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

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

Berlin
August 2023

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

# 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, during the last few centuries, 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. The electrical energy is stored in form of electric charges separated by a potential barrier in a device called a battery, or, precisely, a battery of electrochemical cells. It is 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.

EPR uses the electron spin as a microscopic structural probe to study local molecular environments. 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.

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 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 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.

# 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.