UPPSALA
UNIVERSITET

Designing Quinone-based Organic Batteries

CHRISTIAN STRIETZEL

Dissertation presented at Uppsala University to be publicly examined in Häggsalen, Ångströmslaboratoriet, Lägerhyddsvägen 1, Uppsala, Monday, 24 May 2021 at 09:30 for the degree of Doctor of Philosophy. The examination will be conducted in English. Faculty examiner: Professor Philippe Poizot (Université de Nantes).

Abstract
Strietzel, C. 2021. Designing Quinone-based Organic Batteries. *Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology* 2023. 60 pp. Uppsala: Acta Universitatis Upsaliensis. ISBN 978-91-513-1154-8.

The demand for secondary energy storage is ever increasing, being at the forefront of the transformation to a sustainable society. Conventional batteries, whose electrode materials require mining and high temperature refining, generate substantial carbon dioxide emissions during production. Furthermore, the process for recycling of these batteries is difficult and still at in its infancy. On the contrary, organic batteries could be a sustainable and alternative energy storage solution and is therefore gaining increased attention. While there are several promising organic battery concepts, the focus in of this thesis has been towards batteries using quinones as capacity carrying units. Furthermore, a special emphasis was put on conducting polymers for providing conductivity within the electrode material, predominately in the form of conducting redox polymers. Several battery designs have been explored. All-organic batteries, cycling protons both with an ionic liquid and with a readily available aqueous electrolyte, have been evaluated with promising results concerning rate capabilities and low temperature operation. Hybrid-organic battery designs have shown that quinones easily cycle Lithium ions and act in a dual ion battery with a Manganese oxide cathode. This thesis therefore gives a broad overview on how quinone organic batteries can be designed and provides an outlook on how future development can be focused.

Keywords: conducting polymers, organic electronics, quinones, organic battery, electrochemistry

Christian Strietzel, Department of Materials Science and Engineering, Nanotechnology and Functional Materials, Box 534, Uppsala University, SE-751 21 Uppsala, Sweden.

For my family

About the cover

The cover depicts the painting *Wanderer above the sea of fog* by the German artist Caspar David Friedrich. This painting is considered one of the most defining works during the romantic art period.(1) You may be wondering why I used romantic artwork for the cover of this thesis. Let me explain. In the novel *Zen and the art of motorcycle maintenance,* Robert Pirsig distinguishes between classical and romantic knowledge. In this context, romantic thinking is associated with words such as "imaginative, creative and intuitional", whereas classical thinking is governed by the laws, reasonings and understandings of the underlying mechanisms of a phenomenon.(2) By this definition, the content of this thesis is classical, providing precise definitions on how organic batteries can be composed and how they perform. Importantly, this thesis is a result of almost four years of my work. If I were to describe the work that resulted in this thesis, it would be romantic in nature, i.e., creative and with a large portion of intuition. In my opinion, this thesis is the conclusion of my work and is therefore best summarized by a cover associated with the romantic way of acting and thinking, despite its *classical* content.

List of papers

This thesis is based on the following papers, referred to in the text by their Roman numerals. Reprints were made with permission from the respective publishers. Questions regarding permissions related to the material excerpted should be directed to the respective publisher.

I   Karlsson, <u>C.</u>; <u>Strietzel</u>, C.; Huang, H.; Sjödin, M.; Jannasch, P., Nonstoichiometric Triazolium Protic Ionic Liquids for All-Organic Batteries. *ACS Applied Energy Materials* **2018,** *1* (11), 6451-6462. Doi: 10.1021/acsaem.8b01389

II   Oka, K.; <u>Strietzel, C</u>.; Emanuelsson, R.; Nishide, H.; Oyaizu, K.; Strømme, M.; Sjödin, M., Characterization of PEDOT-Quinone conducting redox polymers in water-in-salt electrolytes for safe and high-energy Li-ion batteries. *Electrochemistry Communications* **2019,** *105*, 106489. Doi: 10.1016/j.elecom.2019.106489

III <u>Strietzel, C</u>.; Sterby, M.; Huang, H.; Strømme, M.; Emanuelsson, R.; Sjödin, M., An Aqueous Conducting Redox-Polymer-Based Proton Battery that Can Withstand Rapid Constant-Voltage Charging and Sub-Zero Temperatures. *Angewandte Chemie International Edition* **2020,** *59* (24), 9631-9638. Doi: 10.1002/anie.202001191

IV Oka, K.; <u>Strietzel, C</u>.; Emanuelsson, R.; Nishide, H.; Oyaizu, K.; Strømme, M.; Sjödin, M., Conducting Redox Polymer as a Robust Organic Electrode-Active Material in Acidic Aqueous Electrolyte towards Polymer–Air Secondary Batteries. *ChemSusChem* **2020,** *13* (9), 2280-2285. Doi: 10.1002/cssc.202000627

V   <u>Strietzel, C</u>.; Oka, K.; Strømme, M.; Emanuelsson, R.; Sjödin, M., An Alternative to Carbon Additives: The Fabrication of Conductive Layers Enabled by Soluble Conducting Polymer Precursors – A Case Study for Organic Batteries. *ACS Applied Materials & Interfaces* **2021,** *13* (4), 5349-5356. Doi: 10.1021/acsami.0c22578

My contribution to the included papers

Paper I. I performed all experiments on the individual electrodes and full battery. The synthesis of the material was not done by me. I contributed to the data analysis and to the writing process.

