from the noise. The low values of  $T_m$  represent a challenge to measure pEPR in materials with  $\langle n \rangle > 10^{20} \text{ cm}^{-3}$ . The alternative, dead-time-free

---

detection schemes[?, ?, ?, ?] may be employed to overcome the limitation imposed by short  $T_m$  in energy storage materials. With the dead-time-free detection, the echo decay transients can be measured at earlier times  $\tau < t_d$ , allowing for detecting the spin echoes from the domains with higher spin concentrations. That would extend the range of the observable local spin concentration  $C$  and allow for precise identification of the charged domains in a battery electrode.

Spin-lattice relaxation times  $T_1$ , measured in the inversion recovery experiments, have revealed two types of domains in a partially charged pDiTBuS film. Both domain types may have comparable spin concentrations and therefore similar  $T_m$ . The “conductive” domains with shorter  $T_1$  are likely to have a more efficient charge transfer kinetics between the TEMPO and the conductive pNiSalen backbone of pDiTBuS, while the “non-conductive” domains with longer  $T_1$  have a weaker interaction between TEMPO and the environment, which implies a lower probability for electron transfer between the TEMPO and the backbone. However, the separation between the two  $T_1$  distributions is rather small and the existence of the two domain types is debatable. The information extracted from the inversion recovery measurements can be used to differentiate between the domains of various charge transport efficiency, which can be used for optimizing the electrode material, such that one predominant type of domains is growing during electropolymerization.

The ability to detect a spin echo signal in a material with densely packed spins, as pDiTBuS, opens the intriguing perspective to apply advanced pulsed pEPR techniques to study novel battery materials on a molecular level. For instance, charge delocalization and intermolecular interactions in organic semiconductors can be observed with pEPR methods, particularly including double resonance techniques[?]. ENDOR was used for measuring charge delocalization in molecular semiconductor dopants [?]; electron-electron double resonance (ELDOR) was used to measure interspin distances between spin-labeled sites in a protein [49] and to observe transient radical formation in photosystems [7]. The presented analysis of the instantaneous diffusion caused by the short microwave pulses and substantial inter-spin interactions provides information on the local spin concentrations in the cathode at various states of charge. Combined, the cwEPR, electrochemical and pEPR data help one to picture the charging of the battery electrode on a microscopic level, allowing for a detailed monitoring of the processes that lead to degradation of the electrode capacity, such as the formation of electrically disconnected domains (“dead mass”), and to improve the film deposition procedure by monitoring its morphology through the  $T_1$  values.

**ME** It is possible to perform a cwEPR experiment on a working organic radical battery.

Degradation of electric capacity of a polymer electrode was attributed to a formation of

electrochemically disconnected domains in the electrode upon repeated recharging.

The significant difference in the number of elementary charges and the number of electron spins in a discharged electrode implies that the closely packed radicals in the discharged electrode pair up into S=0 states. Therefore, a formation of two-particle charge storing unit was observed. The transport of such two-particle units through the electrode film may be more efficient than the single-particle transport, as the total S=0 spin state allows them to recombine with the bipolarons in the NiSalen backbone without obeying the Pauli exclusion principle. The formation of paired spin states between the charge-bearing radicals is increasing the speed of the charge transfer and explains the high charging and discharging rates of TEMPO-Salen RCPs.

cwEPR monitoring of the degradation in pDiTS has shown the extensive release of the mono-nitroxide fragments which indicated that the decomposition of the pDiTS electrode upon is due to the breaking of the Salen-TEMPO linkers. The improved molecular structure of the Salen-TEMPO linkers in pDiTBuS by adding the oxygen atoms to the chains has improved the electrochemical stability of the material and also lead to a more efficient electropolymerization, allowing to grow thicker films that have larger capacity and more intense cwEPR signals.

Study of self-discharged have demonstrated the possibility to measure the concentration of the released mono-nitroxide shuttles and allowed to connect the concentration of the shuttles to the self-discharge rate.

Short spin relaxation times are limiting the application of pulse EPR techniques. Discharged cathode films have high spin concentrations that lead to spin dephasing on a timescale shorter than the dead time of the microwave detector. This limitation can be overcome using longitudinal detection of magnetization.

Spectral distortions caused by the instantaneous diffusion due to the broad-band excitation were simulated numerically and used to estimate the local spin concentrations in the cathode. The incomplete spectral information due to the finite dead time of the detector allows to only give the lower estimate of the local spin concentration.

The echo decay and inversion recovery transients were shown to be polyexponential signals, with individual components corresponding to certain spin concentrations within the electrode. It was possible to do an analytic deconvolution of the devay signals into its exponential components without specifying the number of components, by using the Pade-Laplace analysis.

---

The observation of distribution of the inversion recovery times with longitudinal detection may further increase the sensitivity of the method for detecting the electrically inactive domains in the film. Combining the polyexponential analysis of the inversion recovery transients with the spatially resolved spectroscopic measurements may enable the electron resonance imaging of spin concentrations in a battery cathode. However, the existence of the S=0 states in the discharged cathodes makes this method applicable only to higher states of charge, where the charges are mostly in the S=1/2, EPR active state.

EPR-compatible, polymer electrochemical cells with solid electrolyte were fabricated. These devices are shown to be more stable and longer charging with smaller current can be used to detect spin-dependent charge transport processes in them, by using the electrically detected magnetic resonance techniques.



