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

Ilia Romanovich Kulikov

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Contents

$\vec{e}_x, \vec{e}_y, \vec{e}_z, t$	Laboratory frame of reference
$\vec{\hat{S}}$	Spin operator
$\hat{S}_Z$	Z component of the spin operator
$\mu_B = 9.2740100783(28) \times 10^{-24}$ J/T	Bohr magneton
$\mu_0 = 0.0000000000(00) \times 10^{-00}$ X/X	The permeability of free space
$\vec{B_0} = B_0\vec{e}_z$	Static magnetic field
ORB	organic radical battery
WE	working electrode (cathode)
CE	counter electrode (anode)
RE	reference electrode
SoC	state of charge
ESOC	EPR-detected SoC
CV	cyclic voltammogram
GCD	galvanostatic charge-discharge
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
pDiTBuS	poly-di-TEMPO-Butyl-Salen
PTMA	poly-TEMPO-methacrylate
EDFS	echo-detected field sweep
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

Life needs energy to continue its spread. Plants use photosynthesis to separate carbon from oxygen and to grow. Higher life forms as humans consume energy during the day and during the night, being dependent on the available energy source. While fossil fuels are still the major source of energy and while fire is used to convert the Joules that hold together hydrocarbon molecules into ”horse power” of an engine and kilowatt-hours in the power socket, there are cleaner and more efficient ways to harvest energy. Photosynthesis had inspired the creation of solar panels that convert the sunlight into electricity, the atom had been tamed in the core of a nuclear reactor to power cities; we can extract the energy from sound, wind and waves and from the heat of the planet. Moreover, there are hopes and continuous attempts to achieve nuclear fusion - the creation of an artificial Sun by melting together atomic cores - the virtually inexhaustible and clean source of energy. The oil and gas are limited and unevenly distributed resources, and wind does not always blow, the Sun does not shine at night, the wild Nature is still unpredictable and the extracted energy has to be stored in order to level out its production and consumption.

With the rise of the technological era, over the last century, the energy has been delivered to our homes in form of electricity. The storage of electrical energy is the key ingredient of every power grid, every electrical device. Electric charges separated by a potential barrier can store energy in a device called a battery, or, precisely, a battery of electrochemical cells. It is also possible to store the energy in an electrostatic field between the plates of a capacitor, but due to the technological difficulties, electrochemical cells are commonly used nowadays. An electrochemical cell is an energy storage device that undergoes a chemical reaction to release electrical energy. A simple electrochemical cell consists of two spatially separated materials called electrodes, that have different work functions, or, chemically speaking, reduction-oxidation (redox) potentials. The electrodes are separated with a layer of ions that allow for the transfer of charge between the electrodes when they are connected to each other with a conductor that passes electric current through the consumer and therefore transfers the energy, that is, the battery is plugged into an electric circuit. While the battery 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, that accepts electrons and is being oxidized. The speed, reversibility, released by-products and physical conditions of this reaction are the key factors that define the performance of an electrochemical cell as an energy storage device. This reaction had been a great interest for the field of energy storage, particularly, electrochemistry, where numerous characterization techniques have been developed to optimize the architecture of batteries.

Stable, capacious and powerful batteries have become of great demand for today’s energy driven society [47, 46, 33]. 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 [23, 27], an airplane [18] or a house [4, 13]. Still, the application of lithium ion batteries is limited by irreversible

processes [22, 8, 50] that occur upon extreme operating conditions such as high power demand [49, 12] or over-discharge [26]. 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 the rare earth metals [46] and the toxicity of the manufacturing process [35, 34] is motivating research and development of advanced battery technologies [3]. 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 [25, 19].

Organic radical batteries (ORB) based on redox polymers containing stable radicals [30] have been shown to compete with or even outperform conventional Li based batteries in terms of power densities [41] with the additional benefit of being free from rare precursors, inheriting mechanical properties of plastics and electrical properties of semiconductors [7, 2, 10]. Advanced molecular design techniques allow for tuning of the electrochemical properties of the redox polymers [15], that brings in a rich variety of organic energy storage materials [45, 44, 16] and creates a large room for their optimization.

Redox conductive conjugated polymers containing TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) redox groups, as pDiTBuS (poly-di-TEMPO-Butyl-Salen) shown in Figure 1.1, demonstrate particularly promising energy and power densities [43]. 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.