Paper II. I performed all experiments on the anode material and the battery and advised on the choice of electrolyte to be used. The synthesis was not done by me. I contributed to the data analysis and to the writing process.

Paper III. I codeveloped the polymer precursors and the polymer method that is the basis of this study. I performed most of the experiments and most of the data analysis. The synthesis of the material was not done by me. I wrote the initial manuscript and contributed to the continued writing process.

Paper IV. I codeveloped the method of polymerization that is partly the basis for this study. I codesigned the study and supplied the anode material for the battery. The synthesis of the material was not done by me. I performed the analysis of the data associated with the anode, wrote most of the initial manuscript and contributed to the continued writing process.

Paper V. I developed the electrode formulation method that is the basis for this study. I designed the study, performed all of the experiments, except the synthesis of the material, and performed all the data analysis. I wrote the initial manuscript and contributed to the continued writing process.

Contents

Abbreviations

CC	Constant current
CE	Counter electrode
CP	Conducting polymer
CRP	Conducting redox polymer
CV	Cyclic voltammetry, Constant potential
EDG	Electron donating group
EIS	Electrical impedance spectroscopy
EQCM	Electrochemical quartz crystal microbalance
EWG	Electron withdrawing group
IDA	Interdigitated Array
IL	Ionic liquid
Ox	Oxidation
Q	Quinone
QCM	Quartz crystal microbalance
QH_2	Hydroquinone
QM_2	Metal-quinone
RE	Reference electrode
Red	Reduction
SEI	Solid electrolyte interface
WE	Working electrode

Major symbols

Symbol	Name
ΔG^0	Gibbs free energy
E^0	Standard potential
E	Potential under nonstandard conditions
F	Faraday constant
z	Number of electrons
R	Gas constant, Electrical resistance
T	Temperature
a	Activity
ν	Scan rate
I	Current
α	Transfer coefficient
k^0	Exchange rate constant
t	Time
A	Area
D	Diffusion coefficient
j_0	Exchange current density
Δm	Mass change
Δf	Change in frequency
F_q	Reference frequency
ρ_q	Quartz crystal density
G	Conductance

Redox-active organic electrode materials used in this thesis

Since I will repeatedly refer to different redox-active organic electrode materials that I used in the research presented herein, below is an overview of the chemical structures of these materials and the abbreviations I use for them in this thesis.

pE(NQ)   pE(QH₂)   PNQ@pEPE

pEP(QH₂)E   pEP(NQ)E
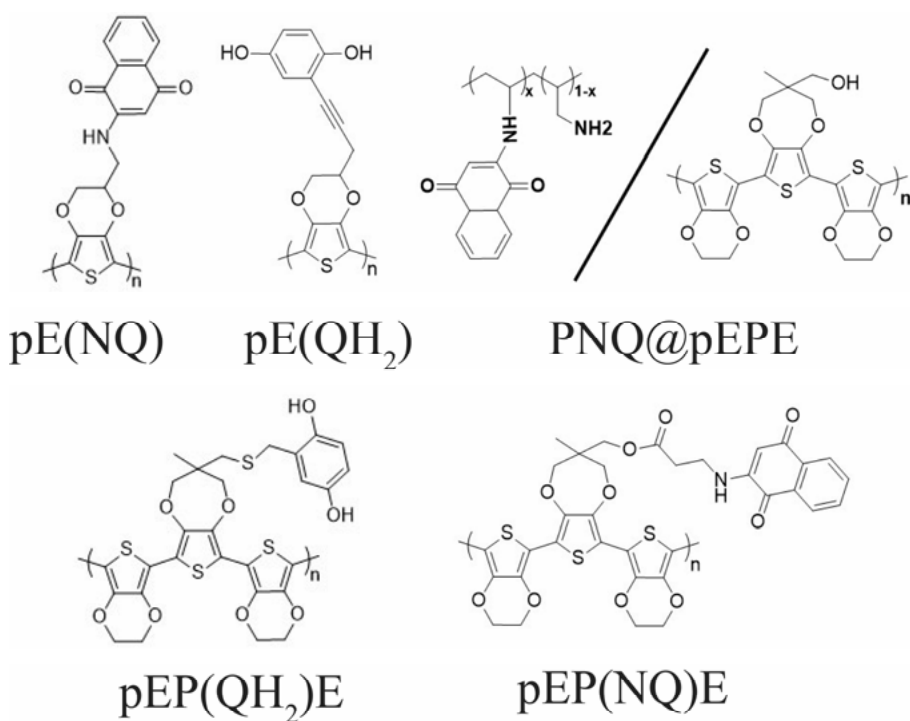
1 Motivation

One of the most important challenges of our time is to meet the sustainability goals set forth by the UN. In particular, man-made climate change needs to be addressed with technologies that enable a high standard of living without the emission of more carbon dioxide into the atmosphere.(3)

Energy storage systems, in particular batteries, are crucial for society to become "carbon-free" while maintaining a high standard of living. Batteries are central not only for replacing fossil fuels in the transport sector but also as a means of storing energy in the electrical energy sector. Electricity production from solar and wind is intermittent, i.e., the production is not constant; thus, energy might not be available during peak demand. Therefore, storing the energy produced over periods of low demand is necessary for utilizing an increasing amount of renewable energy in the electrical grid.