# Bibliography

- [1] R. V. Apraksin, Y. A. Volosatova, A. I. Volkov, P. S. Vlasov, D. A. Lukyanov, I. R. Kulikov, S. N. Eliseeva, and O. V. Levin. Electrochemical synthesis and characterization of poly [ni(ch<sub>3</sub>osalen)] with immobilized poly(styrenesulfonate) anion dopants. *Electrochimica Acta*, 368:137637, 2021.
- [2] Muhammed Aydin and Burak Esat. A polythiophene derivative bearing two electroactive groups per monomer as a cathode material for rechargeable batteries. *Journal of Solid State Electrochemistry*, 19:2275–2281, 8 2015.
- [3] S Bahceci and B Esat. A polyacetylene derivative with pendant tempo group as cathode material for rechargeable batteries. *Journal of Power Sources*, 242:33–40, 2013.
- [4] Allen J. Bard, Larry R. Faulkner, and Henry S. White. *Electrochemical Methods. Fundamentals and Applications*, volume 1. Wiley, 2 edition, 2022.
- [5] Loris Bennett, Bernd Melchers, and Boris Proppe. Curta: A general-purpose high-performance computer at zedat, freie universität berlin. <http://dx.doi.org/10.17169/refubium-26754>, 2020.
- [6] Prateek Bhojane. Recent advances and fundamentals of pseudocapacitors: Materials, mechanism, and its understanding, 1 2022.
- [7] Robert Bittl and Stefan Weber. Transient radical pairs studied by time-resolved epr. *Biochimica et Biophysica Acta - Bioenergetics*, 1707:117–126, 2005.
- [8] C. Boiziau and G. Lecayon. Adhesion of polymers to metals: A review of the results obtained studying a model system. *Surface and Interface Analysis*, 12:475–485, 1988.
- [9] Enrica Bordignon. Epr spectroscopy of nitroxide spin probes. *eMagRes*, 6:235–254, 2017.
- [10] A Carrington and A. D. McLachlan. *Introduction to Magnetic Resonance with Applications to Chemistry and Chemical Physics*. John Weatherhill, inc, 1969.

- [11] Nerea Casado and David Mecerreyes. Chapter 1: Introduction to redox polymers: Classification, characterization methods and main applications, 2021.
- [12] Nerea Casado and David Mecerreyes. *Redox Polymers for Energy and Nanomedicine*. The Royal Society of Chemistry, 2021.
- [13] Harold Cassidy. Electron exchange-polymers. *J. Am. Chem. Soc.*, 71:402–406, 1949.
- [14] C Chatgilialoglu and A Studer. *Encyclopedia of Radicals in Chemistry, Biology and Materials Series*. 2012.
- [15] Davis Thomas Daniel, Steffen Oevermann, Souvik Mitra, Katharina Rudolf, Andreas Heuer, Rüdiger A. Eichel, Martin Winter, Diddo Diddens, Gunther Brunklaus, and Josef Granwehr. Multimodal investigation of electronic transport in ptma and its impact on organic radical battery performance. *Scientific Reports*, 13, 12 2023.
- [16] Davis Thomas Daniel, Conrad Szczenka, Peter Jakes, Rüdiger-A. Eichel, and Josef Granwehr. Laplace inverted pulsed epr relaxation to study contact between active material and carbon black in li–organic battery cathodes. *Physical Chemistry Chemical Physics*, 25:12767–12776, 2023.
- [17] Florian Degen and Marius Schütte. Life cycle assessment of the energy consumption and ghg emissions of state-of-the-art automotive battery cell production. *Journal of Cleaner Production*, 330:129798, 2022.
- [18] Wolfgang Demtröder. *Experimentalphysik 3: Atome, Moleküle und Festkörper*, volume 3. Springer-Verlag, 5 edition, 2016.
- [19] Boucar Diouf and Christophe Avis. The potential of li-ion batteries in ecowas solar home systems. *Journal of Energy Storage*, 22:295–301, 2019.
- [20] Evgenia Dmitrieva, Marco Rosenkranz, Julia S. Danilova, Evgenia A. Smirnova, Mikhail P. Karushev, Irina A. Chepurnaya, and Aleksander M. Timonov. Radical formation in polymeric nickel complexes with n2o2 schiff base ligands: An in situ esr and uv–vis–nir spectroelectrochemical study. *Electrochimica Acta*, 283:1742–1752, 2018.
- [21] D E Eastman. Photoelectric work functions of transition, rare-earth, and noble metals, 1970.
- [22] Sandra S Eaton, Lukas B Woodcock, and Gareth R Eaton. Continuous wave electron paramagnetic resonance of nitroxide biradicals in fluid solution. *Concepts in Magnetic Resonance Part A: Bridging Education and Research*, 47A:1–16, 2018.

## Bibliography

---

- [23] A. Einstein. Relativity - the special and general theory, 1921.
- [24] X. Fan, T. G. Myers, B. A.D. Sukra, and G. Gabrielse. Measurement of the electron magnetic moment. *Physical Review Letters*, 130, 2 2023.
- [25] Chen Fang, Thanh Nhan Tran, Yangzhi Zhao, and Gao Liu. Electrolyte decomposition and solid electrolyte interphase revealed by mass spectrometry, 12 2021.
- [26] M. Fehr, J. Behrends, S. Haas, B. Rech, K. Lips, and A. Schnegg. Electrical detection of electron-spin-echo envelope modulations in thin-film silicon solar cells. *Physical Review B - Condensed Matter and Materials Physics*, 84:1–5, 11 2011.
- [27] R P Feynman. Space-time appxoach to quantum electxotiyynamics. *Physical Review*, 76:769–789, 1949.
- [28] Jan Figgener, Peter Stenzel, Kai Philipp Kairies, Jochen Linßen, David Haberschusz, Oliver Wessels, Georg Angenendt, Martin Robinius, Detlef Stolten, and Dirk Uwe Sauer. The development of stationary battery storage systems in germany – a market review. *Journal of Energy Storage*, 29, 6 2020.
- [29] C Fribe and U S Schubert. High-power-density organic radical batteries. *Topics in Current Chemistry*, 375:1–35, 2017.
- [30] Yangyang Fu, Song Lu, Kaiyuan Li, Changchen Liu, Xudong Cheng, and Heping Zhang. An experimental study on burning behaviors of 18650 lithium ion batteries using a cone calorimeter. *Journal of Power Sources*, 273:216–222, 1 2015.
- [31] Yangyang Fu, Song Lu, Kaiyuan Li, Changchen Liu, Xudong Cheng, and Heping Zhang. An experimental study on burning behaviors of 18650 lithium ion batteries using a cone calorimeter. *Journal of Power Sources*, 273:216–222, 1 2015.
- [32] Walther Gerlach and Otto Stern. Der experimentelle nachweis der richtungsquantelung im magnetfeld. *Zeitschrift für Physik*, 9:348–352, 1922.
- [33] Nicolas Goujon, Nerea Casado, Nagaraj Patil, Rebeca Marcilla, and David Mecerreyes. Organic batteries based on just redox polymers: Abstract. *Progress in Polymer Science*, 122:101449, 2021.
- [34] Cristina Grosu, Chiara Panosetti, Steffen Merz, Peter Jakes, Stefan Seidlmayer, Sebastian Matera, Rüdiger a Eichel, Josef Granwehr, and Christoph Scheurer. Revisiting the storage capacity limit of graphite battery anodes : Spontaneous lithium overintercalation at ambient pressure. *PRX Energy*, 2:1–14, 2023.

