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

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Contents

Summary

This monograph represents a series of spectroscopic studies aimed at a comprehensive description of the storage and transport of elementary charges in redox conductive polymers, that have applications in electrochemical energy storage devices. A specific class of TEMPO-Salen polymers is considered. In the beginning, we present an overview of the available charge-transport and charge-storage models for redox conductive polymers and indicate, how the models can be refined by using the toolbox of spin resonance spectroscopy. We then describe the spectroscopic and electrochemical methods that will be used to obtain the information on the undisclosed charge transport and storage mechanisms. Next chapter is devoted to the fabrication of a TEMPO-Salen electrochemical cell inside an X-Band EPR sample tube, that is used for operando spectroscopic experiments. The discussion of the operando spectroscopic data takes place in the next chapter. The chapter after that describes a magnetic resonance experiment with electrical detection on the working electrochemical cell. Then, we focus on the application of pulsed EPR techniques to study domain formation in the redox conductive polymer films. We will further consider the attempts to observe electrically detected magnetic resonance signals in a slowly charging TEMPO-Salen electrochemical cell. Afterwards, we present and discuss the deep-trap-dominated semiconductor model of storage and transport of charge in densely packed redox conductive polymers. Finally, in the Chapter Conclusions and Outlook, we summarize the monograph and sketch a roadmap for the future investigations.

IoT	internet of things
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 [44, 43, 32]. 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 [22, 26], an airplane [17] or a house [4, 12]. Still, the application of lithium ion batteries is limited by irreversible

processes [21, 8, 47] that occur upon extreme operating conditions such as high power demand [46, 11] or over-discharge [25]. 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 [43] and the toxicity of the manufacturing process [34, 33] 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 [24, 18].

Organic radical batteries (ORB) based on redox polymers containing stable radicals [29] have been shown to compete with or even outperform conventional Li based batteries in terms of power densities [38] with the additional benefit of being free from rare precursors, inheriting mechanical properties of plastics and electrical properties of semiconductors [7, 2, 9]. Advanced molecular design techniques allow for tuning of the electrochemical properties of the redox polymers [14], that brings in a rich variety of organic energy storage materials [42, 41, 15] 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 [40]. 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.

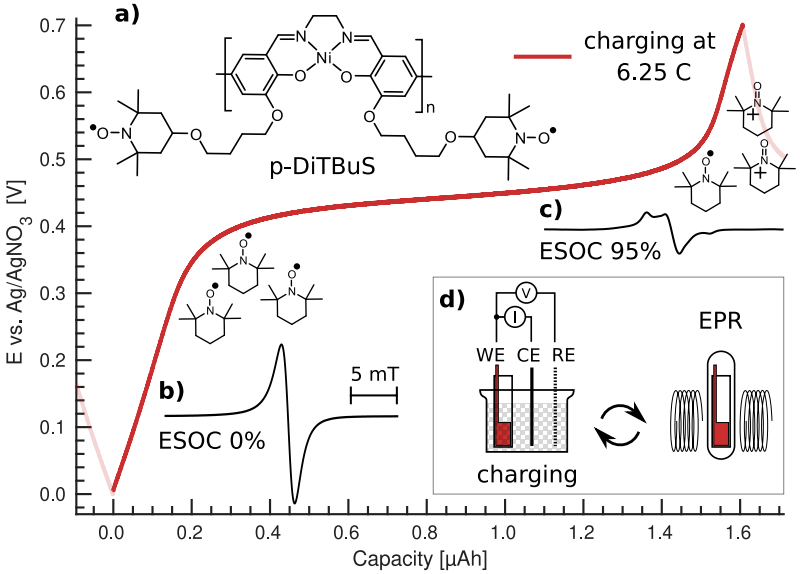

Figure 1.1: Galvanostatic charge-discharge curve for a pDiTBuS cathode film at 10 µA (6.25 C), chemical structure of pDiTBuS (a), normalized cwEPR spectral signatures for reduced (b) and oxidized (c) states. Scheme of the ex-situ EPR measurement on the pDiTBuS half cell (d).

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[38, 45], operando optical microscopy [28], neutron imaging [25] and X-ray diffraction [35] 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 [31, 27, 23, 1]. NMR was used to study dendrite formation, electrolyte dynamics and intercalation of Li ions[20, 10] in Li cells, including operando imaging [37].

Operando continuous-wave EPR (cwEPR) was applied to study redox kinetics of inorganic battery cathodes [30], radical formation and spin densities in redox polymers [5] and in organic electrochemical cells [13, 19].