Although lead acid battery systems are still very common, lithium-ion battery technology is at the heart of future electrical storage and is used both in transport and as grid storage. Unfortunately, lithium-ion batteries require access to minerals that are only available in certain parts of the world, e.g., cobalt, a key component in lithium-ion battery cathodes, is mostly mined in Congo. Additionally, refining the minerals for ready-to-use battery materials requires considerable energy. Furthermore, recycling of these materials is still in its infancy.(4) In short, lithium-ion battery technologies have their own shortcomings in regard to sustainability and a "carbon-free" society.

To achieve a sustainable battery life cycle, the use of organic battery materials has been proposed.(5) Organic battery materials are made from abundant and readily available elements, i.e., carbon, oxygen, nitrogen and sulfur, and this type of active battery material can theoretically be sustainable in regard to production and recycling. Therefore, there has been recent research interest in hybrid-organic batteries, i.e., batteries with a lithium anode and an organic cathode, and all-organic batteries. Apart from being sustainable, these types of batteries reveal new and exciting battery designs, ranging from flexible batteries to application-specific designs.

The work comprised in this thesis aims to further research on hybrid-organic and all-organic batteries, with a special emphasis on water-based systems, which are of particular interest from a sustainability point of view.

2 Aims of this thesis

The overall aim of this thesis was to design different quinone-based organic batteries utilizing electrode materials that use a conducting polymer as a means of charge transport. In most studies presented herein, the redox-active pendant group has been directly attached to the conducting polymer, forming a conducting redox polymer. I have also explored how a conducting polymer mixed with a redox polymer compares to conducting redox polymer-based electrode materials. Several important aspects of these types of batteries have been studied:

- Different electrolytes have been evaluated, including ionic liquid (**Paper I**), water-in-salt (**Paper II**) and aqueous (**Papers III, IV** and **V**) electrolytes
- Different ways of processing and coating the electrodes, including electropolymerization (**Papers I** and **II**), chemical polymerization (**Paper IV**), and a novel so-called postdeposition polymerization (**Papers III and V**)
- Different modes of charging (**Paper III**)
- Different electrode configurations including all-organic batteries (**Papers I** and **III**) and hybrid-organic batteries (**Papers II, IV** and **V**)

3 Batteries

3.1 General considerations and methods of evaluating electrode materials

3.1.1 The battery

In its simplest form, a battery can be defined as a device converting chemical energy into electrical energy. This conversion is driven by an electrochemical redox (reduction-oxidation) reaction. This process is irreversible in a primary battery; however, in a secondary battery, this reaction can be reversed.[*]

I will treat the battery as a two-component system, with the electrodes, anode and cathode, on the one hand and the electrolyte on the other hand.

Battery operation can be illustrated as follows: During discharge, the anode, or negative electrode (-), is oxidized, thus supplying electrons to the external circuit. Simultaneously, the cathode, or positive electrode (+), is reduced, accepting electrons from the external circuit. Importantly, the ions in the electrolyte, which have to be electrically insulating to prevent a short circuit, counterbalance the reactions occurring at the electrodes. In secondary batteries, as mentioned earlier, the electrode reactions can be reversed through a charging process. (Figure 1)

For most practical purposes, the most important aspects of a battery are its energy content (per weight or per volume) and rate capability, and to a lesser degree, the safety and environmental aspects of the battery. The energy content is a function of the respective electrode materials, depending on their redox chemistry, that is, the voltage difference (potential) between the reaction at the anode and the cathode and the number of electrons participating in the reactions (capacity). The rate capability is an interplay between the kinetics of the redox reactions and mass transport, both in the electrodes and through the electrolyte. In the following chapters, I will discuss how electrode materials can be designed and studied, which kind of electrolytes can be used and how these components can be used to build (secondary) organic batteries.

---

[*] To be precise, instead of using the term *battery*, the term *cell* should be used as several electrochemical cells often make up a *battery*. In this thesis, I will ignore this fact and will use cell and battery interchangeably, with both terms referring to a single battery cell.
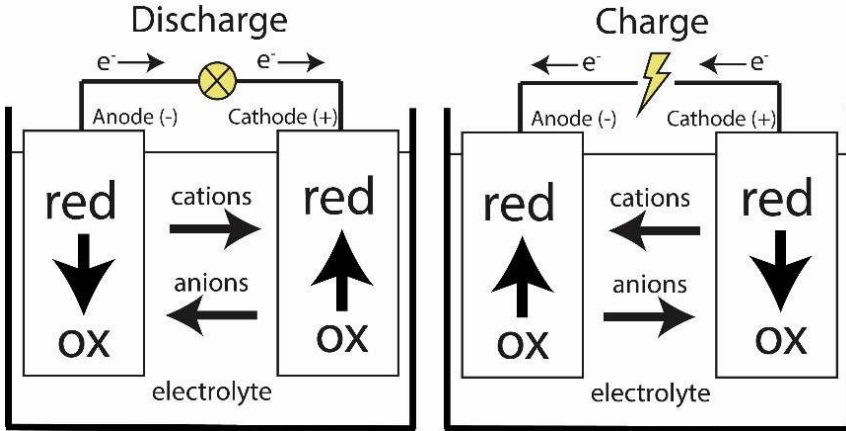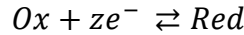
Figure 1. Battery operation during discharge (left) and charge (right).