- [35] Ting Guan, Shun Sun, Fengbin Yu, Yunzhi Gao, Peng Fan, Pengjian Zuo, Chunyu Du, and Geping Yin. The degradation of  $\text{LiCoO}_2$ /graphite batteries at different rates. *Electrochimica Acta*, 279:204–212, 2018.
- [36] Karin Halbmair, Jan Seikowski, Igor Tkach, Claudia Höbartner, Deniz Sezer, and Marina Bennati. High-resolution measurement of long-range distances in rna: Pulse epr spectroscopy with tempo-labeled nucleotides. *Chemical Science*, 7:3172–3180, 2016.
- [37] Padinhare Cholakkal Harikesh, Chi-Yuan Yang, Deyu Tu, Jennifer Y. Gerasimov, Abdul Manan Dar, Adam Armada-Moreira, Matteo Massetti, Renee Kroon, David Bliman, Roger Olsson, Eleni Stavrinidou, Magnus Berggren, and Simone Fabiano. Organic electrochemical neurons and synapses with ion mediated spiking. *Nature Communications*, 13:901, 12 2022.
- [38] Xiyue He and Xuelai Zhang. A comprehensive review of supercapacitors: Properties, electrodes, electrolytes and thermal management systems based on phase change materials, 12 2022.
- [39] Alan J Heeger. Semiconducting and metallic polymers: The fourth generation of polymeric materials. *The Journal of Physical Chemistry B*, 105:8475–8491, 9 2001.
- [40] Edward H. Hellen. Padé–laplace analysis of signal averaged voltage decays obtained from a simple circuit. *American Journal of Physics*, 73:871–875, 2005.
- [41] Edward H. Hellen. Padé–laplace analysis of signal averaged voltage decays obtained from a simple circuit. *American Journal of Physics*, 73:871–875, 9 2005.
- [42] Takuma Hirasawa, Mika Yoshida, and Shin’ya Obara. Battery control for leveling the amount of electricity purchase in smart-energy houses. *International Journal of Energy Research*, 45:807–823, 2021.
- [43] Peng Hu, Xuexia He, and Hui Jiang. Greater than  $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ : A breakthrough of organic semiconductors for field-effect transistors, 6 2021.
- [44] Q Huang, E D Walter, L Cosimbescu, D Choi, and J P Lemmon. In situ electrochemical-electron spin resonance investigations of multi-electron redox reaction for organic radical cathodes. *Journal of Power Sources*, 306:812–816, 2016.
- [45] Ian E. Jacobs, Yue Lin, Yuxuan Huang, Xinglong Ren, Dimitrios Simatos, Chen Chen, Dion Tjhe, Martin Statz, Lianglun Lai, Peter A. Finn, William G. Neal, Gabriele D’Avino, Vincent Lemaur, Simone Fratini, David Beljonne, Joseph

## Bibliography

---

- Strzalka, Christian B. Nielsen, Stephen Barlow, Seth R. Marder, Iain McCulloch, and Henning Sirringhaus. High-efficiency ion-exchange doping of conducting polymers. *Advanced Materials*, 34, 6 2022.
- [46] T Janoschka, M D Hager, and U S Schubert. Powering up the future: Radical polymers for battery applications. *Adv. Mater.*, 24:6397–6409, 2012.
- [47] Tobias Janoschka, Christian Friebe, Martin D. Hager, Norbert Martin, and Ulrich S. Schubert. An approach toward replacing vanadium: A single organic molecule for the anode and cathode of an aqueous redox-flow battery. *ChemistryOpen*, 6:216–220, 2017.
- [48] Tobias Janoschka, Christian Friebe, Martin D. Hager, Norbert Martin, and Ulrich S. Schubert. An approach toward replacing vanadium: A single organic molecule for the anode and cathode of an aqueous redox-flow battery. *ChemistryOpen*, 6:216–220, 2017.
- [49] G Jeschke. Deer distance measurements on proteins. *Annual Review of Physical Chemistry*, Vol 63, 63:419–446, 2012.
- [50] Josef Kadlec, Radoslav Cipin, Dalibor Cervinka, Pavel Vorel, and Bohumil Klima. Li-ion accumulators for propulsion system of electric airplane vut 051 ray. *Journal of Solid State Electrochemistry*, 18:2307–2313, 2014.
- [51] Y Kanzaki, S Mitani, D Shiomi, Y Morita, T Takui, and K Sato. Microscopic behavior of active materials inside a tcnq-based lithium-ion rechargeable battery by in situ 2d esr measurements. *Acs Applied Materials & Interfaces*, 10:43631–43640, 2018.
- [52] T Katsumata, M Satoh, J Wada, M Shiotsuki, F Sanda, and T Masuda. Polyacetylene and polynorbornene derivatives carrying tempo. synthesis and properties as organic radical battery materials. *Macromolecular Rapid Communications*, 27:1206–1211, 2006.
- [53] M Khodeir, B Ernould, J Brassinne, S Ghiassinejad, H Jia, S Antoun, C Friebe, U S Schubert, Z Kochovski, Y Lu, E Van Ruymbeke, and J F Gohy. Synthesis and characterisation of redox hydrogels based on stable nitroxide radicals. *Soft Matter*, 15:6418–6426, 2019.
- [54] Jihyeon Kim, Youngsu Kim, Jaekyun Yoo, Giyun Kwon, Youngmin Ko, and Kisuk Kang. Organic batteries for a greener rechargeable world. *Nature Reviews Materials*, 8:54–70, 2023.