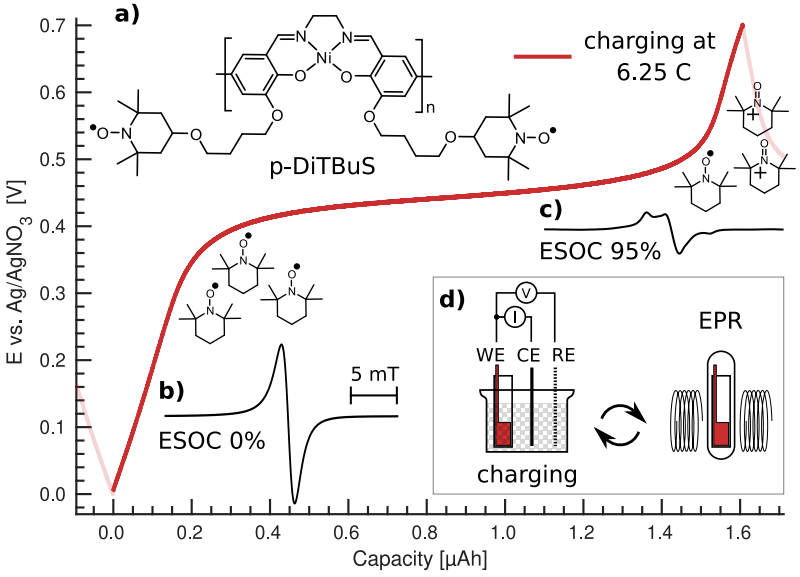

Figure 1.1: Galvanostatic charge-discharge curve for a pDiTBuS cathode film at 10 µA (6.25 C), chemical structure of pDiTBuS (a), normalized cwEPR spectral signatures for reduced (b) and oxidized (c) states. Scheme of the ex-situ EPR measurement on the pDiTBuS half cell (d).

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 and ex-situ. Together

with electrochemical characterization as the standard method for studying the properties of energy storage materials[41, 48], operando optical microscopy [29], neutron imaging [26] and X-ray diffraction [36] were applied to monitor irreversible structural deformations during extreme charging of Li cells.

UV and IR spectroscopy turned out to be particularly useful for studying organic energy-storage materials. For instance, it was possible to observe formation of positive polarons in the NiSalen backbone of the pDiTBuS upon its oxidation [5]. 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 can be applied to obtain structural information on the battery electrodes on the molecular level [32, 28, 24, 1]. NMR was used to study dendrite formation, electrolyte dynamics and intercalation of Li ions[21, 11] in Li cells, including operando imaging [40].

Operando continuous-wave EPR (cwEPR) was applied to study redox kinetics of inorganic battery cathodes [31], radical formation and spin densities in redox polymers [5] and in organic electrochemical cells [14, 20].

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 [37] as in spin-labelled proteins [17, 42]. In addition, the hyperfine coupling between electron and nuclear spins in close vicinity can be measured by electron spin echo envelope modulation (ESEEM) and 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 seminconductors [6].

EDMR is allowing to manipulate the spin of an electron that tunnels through a disordered media such as the amorphous silicon in a solar cell, through intertwined fragments of conjugated polymers in an organic solar cell or an organic field-effect transistor.

Chapter 2

Electrochemical Energy Storage in Redox Conductive Polymers

DiTS is a molecule that can efficiently store upto three electric charges. When polymerized, it can grow into a film that performs well as a cathode in an electrochemical cell.

Chapter 3

Operando EPR Spectroscopy of Energy Storage Materials

3.1 Electron Paramagnetic Resonance

3.1.1 Spin Hamiltonian

The electron bears an internal angular momentum that is called spin. Spin combines with the charge of the electron to endow the electron with a magnetic moment. The magnetic moment of the electron is quantized: $\mu_e = \mu_B g S$ [9], where S is the spin quantum number, the eigenvalue of the spin operator $\vec{\hat{S}}$, that equals $S = 1/2$ for an electron. When an electron is placed in a static magnetic field $\vec{B_0} = B_0 \vec{e_z}$, its magnetic moment precesses about the field direction with the Larmor frequency $\omega_L = \gamma B_0$, where $\gamma = \frac{g_e \mu_B}{\hbar} = 28.025$ GHz/T is the gyromagnetic ratio of the electron and g_e is the electron g factor. The projection of the electron's magnetic moment on the direction of the magnetic field can take only discrete values between $-S = -1/2$ and $S = 1/2$, so that the eigenvalues of the z component of the spin operator are also discrete: $\hat{S}_Z|\uparrow\rangle = +\frac{\hbar}{2}|\uparrow\rangle$, $\hat{S}_Z|\downarrow\rangle = -\frac{\hbar}{2}|\downarrow\rangle$. The two eigenfunctions of $\hat{S}_Z$ are called the spin-up state $|\uparrow\rangle$ and the spin-down state $|\downarrow\rangle$. The two corresponding eigenvalues $\pm\frac{\hbar}{2}$ define the energy difference between the states $|\uparrow\rangle$ and $|\downarrow\rangle$, that is known as the Zeeman splitting.