3.1.2 The redox reaction

As mentioned earlier, the redox reactions occurring in the electrode material are at the heart of the battery. In the simplest form, a half-cell reaction can be written as follows:

$$Ox + ze^- \rightleftarrows Red$$

where z is the number of electrons participating in the reaction. The change, i.e., the decrease in Gibbs free energy (ΔG^0), is related to the standard potential (E^0) as follows:

$$\Delta G^0 = -zFE^0 \tag{1}$$

where F is the Faraday constant and z is the number of electrons. The standard potential (E^0) only applies under standard conditions, and all species have an activity of 1. The Nernst equation can be used to calculate the potential under nonstandard conditions (E):

$$E = E^0 + \frac{RT}{zF} \ln \frac{a_{ox}}{a_{red}} \tag{2}$$

Here, R is the gas constant, T is the temperature, a_{ox} denotes the activity of the oxidized species, and a_{red} is the activity of the reduced species. The potential at which the redox reaction takes place is important since the difference between the reaction occurring at the anode and the cathode determines the cell potential of the battery, which is directly proportional to the energy content of

the cell. Furthermore, when using a redox-active material as an electrode material in a secondary battery, it is important that the redox reaction is reversible. This reversibility requires that both the oxidized and reduced forms of the material are stable and that no side reactions occur during the redox reaction. Different methods of evaluating the redox reactions of electrode materials, together with the mass transport, will be discussed in the following sections.

3.1.3 Evaluating individual electrodes: The three-electrode setup

When studying the redox reaction of an electrode, there are two signals of interest, the current consumed by the reaction and the potential where the reaction occurs on the electrode versus some kind of reference. The setup (*Figure 2*) for studying an electrode material therefore preferably consists of a working electrode (WE), which is the electrode to be studied, a reference electrode (RE) with a known and constant potential and a counter electrode (CE) through which the current generated or consumed at the WE flows (Figure 2). In principle, there are several different REs and CEs to choose from. In aqueous electrolytes, Ag/AgCl is often used as an RE, while a platinum wire is used as a CE. In organic electrolytes Ag/AgCl cannot be used as an RE. Instead of Ag/Ag$^+$ or a quasi-reference, a platinum wire can be used. Both are then calibrated with an internal reference using the Fc/Fc$^+$ redox pair.
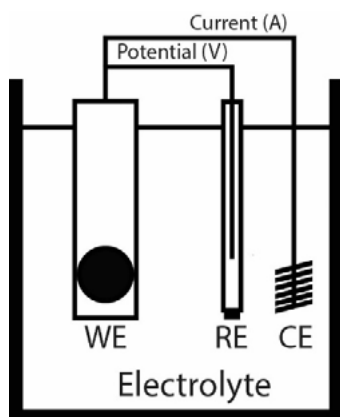

Figure 2. The three-electrode setup. The WE and RE are connected to provide the potential (V), and the WE and CE are connected to provide the current (A).

3.1.4 Basic electrochemical techniques

Cyclic voltammetry

Cyclic voltammetry (CV) is a popular method for electrochemical characterization and can reveal considerable information to a trained eye. During the

measurement, the potential is changed in a constant manner, i.e., a certain number of volts per second (V/s), which is denoted as the scan rate (ν). If any redox-active species are present, either on the surface bound to the WE or in the solution in contact with the WE, a redox reaction will produce a current response. The response of current versus potential, which I will explain in more detail below, is of interest when performing a CV experiment.

In principle, one can categorize the CV response into three different cases: 1) the thermodynamic equilibrium for a dissolved redox species at the electrode, 2) the thermodynamic equilibrium for a surface-bound species and 3) the apparent irreversible redox reaction for a surface-bound species.

1) In the case of a dissolved redox species with a reversible redox reaction, the reaction is diffusion limited, and importantly, the peak current i_p is proportional to $\sqrt{\nu}$, i.e., $\ln(i_p)$ versus $\ln(\nu)$ will have a slope of 0.5. Furthermore, the peak potential E_p is provided by:

$$E_p = E_{1/2} + 1.109 \frac{RT}{zF} \qquad (3)$$

where, in most cases, $E_{1/2}$ is equal to the formal potential E^0.

2) In the thermodynamic equilibrium for a surface-bound species, the peak current (i_p) is proportional to the scan rate (ν). Notably, the peak potential (E_p) is the same as the formal potential (E^0). Often, this case is valid for thin layers on an electrode with a low to moderate scan rate (ν).

3) At high scan rates, in the case of a surface-bound species, the peak current can still be directly proportional to the scan rate if the reaction is not limited by diffusion, although the system is no longer in thermodynamic equilibrium. It is important to note that in thick layers, due to the internal resistance of the material, a lower than expected peak current can be observed at the same time as the peak considerably broadens. This result can be attributed to the inner resistance of the material. Furthermore, the oxidation and reduction peaks will separate, and the current of the respective back-reaction decreases exponentially with an increasing overpotential, η (E_p-E^0). Therefore, when the peak separation is high enough, i.e., more than 200 mV, the CV response can be treated as an irreversible reaction, and the peak potential is provided by:

$$E_p = E^{0'} + \frac{RT}{\alpha F} \ln \left(\frac{RT}{\alpha F} \frac{k^0}{v} \right) \qquad (4)$$

where α is the transfer coefficient and k^0 is the exchange rate constant. This equation is useful when determining the exchange rate constant, which provides information on the kinetics of the system. An E_p versus $\ln(v)$ plot will yield the exchange rate constant.

Galvanostatic measurements

Another popular method for electrochemical characterization is the galvanostatic measurement method. Instead of a potential sweep, in this method, a constant current is applied, and the potential is monitored. Apart from resembling common battery charge-discharge cycles, this method is also useful to identify side reactions that might occur. As mentioned earlier, in a secondary battery, the complete chemical reversibility of all redox reactions is important for the battery to withstand subsequent charge-discharge cycles. The reversibility of the redox reactions, also called the columbic efficiency, can be easily probed using constant-current measurements, i.e., galvanostatic measurements. In a special case of this method, the current can be set to zero, which is of special interest when studying the self-discharge of an electrode material.