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 [36] as in spin-labelled proteins [16, 39]. 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 Electron Paramagnetic Resonance Spectroscopy of Energy Storage Materials

EPR uses spin as a probe.

Chapter 4

Pulsed Electron Paramagnetic Resonance Spectroscopy of Densely Packed Nitroxide Radicals

EPR uses spin as a probe and that spin is coupled to the environment.

4.1 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.

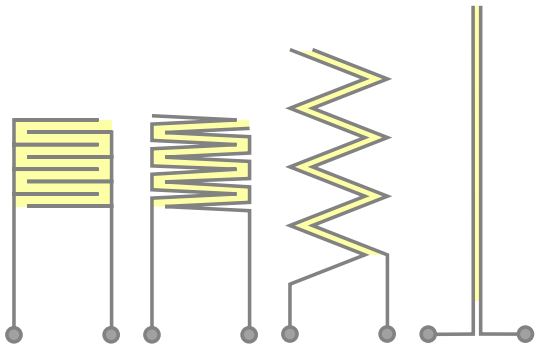

Figure 6.1: Transformation of the meander-shaped electrode grid into two linear electrodes

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.

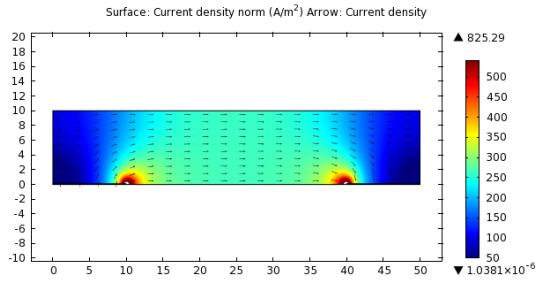

Figure 6.2: Distribution of electric current in a thick polymer film. The current is uniform in the middle of the film. Let us see, whether we can apply the simple, bulk formula to this structure.

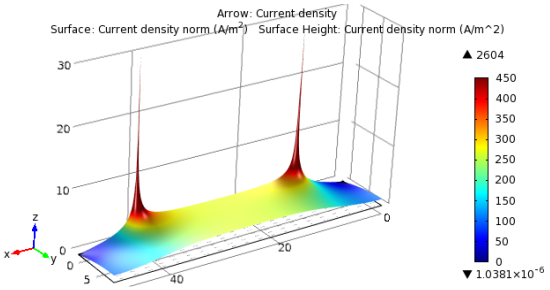

Figure 6.3: Thick film. The current is uniform in the middle of the film. It is better seen on this 3d plot. Let us see, whether we can apply the simple, bulk formula to this structure. I think we do not gain a lot of error by saying that the current is uniform within the whole film.

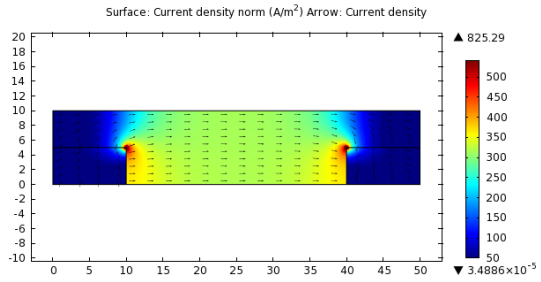

Figure 6.4: Distribution of electric current in an intermediate polymer film

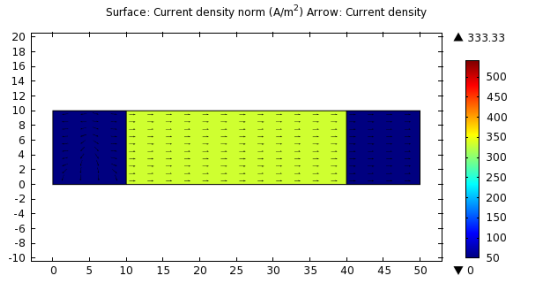

Figure 6.5: Distribution of electric current in a thin polymer film

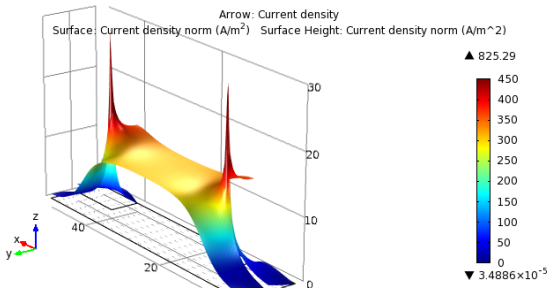

Figure 6.6: Very high values of the computed distribution of the current density in a film of intermediate thickness due to the sharp edges of the contacts.

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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