The energy of an unpaired electron placed in the external magnetic field $\vec{B_0}$ is the eigenvalue of the spin Zeeman Hamiltonian: $\hat{H}_{EZ} = \mu_B g \vec{B_0} \cdot \vec{\hat{S}}$. In the laboratory frame of reference $\vec{B_0} \parallel \vec{e_z}$, $\left[\hat{H}_{EZ}, \hat{S}_z\right] = 0$, so $\hat{H}$ and $\hat{S}_Z$ share the eigenfunctions $|\uparrow\rangle$ and $|\downarrow\rangle$. The Zeeman energies of the electron are $E^{\pm}_{EZ} = \pm\frac{\hbar}{2}\mu_B g B_0$.

A proton also bears an internal angular momentum $S = 1/2$ that results in a magnetic moment $\mu_p = \mu_e \frac{m_e}{m_p}$, that is $\frac{m_e}{m_p} \approx 1836$ times smaller than the electron's magnetic moment. A neutron bears no charge but still has an internal angular momentum $S = 1/2$. An atomic nucleus that consists of protons and neutrons can have a magnetic moment, depending on the mutual orientations of their spins and on 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 $\mu_N = \mu_B g_N \frac{m_e}{m_N} I$ that splits into three Zeeman energy levels corresponding to $I = -1, 0, +1$, analogously to the electron with $S = 1/2$. The nuclear Zeeman splitting is more than three orders of magnitude weaker than the electron Zeeman splitting because of the difference in the masses of the particles.

The magnetic moments of an electron and a magnetic nucleus, such as nitrogen, couple in the hyperfine interaction [38]: $H_{HF} = \vec{\hat{S}} \mathbf{A} \vec{\hat{I}} = H_F + H_{DD}$ with the hyperfine tensor $\mathbf{A}$. The isotropic part $H_F = a_{iso} \vec{\hat{S}} \vec{\hat{I}}$, or the Fermi contact interaction, scales with the probability density of the electron at the position of the nucleus $a_{iso} = \frac{2}{3}\frac{\mu_0}{\hbar} g_e \beta_e g_n \beta_n |\psi(0)|^2$. The anisotropic part $H_{DD} = \vec{\hat{S}} \mathbf{T} \vec{\hat{I}}$ with the dipolar coupling tensor $\mathbf{T}$

takes into account the anisotropic dipole-dipole coupling between the magnetic moments of the electron and the nucleus.

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. The interaction between the asymmetrically distributed charge and the gradient of the electric field at the nucleus is given by the nuclear quadrupole Hamiltonian $H_{NQ} = \vec{I}\mathbf{P}\vec{I}$ with the nuclear quadrupole tensor $\mathbf{P}$ that describes the coupling of the nuclear quadrupole moment to the electric field gradient.

In a system of closely placed electrons, such as in a film of densely packed nitroxide radicals, the electron orbitals may overlap significantly and the radicals may exchange electrons. The energy required to exchange the electrons is called the Heisenberg 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 delocalization [39]. 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 $S = 1$.

The dipole-dipole interaction between the two neighboring electron spins contributes one more term to the spin Hamiltonian: $H_{dd} = \vec{S_1}\mathbf{D}\vec{S_2}$ that depends on the distance between the spins.

Chapter 4

Pulsed Electron Paramagnetic Resonance Spectroscopy of Densely Packed Nitroxide Radicals

4.1 Coherent Spin Motion under Pulsed Microwave Field

When a spin system is excited with a microwave pulse, its

4.2 Three-Dimensional Electron Gas with Inter-Spin Interactions

The observations of pulsed EPR spectra in densely packed nitroxide radicals have risen questions regarding the physical model that would be able to describe these systems. So far no model for such system could explain the results of the distorted EPR spectra and an attempt was made to introduce the inter-spin interactions in the three-dimensional electron gas that appears to be the most accurate model of a polymer cathode film.

Chapter 5

Longitudinally Detected Electron Paramagnetic Resonance in Systems with Short Relaxation Times

LOD lets us look behind the protection pulse.

Chapter 6

Electrically Detected Electron Paramagnetic Resonance on a Cathode of an Organic Radical Battery

With EDMR we observe the hopping charge as it travels to the charge bearing group through the electrode.

6.1 Distribution of Current Density in On-Substrate Meander-Shaped Electrodes

Meander-shaped electrodes shown in Figure 6.1 are used to study properties of thin conductive films. The distribution of electric potential and the current within a film of poor conductivity and a finite thickness be not obvious.