Since cyclic voltammetry is a very popular method for evaluating data, galvanostatic measurements can be visualized by deriving the amount of charge with respect to the potential, which results in a so-called $\frac{dQ}{dV}$ plot. This plot resembles a typical CV experiment response, although the data are acquired by a galvanostatic experiment.

Amperometric measurements

In amperometric measurements, a constant voltage, or potential step, is applied, and the current response as a function of time is recorded. In many experiments, the current (i) response with respect to time (t) can be described with the Cottrell equation:

$$i = \frac{zFAc\sqrt{D}}{\sqrt{\pi t}} \qquad (5)$$

where A is the area of the electrode, c is the concentration of the redox species and D is the diffusion coefficient. It is important to mention that this equation only applies to planar electrodes (such as a glassy carbon disc) in a system under diffusion control. Therefore, this equation can be used to determine whether the redox reaction that is studied with the potential step is limited by diffusion, i.e., plotting i vs. $t^{-1/2}$ provides a linear curve.

Potential step measurements can also be used to acquire a Tafel plot, which contains information about the kinetics and exchange current density (j_0) of a redox reaction. I will only briefly explain this procedure. In a Tafel plot, log i is plotted versus the overpotential (η), and the slope contains information about j_0. The different overpotentials and currents are acquired through different potential steps (which results in overpotentials) and the initial current observed as a result of the potential step is recorded. It is important that the kinetics are rather simple, and the overpotential is sufficient so the back-reaction can be neglected; additionally, it is important that the kinetics dominate the current response, i.e., the reaction is not limited by mass transfer.

3.1.5 *In situ* EQCM

Another aspect that is interesting to study when evaluating electrode materials is the mass change that occurs during an electrochemical experiment, as described above. This can be done by using a quartz crystal microbalance (QCM), which can also work as an electrode, resulting in an electrochemical quartz crystal microbalance (EQCM). EQCM employs the piezoelectric effect, in which an electric current results in vibrations in the quartz crystal.(6) Depending on the mass of the crystal, the crystal will change its vibration frequency; during EQCM, the electrode mass includes any deposited material. A high mass results in a low frequency; in contrast, a low mass results in a high vibrational frequency. The relationship between the mass change and change in frequency was described by Sauerbrey in 1959:(7)

$$\Delta m = -\Delta f \frac{A(\rho_q \times \mu_q)^{1/2}}{2(Fq^2)} \qquad (6)$$

where Δm is the mass change, Δf is the change in frequency, A is the area, F_q is the reference frequency, ρ_q is the quartz crystal density and μ_q is the AT-cut quartz constant.

It is important to mention that the Sauerbrey equation is valid only for thin and rigid electrodes. Since good EQCM devices can determine mass changes down to a few ng/cm^2, EQCM is a valuable method when studying the movement of ion and solvent molecules during the oxidation or reduction of an electrode material.

3.1.6 Evaluating batteries: The two-electrode setup

All of the methods described above can also be used to evaluate a battery. For example, the battery can be galvanostatically charged, and the potential can be monitored; moreover, through a potential step, the current response can be

monitored (Figure 3). In **Paper III**, for example, we describe how an all-organic proton battery can be charged using both a constant current (CC) and a constant potential (CV) followed by a constant-current discharge.

When batteries are evaluated, oftentimes there is extra emphasis on the rate at which the battery can be charged and discharged. In principle, determining the rate capabilities of a battery only consists of galvanostatic measurements at different currents; thus, the battery community often refers to *C-rates*. In this case, *1C* is defined by the current in a galvanostatic experiment necessary to charge or discharge the battery in one hour.
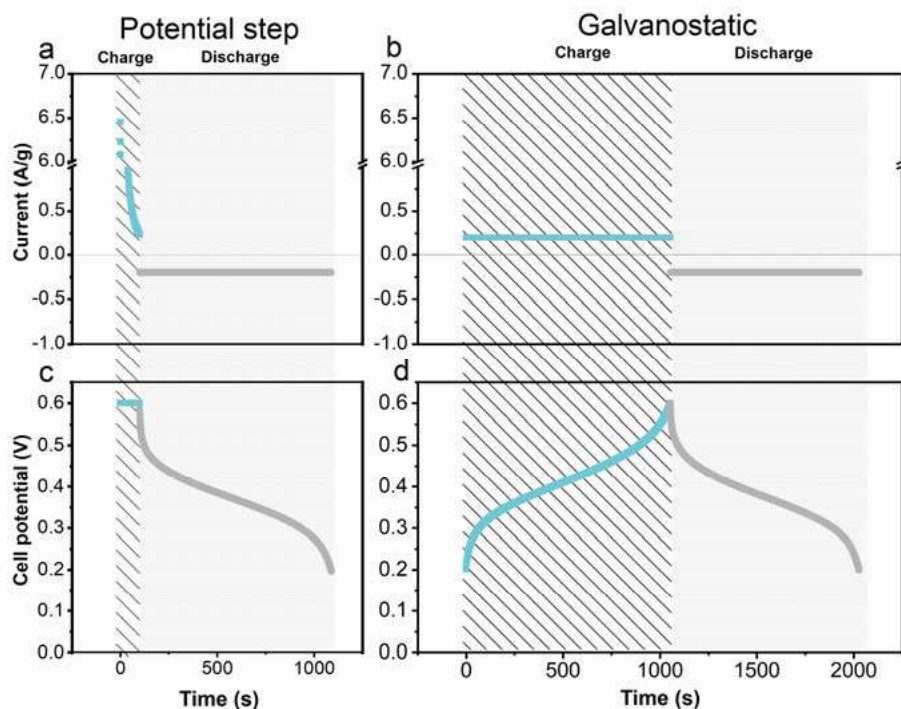

Figure 3. Comparison between the galvanostatic charge and potential step charge in a two-electrode setup. The graphs at the top (a and b) show the current response, whereas the graphs at the bottom (c and d) show the potential response.