- [55] H Koezuka, A Tsumura, and T Ando. Field-effect transistor with polythiophene thin film, 1987.
- [56] Kenichiroh Koshika, Naoki Sano, Kenichi Oyaizu, and Hiroyuki Nishide. An aqueous, electrolyte-type, rechargeable device utilizing a hydrophilic radical polymer-cathode. *Macromolecular Chemistry and Physics*, 210:1989–1995, 11 2009.
- [57] Ilia Kulikov, Naitik A. Panjwani, Anatoliy A. Vereshchagin, Domenik Spallek, Daniil A. Lukianov, Elena V. Alekseeva, Oleg V. Levin, and Jan Behrends. Spins at work: probing charging and discharging of organic radical batteries by electron paramagnetic resonance spectroscopy. *Energy and Environmental Science*, 15:3275–3290, 2022.
- [58] Ilia Kulikov, Anatoliy A. Vereshchagin, Daniil A. Lukianov, Oleg V. Levin, and Jan Behrends. A nitroxide-containing cathode material for organic radical batteries studied with pulsed epr spectroscopy. *Journal of Magnetic Resonance Open*, 16-17, 12 2023.
- [59] Ilya Kuprov. *Spin: From Basic Symmetries to Quantum Optimal Control*. Springer International Publishing, 1 2023.
- [60] T. Kushida and J. C. Murphy. Volume dependence of the knight shift in lithium. *Physical Review B*, 21:4247–4250, 1980.
- [61] Anna Köhler and Heinz Bässler. Electronic processes in organic semiconductors, 2015.
- [62] Fredrik Larsson, Petra Andersson, Per Blomqvist, and Bengt Erik Mellander. Toxic fluoride gas emissions from lithium-ion battery fires. *Scientific Reports*, 7:1–13, 12 2017.
- [63] C H Lee, G Yu, D Moses, K Pakbaz, C Zhang, N S Sariciftci, A J Heeger, and F Wudl. Sensitization of the photoconductivity of conducting polymers by c60: Photoinduced electron transfer, 1993.
- [64] Yong Hee Lee, Joo Seong Kim, Jonghyeon Noh, Inhwa Lee, Hyeong Jun Kim, Sunghun Choi, Jeongmin Seo, Seokwoo Jeon, Taek Soo Kim, Jung Yong Lee, and Jang Wook Choi. Wearable textile battery rechargeable by solar energy. *Nano Letters*, 13:5753–5761, 2013.
- [65] Chao Li, Ming Shen, and Bingwen Hu. Solid-state nmr and epr methods for metal ion battery research. *Wuli Huaxue Xuebao/Acta Physico - Chimica Sinica*, 36:1–16, 2019.

## Bibliography

---

- [66] Jiahao Liang, Thomas M. Fuchs, Rolf Schäfer, and Vitaly V. Kresin. Strong permanent magnet gradient deflector for stern-gerlach-type experiments on molecular beams. *Review of Scientific Instruments*, 91, 5 2020.
- [67] Chaofeng Liu, Zachary G. Neale, and Guozhong Cao. Understanding electrochemical potentials of cathode materials in rechargeable batteries, 3 2016.
- [68] Xiangli Liu, Yougang Mao, Errol V. Mathias, Collin Ma, Osmundo Franco, Yong Ba, Julia A. Kornfield, Tieli Wang, Lijun Xue, Bing Sen Zhou, and Yun Yen. Study the property of double-ended fluoroalkyl poly(ethylene glycol) hydrogel as a depot for hydrophobic drug delivery using electron paramagnetic resonance technique and cell proliferation assay. *Journal of Sol-Gel Science and Technology*, 45:269–278, 3 2008.
- [69] Yong Lu and Jun Chen. Prospects of organic electrode materials for practical lithium batteries. *Nature Reviews Chemistry*, 4:127–142, 2020.
- [70] Oana R. Luca, Jeffrey L. Gustafson, Sean M. Maddox, Aidan Q. Fenwick, and Daryl C. Smith. Catalysis by electrons and holes: Formal potential scales and preparative organic electrochemistry, 7 2015.
- [71] Tianyi Ma, Siyuan Wu, Fang Wang, Joseph Lacap, Chunjing Lin, Shiqiang Liu, Mohan Wei, Weijian Hao, Yunshi Wang, and Jae Wan Park. Degradation mechanism study and safety hazard analysis of overdischarge on commercialized lithium-ion batteries. *ACS Applied Materials and Interfaces*, 12:56086–56094, 2020.
- [72] Praveen Kumar Reddy Maddikunta, Gautam Srivastava, Thippa Reddy Gadekallu, Natarajan Deepa, and Prabadevi Boopathy. Predictive model for battery life in iot networks. *IET Intelligent Transport Systems*, 14:1388–1395, 2020.
- [73] Christoph Meier, Jan Behrends, Christian Teutloff, Oleksandr Astakhov, Alexander Schnegg, Klaus Lips, and Robert Bittl. Multi-frequency edmr applied to microcrystalline thin-film silicon solar cells. *Journal of Magnetic Resonance*, 234:1–9, 2013.
- [74] Alice J. Merryweather, Quentin Jacquet, Steffen P. Emge, Christoph Schnedermann, Akshay Rao, and Clare P. Grey. Operando monitoring of single-particle kinetic state-of-charge heterogeneities and cracking in high-rate li-ion anodes. *Nature Materials*, 21:1306–1313, 2022.
- [75] S Muench, A Wild, C Fribe, B Haupler, T Janoschka, and U S Schubert. Polymer-based organic batteries. *Chemical Reviews*, 116:9438–9484, 2016.