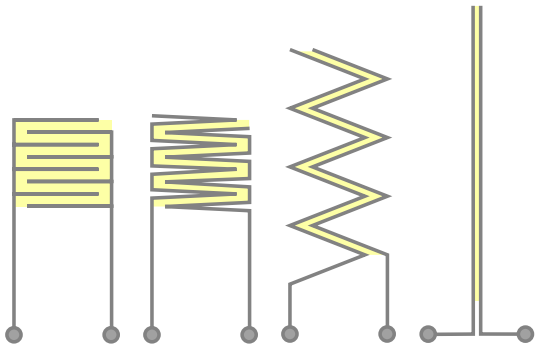

Figure 6.1: Transformation of the meander-shaped electrode grid into two linear electrodes

A numerical solution was found to the distribution of the current density $\vec{j}$ within a film of a finite thickness, connected by two metal electrodes. Two cases were considered, a thick film and a thin film.

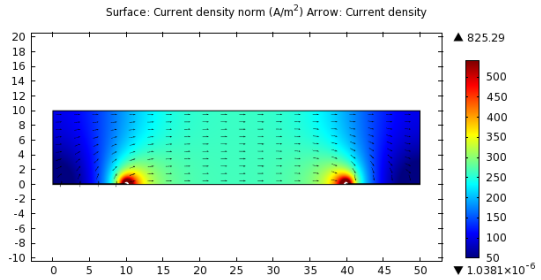

Figure 6.2: Distribution of electric current in a thick polymer film. The current is uniform in the middle of the film. Let us see, whether we can apply the simple, bulk formula to this structure.

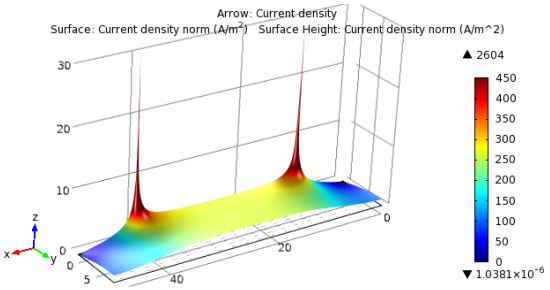

Figure 6.3: Thick film. The current is uniform in the middle of the film. It is better seen on this 3d plot. Let us see, whether we can apply the simple, bulk formula to this structure. I think we do not gain a lot of error by saying that the current is uniform within the whole film.

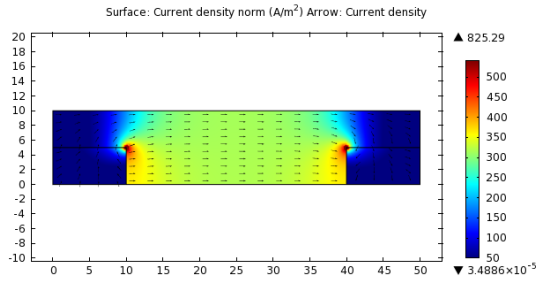

Figure 6.4: Distribution of electric current in an intermediate polymer film

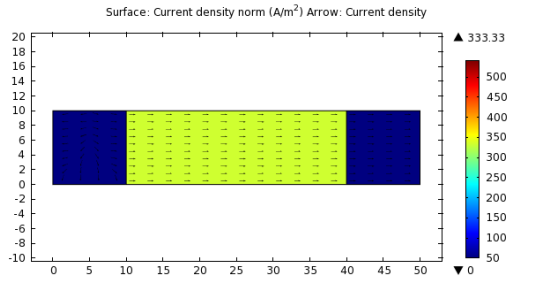

Figure 6.5: Distribution of electric current in a thin polymer film

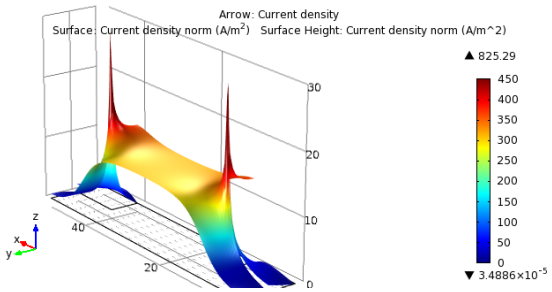

Figure 6.6: Very high values of the computed distribution of the current density in a film of intermediate thickness due to the sharp edges of the contacts.

Chapter 7

The Deep-Trap Model of a TEMPO-Salen Electrode Film

A DiTBuS/DiTS film can be seen as a p-type, molecular semiconductor (the poly-Salen backbone) that is heavily doped with low-energy traps for holes ($TEMPO^{\bullet}$).

Chapter 8

Conclusions and Outlook

What hasnt worked so far is the EDMR. It would be super cool to see the signal, but my devices don't live that long. LOD also did not work up to now. Adjusting the pulse train rate to the eigenfrequency of the ENDOR coils turned out to be an irresistible obstacle.

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