3.2 Organic electrodes

In this section, different types of organic electrode materials and their use in electrodes will be discussed. A more extensive discussion on conducting redox polymer electrodes, which have been the focus of this thesis, will be presented in chapter 4. Several organic electrode materials have been studied. One approach is to simply use an organic molecule that is redox active; thus,

it can work as an electrode material in the battery, which was reported by Armand in 2009.(8) One major challenge with the use of organic battery materials is inhibiting their dissolution, so recently, an increasing number of organic battery concepts have focused on redox polymers, where the redox-active group is attached to or incorporated into a polymer backbone to inhibit dissolution.(9) From the pioneering work of Nishide(10-12), the immobilization of a wide range of different redox-active groups on a polymer have been studied. These include carbonyl-based(13), organosulfur-based(14) and radical-based(15) redox polymers. In most of these battery concepts, only one electrode, usually the cathode, has been organic, while the other electrode usually contains metals in the form of lithium or sodium. This setup results in a rather high potential and establishes organic electrodes as substitutes for cathode materials that are often considered the most problematic for conventional battery sustainability. Interestingly, some all-organic batteries, in which both the anode and cathode are organic electrode materials, have been shown.(16, 17)

Apart from the dissolution problem of redox-active group in an electrolyte, another challenge for organic electrode materials is to provide electrical conductivity. Electrical conductivity is important for transporting electrons generated or consumed by the redox reaction at an electrode to or from current collectors. In most of the abovementioned battery concepts, many carbon additives have to be used (usually between 20% - 80%), which considerably decreases the amount of redox-active material in the electrode composition. In chapter 4, I will discuss how this can be addressed using *conducting* redox polymers. In the coming section, I will provide a short overview of how electrodes can be coated and formulated together with binders and carbon additives in conventional redox polymers.

## Coating electrode surfaces and carbon additives
In conventional redox polymer electrodes, both the binder for adhesion and the carbon additive that supplies conductivity have to be used in the electrode formulation. There are several carbon additives (carbon particles) available, such as SuperP, mesoporous carbon, vapor-grown carbon fibers and carbon nanotubes. The binder poly(vinylidene difluoride) (PVDF) is most commonly used because it has dissolution properties similar to those of typically used redox polymers. Since PVDF requires N-methyl-2-pyrrolidone (NMP) as the solvent, which is toxic, water-based slurries containing carboxylmethylcellulose (CMC) have recently been explored. Several options exist for processing additives together with redox polymers; common in all these procedures is the goal to achieve a homogenous mixture and an electrode coating that is porous enough to allow electrolyte penetration, i.e., ion transport.

In its simplest form, all components of electrodes can be mixed in their solid form, e.g., using ball milling. This method can lead to a uniform distri-

bution for certain redox polymers but can also result in nonhomogenous electrodes, especially if the particle size of the redox polymer is too large. In many contexts, the dissolution of both the polymer and binder, e.g., in NMP, results in a better distribution and larger contact area between the redox polymer and carbon additive. For this method, the drying process is crucial, and when not optimized, the electrode composition can be brittle and easily cracks. Another option for processing is to use water-based slurries, i.e., the use of water-suspended CMC as the binder. In that case, all components are in their solid form, but good mixing and homogenous electrodes are achieved by suspending the components in water, followed by a drying step. Another, more exotic method that can be used for certain polymers is to perform *in situ* polymerization together with carbon and binder additives.(9)
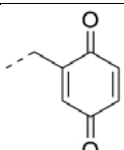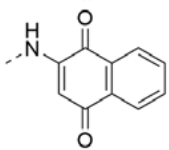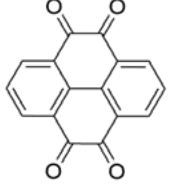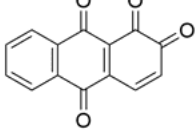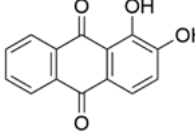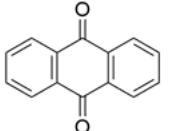
3.3 Quinones as a redox-active group

As mentioned earlier, the aim of this thesis is to study organic batteries using quinones as the redox-active group in electrode materials. In principle, the quinone redox reaction is shown in Schematic 1. Here, *para*-benzoquinone (Q) reacts with two electrons and two cations, either metal ions or protons, to result in a hydroquinone (QH_2) or a metal-quinone (QM_2).
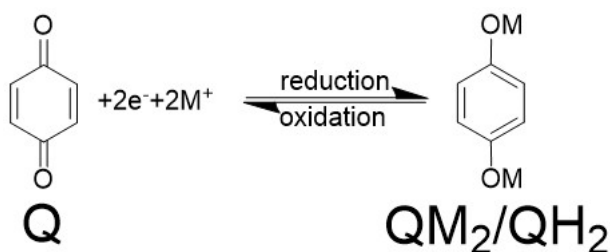
Schematic 1. Quinone reaction scheme

There has been considerable research on using quinones as electrode materials in hybrid-organic batteries, which primarily cycle lithium ions in organic electrolytes.(13, 18-21) Quinones in aqueous systems and particularly all-organic aqueous quinone batteries are much rarer. Table 1 provides a short overview of different quinone electrodes that have been studied in aqueous electrolytes.