- [76] K Nakahara, S Iwasa, M Satoh, Y Morioka, J Iriyama, M Suguro, and E Hasegawa. Rechargeable batteries with organic radical cathodes. *Chem. Phys. Lett.*, 359:351–354, 2002.
- [77] Roland Neueder. Ion mobilities, 2014.
- [78] David B Newell and Eite Tiesinga. The international system of units (si):, 8 2019.
- [79] Arvid Niemöller, Peter Jakes, Rüdiger A. Eichel, and Josef Granwehr. In operando epr investigation of redox mechanisms in  $\text{LiCoO}_2$ . *Chemical Physics Letters*, 716:231–236, 2019.
- [80] Arvid Niemöller, Peter Jakes, Svitlana Eurich, Anja Paulus, Hans Kungl, Rüdiger A. Eichel, and Josef Granwehr. Monitoring local redox processes in  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  battery cathode material by in operando epr spectroscopy. *Journal of Chemical Physics*, 148:1–10, 2018.
- [81] H Nishide, S Iwasa, Y J Pu, T Suga, K Nakahara, and M Satoh. Organic radical battery: nitroxide polymers as a cathode-active material. *Electrochimica Acta*, 50:827–831, 2004.
- [82] Hiroyuki Nishide, Kenichiro Koshika, and Kenichi Oyaizu. Environmentally benign batteries based on organic radical polymers. volume 81, pages 1961–1970, 2009.
- [83] Naoki Nitta, Feixiang Wu, Jung Tae Lee, and Gleb Yushin. Li-ion battery materials: Present and future. *Materials Today*, 18:252–264, 2015.
- [84] Cavendish Laboratory University of Cambridge. Organic semiconductors, 2018.
- [85] D E O’reilly. Exchange narrowing in electron paramagnetic resonance of ruby. *Chemical Physics Letters*, 10:239–241, 1971.
- [86] Dongxu Ouyang, Jingwen Weng, Mingyi Chen, Jiahao Liu, and Jian Wang. Experimental analysis on the degradation behavior of overdischarged lithium-ion battery combined with the effect of high-temperature environment. *International Journal of Energy Research*, 44:229–241, 2020.
- [87] Rikard Owenius, Maria Engström, Mikael Lindgren, and Martina Huber. Influence of solvent polarity and hydrogen bonding on the epr parameters of a nitroxide spin label studied by 9-ghz and 95-ghz epr spectroscopy and dft calculations. *Journal of Physical Chemistry A*, 105:10967–10977, 2001.

## Bibliography

---

- [88] Kenichi Oyaizu, Hanae Tatsuhira, and Hiroyuki Nishide. Facile charge transport and storage by a tempo-populated redox mediating polymer integrated with polyaniline as electrical conducting path. *Polymer Journal*, 47:212–219, 2 2015.
- [89] Dirac P. A. M. The quantum theory of the electron. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 117:610–624, 1928.
- [90] Yuepeng Pang, Jinyu Pan, Junhe Yang, Shiyou Zheng, and Chunsheng Wang. Electrolyte/electrode interfaces in all-solid-state lithium batteries: A review, 6 2021.
- [91] Jens F. Peters, Manuel Baumann, Benedikt Zimmermann, Jessica Braun, and Marcel Weil. The environmental impact of li-ion batteries and the role of key parameters – a review. *Renewable and Sustainable Energy Reviews*, 67:491–506, 2017.
- [92] M. H. Poincaré. Sur la dynamique de l'électron. *Rend. Circ. Matem. Palermo*, pages 129–175, 12 1906.
- [93] Anna Pražanová, Vaclav Knap, and Daniel Ioan Stroe. Literature review, recycling of lithium-ion batteries from electric vehicles, part i: Recycling technology. *Energies*, 15:1–29, 2022.
- [94] Kevin J. Rhodes, Roberta Meisner, Melanie Kirkham, Nancy Dudney, and Claus Daniel. In situ xrd of thin film tin electrodes for lithium ion batteries. *Journal of The Electrochemical Society*, 159:A294–A299, 2012.
- [95] Philip Rohland, Erik Schröter, Oliver Nolte, George R. Newkome, Martin D. Hager, and Ulrich S. Schubert. Redox-active polymers: The magic key towards energy storage – a polymer design guideline progress in polymer science, 2 2022.
- [96] J. J. Sakurai and Jim Napolitano. *Modern Quantum Mechanics*. Dorling Kinder-sley Pvt. Ltd., 2 edition, 2014.
- [97] K. M. Salikhov, S. A. Dzuba, and A. M. Raitsimring. The theory of electron spin-echo signal decay resulting from dipole-dipole interactions between paramagnetic centers in solids. *Journal of Magnetic Resonance*, 42:255–276, 1981.
- [98] K M Salikhov and N E Zavoiskaya. Zavoisky and the discovery of epr, 2015.
- [99] Kan Sato, Rieka Ichinoi, Ryusuke Mizukami, Takuma Serikawa, Yusuke Sasaki, Jodie Lutkenhaus, Hiroyuki Nishide, and Kenichi Oyaizu. Diffusion-cooperative model for charge transport by redox-active nonconjugated polymers. *Journal of the American Chemical Society*, 140:1049–1056, 1 2018.

- [100] Pierre Olivier Schwartz, Marijana Pejic, Mario Wachtler, and Peter Bäuerle. Synthesis and characterization of electroactive pedot-tempo polymers as potential cathode materials in rechargeable batteries. *Synthetic Metals*, 243:51–57, 9 2018.
- [101] A Schweiger and G Jeschke. *Principles of Pulse Electron Paramagnetic Resonance*. Oxford University Press, 2001.
- [102] J Schwinger. On quantum-electrodynamics and the magnetic moment of the electron. *Physical Review*, 73:416–417, 1948.
- [103] Yongchao Shi and Mingxue Tang. Nmr/epr investigation of rechargeable batteries. *Wuli Huaxue Xuebao/Acta Physico - Chimica Sinica*, 36:1–13, 2019.
- [104] By Hideki Shirakawa, Edwin J Louis, Alan G Macdiarmid, C H W A N K Chiang, and Alan J HEEGERt. Synthesis of electrically conducting organic polymers : Halogen derivatives of polyacetylene, (ch), 1977.
- [105] Domenik Spallek. Spin-dependent processes in organic radical batteries, master thesis, 6 2022.
- [106] H. Staudinger. Über polymerisation. *European Journal of Inorganic Chemistry*, 53:1073–1085, 6 1920.
- [107] Stefan Stoll and Arthur Schweiger. Easyspin, a comprehensive software package for spectral simulation and analysis in epr. *Journal of Magnetic Resonance*, 178:42–55, 1 2006.
- [108] Juliusz Sworakowski. How accurate are energies of homo and lumo levels in small-molecule organic semiconductors determined from cyclic voltammetry or optical spectroscopy. *Synthetic Metals*, 235:125–130, 1 2018.
- [109] Hiroyuki Takeo Nishide and Suga. Organic radical battery. *Journal of the Society of Mechanical Engineers*, 110:194–195, 2007.
- [110] J.-M Tarascon and M Armand. Issues and challenges facing rechargeable lithium batteries, 2001.
- [111] Nir Tessler, Yevgeni Preezant, Noam Rappaport, and Yohai Roichman. Charge transport in disordered organic materials and its relevance to thin-film devices: A tutorial review. *Advanced Materials*, 21:2741–2761, 2009.
- [112] Yu. V. Toropov, S. A. Dzuba, Yu. D. Tsvetkov, V Monaco, F Formaggio, M Crisma, C Toniolo, and J. Raap. Molecular dynamics and spatial distribution of toac spin-labelled peptaibols studied in glassy liquid by echo-detected epr spectroscopy. *Applied Magnetic Resonance*, 15:237–246, 1998.

## Bibliography

---

- [113] Wu-Ki. Tung. *Group theory in physics*. World Scientific, 1985.
- [114] Anatolii. A. Vereshchagin, Daniil A. Lukyanov, Ilia R. Kulikov, Naitik A. Pan-jwani, Elena A. Alekseeva, Jan Behrends, and Oleg V. Levin. The fast and the spacious: A [ni(salen)]-tempo redox-conducting polymer for organic batteries. *Batteries and Supercaps*, 4:336–346, 2020.
- [115] Anatoliy A. Vereshchagin, Arseniy Y. Kalnin, Alexey I. Volkov, Daniil A. Lukyanov, and Oleg V. Levin. Key features of tempo-containing polymers for energy storage and catalytic systems. *Energies*, 15:1–50, 2022.
- [116] Shaoyang Wang, Fei Li, Alexandra D. Easley, and Jodie L. Lutkenhaus. Real-time insight into the doping mechanism of redox-active organic radical polymers. *Nature Materials*, 18:69–75, 1 2019.
- [117] John A. Weil and James R. Bolton. *Electron Paramagnetic Resonance Elementary Theory and Practical Applications*. Wiley, 2nd edition, 2007.
- [118] Ting Ting Wu, Gao Le Dai, Jin Jia Xu, Fang Cao, Xiao Hong Zhang, Yu Zhao, and Yu Min Qian. Structural design of organic battery electrode materials: from dft to artificial intelligence, 10 2023.
- [119] Y Xie, K Zhang, Y Yamauchi, K Oyaizu, and Z F Jia. Nitroxide radical polymers for emerging plastic energy storage and organic electronics: fundamentals, materials, and applications. *Materials Horizons*, 8:803–829, 2021.
- [120] Yuan Xie, Kai Zhang, Yusuke Yamauchi, Kenichi Oyaizu, and Zhongfan Jia. Nitroxide radical polymers for emerging plastic energy storage and organic electronics: Fundamentals, materials, and applications. *Materials Horizons*, 8:803–829, 2021.
- [121] Chengjian Xu, Qiang Dai, Linda Gaines, Mingming Hu, Arnold Tukker, and Bernhard Steubing. Future material demand for automotive lithium-based batteries. *Communications Materials*, 1:1–10, 2020.
- [122] Lihuan Xu, Fang Yang, Chang Su, Lvlv Ji, and Cheng Zhang. Synthesis and properties of novel tempo-contained polypyrrole derivatives as the cathode material of organic radical battery. *Electrochimica Acta*, 130:148–155, 6 2014.
- [123] He Yan, Zhihua Chen, Yan Zheng, Christopher Newman, Jordan R. Quinn, Florian Dötz, Marcel Kastler, and Antonio Facchetti. A high-mobility electron-transporting polymer for printed transistors. *Nature*, 457:679–686, 2 2009.
- [124] H T Yi, Y N Gartstein, and V Podzorov. Charge carrier coherence and hall effect in organic semiconductors. *Scientific Reports*, 6:1–11, 2016.

- [125] Hyun Deog Yoo, Elena Markevich, Gregory Salitra, Daniel Sharon, and Doron Aurbach. On the challenge of developing advanced technologies for electrochemical energy storage and conversion. *Materials Today*, 17:110–121, 2014.
- [126] E K Zavoisky. Paramagnetic relaxation of liquid solutions for perpendicular fields. *Zhur. Eksperiment. i Theoret. Fiz.*, 15:344–350, 1945.
- [127] E K Zavoisky. Spin-magnetic resonance in paramagnetics. *Journal of Physics*, 9:245, 1945.
- [128] Clara Zens, Christian Fribe, Ulrich S. Schubert, Martin Richter, and Stephan Kupfer. Tailored charge transfer kinetics in precursors for organic radical batteries – a joint synthetic-theoretical approach. *ChemSusChem*, e202201679:1–14, 2022.
- [129] Guangxu Zhang, Xuezhe Wei, Siqi Chen, Guangshuai Han, Jiangong Zhu, and Haifeng Dai. Investigation the degradation mechanisms of lithium-ion batteries under low-temperature high-rate cycling. *ACS Applied Energy Materials*, 5:6462–6471, 2022.
- [130] Qingsong Zhang, Tiantian Liu, and Qiong Wang. Experimental study on the influence of different heating methods on thermal runaway of lithium-ion battery. *Journal of Energy Storage*, 42:1–9, 10 2021.
- [131] Yiren Zhang, Albert M. Park, Stephen R. McMillan, Nicholas J. Harmon, Michael E. Flatté, Gregory D. Fuchs, and Christopher K. Ober. Charge transport in conjugated polymers with pendent stable radical groups. *Chemistry of Materials*, 30:4799–4807, 7 2018.
- [132] Evan Wenbo Zhao, Erlendur Jónsson, Rajesh B. Jethwa, Dominic Hey, Dongxun Lyu, Adam Brookfield, Peter A.A. Klusener, David Collison, and Clare P. Grey. Coupled *in situ* nmr and epr studies reveal the electron transfer rate and electrolyte decomposition in redox flow batteries. *Journal of the American Chemical Society*, 143:1885–1895, 2 2021.
- [133] Wenbo Zhou, Wenjie Liu, Meng Qin, Zhidong Chen, Juan Xu, Jianyu Cao, and Jun Li. Fundamental properties of tempo-based catholytes for aqueous redox flow batteries: effects of substituent groups and electrolytes on electrochemical properties, solubilities and battery performance. *RSC Advances*, 10:21839–21844, 6 2020.
- [134] Lingyun Zhu, Yuanping Yi, Yuan Li, Eung Gun Kim, Veaceslav Coropceanu, and Jean Luc Brédas. Prediction of remarkable ambipolar charge-transport characteristics in organic mixed-stack charge-transfer crystals. *Journal of the American Chemical Society*, 134:2340–2347, 2 2012.