Table 1. Different quinone-based electrode materials that have been studied in aqueous electrolytes
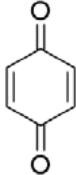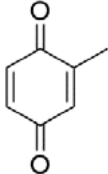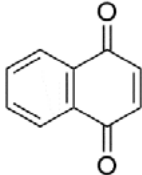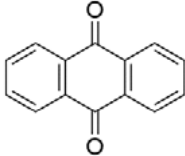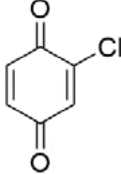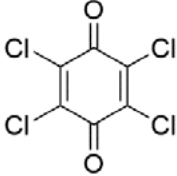
Name	Quinone pendent group structure	Electrolyte	Potential vs SHE (V)	Discharge capacity based on the whole electrode composition (mAh/g)	References
EP(Q)E		0.5 M H_2SO_4 (aq)	0.67	80	This work*
EP(NQ)E		0.5 M H_2SO_4 (aq)	0.27	68	This work*
PTO		4.4 M H_2SO_4 (aq)	0.51	198	(22)*,(23, 24)
Alizarin (pos)		1 M H_2SO_4 (aq)	1.05	48	(25)*
Alizarin (neg)		1 M H_2SO_4 (aq)	0	48	(25)*
Anthra-quinone		30 wt% NaOH(aq)	-0.6	217	(26)*,(22, 27-29)

* Reference for the electrolyte, capacity and potential values

As shown in Table 1, the potential of different quinones that have been studied can vary considerably. In most cases, the potential of quinone can be tuned by either using electron withdrawing groups (EWGs) or electron donating groups (EDGs). EWGs increase the formal potential of the quinone redox reaction since the oxygen is electron poor and consequently will be easier to reduce. The opposite is of course true for EDGs. Furthermore, annulation will stabilize the oxidized quinone form, further reducing its potential. In Table 2, different

quinones with their corresponding formal potentials are listed. It is important to mention that these are calculated values and might differ from experimentally obtained values. In particular, the electrolyte that is used can affect how functional groups affect the quinone potential. When substituting hydroquinoids with fluorides as an EWG in aqueous electrolytes, the electron donating effect of the water molecules counteracts the effect of the fluoride substitution on the benzene ring. (30)

Table 2. Quinone structure, formal potential and electronic properties of substituents(31)

Name	Quinone structure	E^0 vs SHE	Electronic properties of substituents
1,4-benzoquinone		0.64	
2-methyl-1,4-benzo-quinone		0.60	EDG
1,4-naphthoquinone		0.38	EDG
9,10-Anthraquinone		0.09	EDG
2-chloro-1,4-benzo-quinone		0.68	EWG
Tetrachloro-1,4-ben-zoquinone		0.70	EWG

26

Effect of proton activity on the formal potentials of quinone in aqueous electrolytes

The redox reaction from Q to QH$_2$ involves two electrons and two protons. According to the Nernst equation (Equation 7), the formal potential is therefore dependent on proton activity. When standard conditions exist while proton activity is $\neq 1$, the formal potential of the redox reaction is dependent on the pH according to Equation 7. For example, a high proton activity or low pH results in a high formal potential, since the reduction of Q to QH$_2$ is easier.

$$E^{0\prime} = E^0 + \frac{RT}{2F} ln\left(\frac{[Q][H^+]^2}{[QH_2]}\right) = E^0 + \frac{RT}{2F} 2ln([H^+])$$
$$= E^0 - 59mV \times pH \qquad (7)$$

The change in the formal potential as a function of pH is important when designing an electrode material. The formal potential needs to fall within the potential window of the electrolyte and, if used with a conducting polymer backbone, needs to be redox matched with the conducting polymer. Both of these aspects will be further discussed later in the thesis.

3.4 Electrolytes

An important aspect of a battery system is the electrolyte, which conducts the ions necessary to counterbalance the redox reactions at the respective electrodes. Most importantly, there are two electrolyte properties that must be considered when choosing one for organic batteries. First, and most importantly, the electrolyte has to be stable at potentials where redox reactions at the electrodes occur. Figure 4 shows a comparison of the stability window for the different electrolytes used in this thesis when measured with a glassy carbon electrode. Second, the ion conduction has to be high, i.e., the solution resistance, as measured by electrical impedance spectroscopy (EIS), has to be low. Table 3 shows an overview of electrolytes and their conductivity. In the coming sections, the electrolytes used in the different studies for this thesis are discussed in more detail.
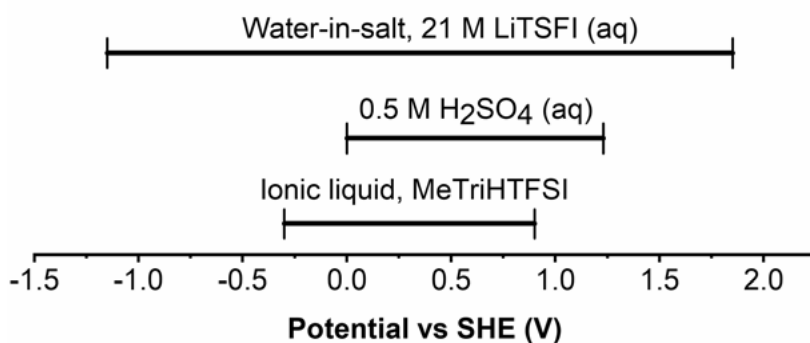
Figure 4. Stability window of different electrolytes vs SHE as reference; 21 M LiTSFI (aq), 0.5 M H₂SO₄ and MeTriHTFSI.