# **Appendix A: Electron Magnetic Resonance Environment**

A python-based interactive program EMRE (Electron Magnetic Resonance Environment) was developed to interconnect and control the EPR spectrometer and to simultaneously operate the electrochemical device under testing. The program allows one to perform electrochemical measurements such as cyclic voltammetry and galvanostatic charge-discharge cycling and to simultaneously record cwEPR spectra with customizable, lab-built and commercial EPR spectrometers. Most of the redox conductive films considered in this thesis were manufactured using EMRE. Some of the potential-dependent spectra and degradation studies were carried out using EMRE. The source code of the program and the documentation is available at the remote repository: <https://github.com/rst030/EMRE>.



## **Appendix B: Calculations of Spin Density in DiTS**

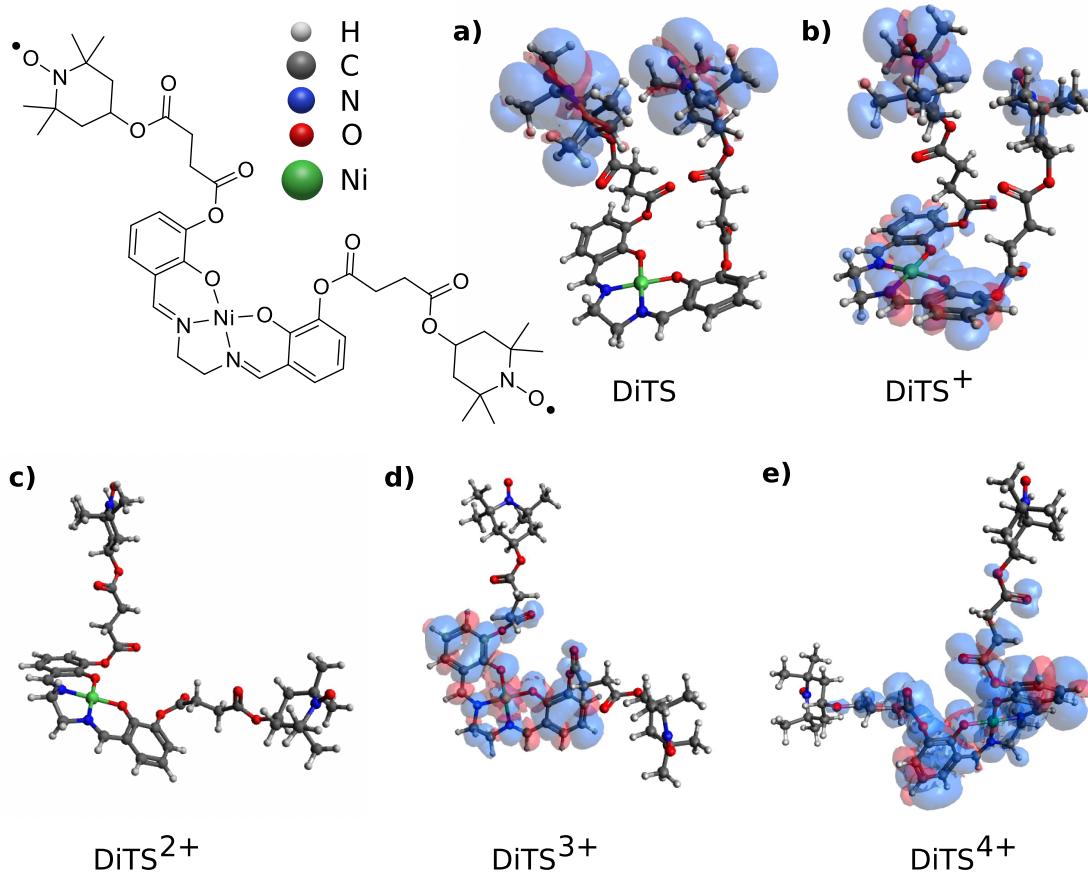
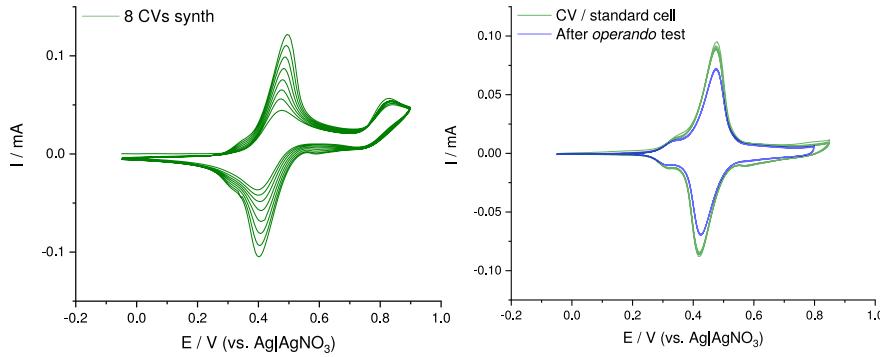


Figure 6.1: Spin density in a single DiTS monomer unit for various oxidation states (isovalue: 0.01) calculated with density-functional theory in ORCA [?], using the def2-TZVP functional basis set for the geometry optimization and the calculations of the spin density. The calculations were carried out at the high-performance computing cluster Curta of the Free University of Berlin [5]. a): neutral DiTS with two TEMPO radicals, b) singly oxidized DiTS (one hole injected), b) doubly oxidized DiTS showing no spin density, c)  $\text{DiTS}^{3+}$  showing a positive polaron localized on the NiSalen backbone, d)  $\text{DiTS}^{4+}$  showing increased spin density on the backbone. Calculations performed by Marcel Gauglitz.

## **Appendix C: Sample Information**

a) p-DiTS In-operando SEC cwEPR study at room temperature (Figure 4)

CV: 8 CV cycles, 50 mV/s

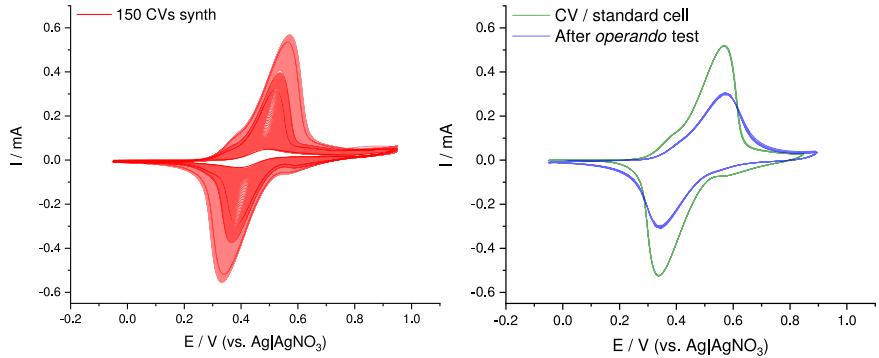


cwEPR Parameters: Attenuation 22 dB, Modulation Amplitude 0.5 mT, Modified Tube

---

b) p-DiTS In-operando SEC cwEPR study at room temperature (Figure 5a)

CV: 150 CV cycles, 50 mV/s

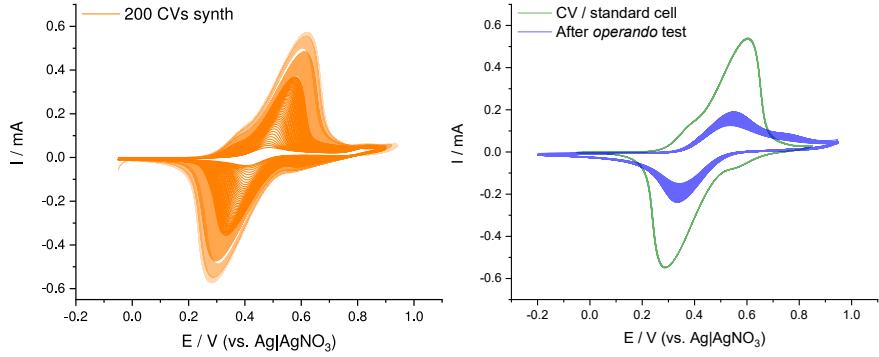


cwEPR Parameters: Attenuation 22 dB, Modulation Amplitude 0.5 mT, Modified Tube

---

c) p-DiTS In-operando SEC cwEPR study at room temperature (Figure 5b)

CV: 200 CV cycles, 50 mV/s



cwEPR Parameters: Attenuation 22 dB, Modulation Amplitude 0.5 mT, Modified Tube

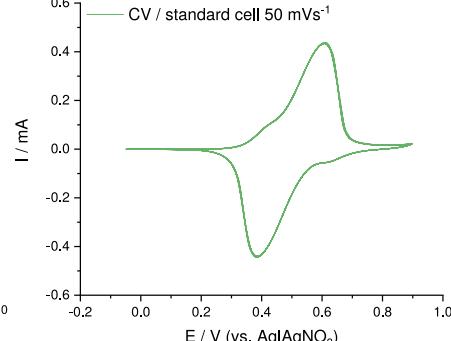
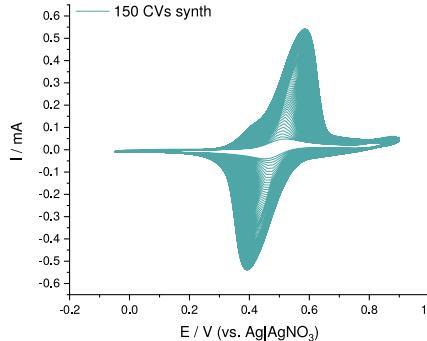
## Bibliography

---

d) p-DiTS In-operando SEC cwEPR study at room temperature (Figure 6)

CV:

150 CV cycles, 50 mV/s



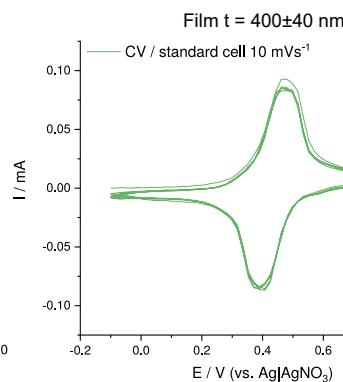
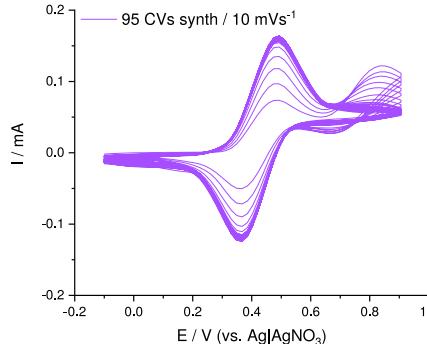
cwEPR Parameters: Attenuation 22 dB, Modulation Amplitude 0.5 mT, Modified Tube

---

e) p-DiTS Ex-situ SEC cwEPR at 150 K (Figure 7a)

CV:

95 CV cycles, 10 mV/s



cwEPR Parameters: Attenuation 22 dB, Modulation Amplitude 0.5 mT, 150 K, Standard Tube

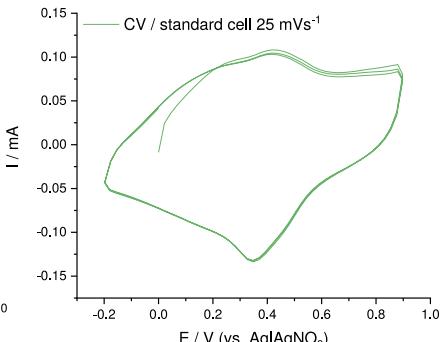
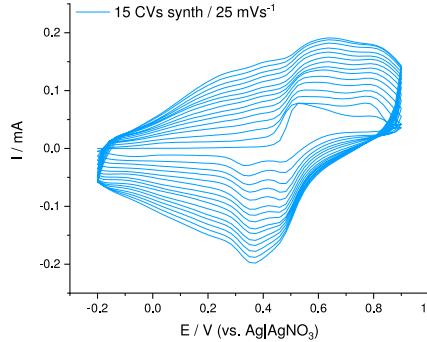
---

f) p-NiMeOSalen Ex-situ SEC cwEPR study at 150 K (Figure 7b)

CV:

15 CV cycles, 25 mV/s

Film t = 900±100 nm



cwEPR Parameters: Attenuation 22 dB, Modulation Amplitude 0.5 mT, 150 K, Standard Tube

Figure 6.2: Sample information. Deposition CV curves, Cleaning CV curves, EPR parameters, Figure references.