Table 3. Conductivities of different electrolytes that were used in the quinone-based organic batteries in this thesis.

Electrolyte	Conductivity	Reference
Aqueous, 0.5 M H_2SO_4	200 mS cm^{-1}	(32)
Water-in-salt, 21 M LiTSFI (aq)	10 mS cm^{-1}	(33)
Nonstoichiometric ionic liquid, triazole based, MeTriHTFSI	25 mS cm^{-1}	(34)

3.4.1 Aqueous electrolytes

Due to its abundance, one of the simplest electrolytes to consider when designing a battery is using aqueous solutions. One major advantage of aqueous electrolytes is their very low solution resistance, which is an order of magnitude lower than that of other electrolytes (Table 3). Furthermore, aqueous

electrolytes are generally abundant and inexpensive. On the other hand, the potential window of aqueous electrolytes is limited by the oxygen reduction reaction at 1.23 V vs. SHE and the hydrogen evolution reaction at 0 V SHE, resulting in an effective stability window of 1.23 V.(35) In practice, these values can differ slightly due to kinetic effects. For different WEs, e.g., platinum, glassy carbon or gold, the actual potential for hydrogen and oxygen evolution will be different due to these kinetic effects.

3.4.2 Ionic liquids

Another class of electrolytes is ionic liquids (ILs). This type of electrolyte consists of a salt that has a melting point below 100 °C(36), and in certain cases, can even be in liquid form at room temperature, i.e., room-temperature ionic liquids. Most importantly, ILs are free from solvent molecules, which provides them with interesting properties, most importantly in regard to electrochemical stability.(37) Ideally, in the case of polymers that can cycle protons, the ionic liquid also enables proton transport. In **Paper II,** we therefore explored nonstoichiometric protic ionic liquids, which have a slightly different charge transfer mechanism than the mechanism exhibited by conventional ionic liquids, namely, vehicular diffusion (as also observed in conventional ionic liquids), proton hopping and structure diffusion (both of which only occur in protic ionic liquids). The different mechanisms are illustrated in Figure 5.
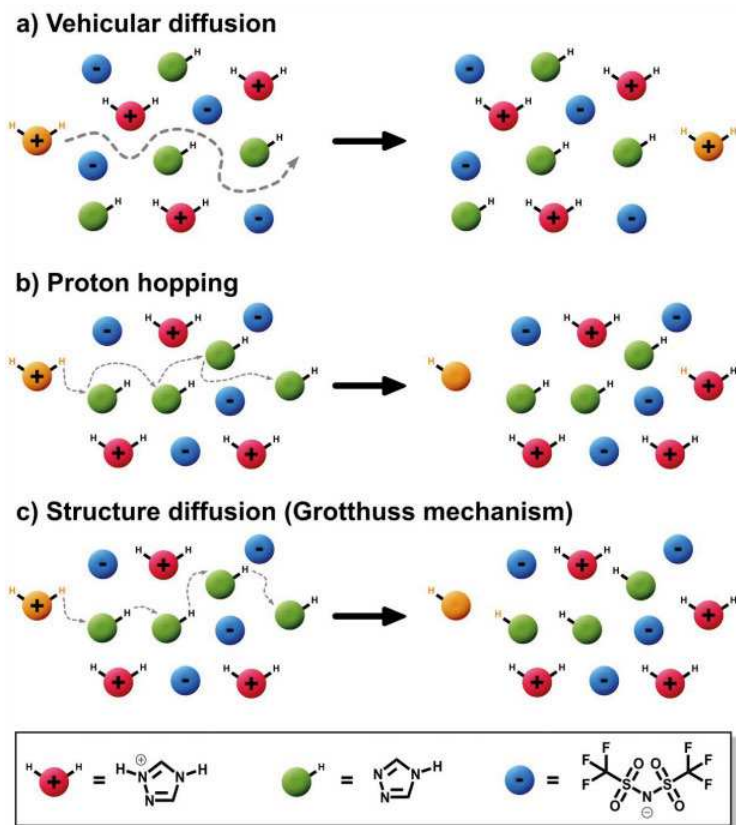
Figure 5. Different charge transfer mechanisms that are exhibited by protic ionic liquids. Vehicular diffusion, proton hopping and structure diffusion. Reproduced from Paper I © 2018 American Chemical Society.

3.4.3 Commercial lithium electrolytes

Apart from all-organic batteries, organic battery materials can also be used as cathode materials together with a commercial lithium-ion anode. In this hybrid-organic battery design, commercial lithium-ion battery electrolytes are of interest. Again, properties such as the electrochemical window and conductivity are important. However, instead of only relying on the electrochemical stability window of the electrolyte, the operating potential can be increased by forming an interface at not only the electrode that is an ionic conductor but also an electrical insulator, thus shielding the electrolyte from the actual potential at the electrodes. This layer, formed at the anode, is called the solid electrolyte interface (SEI), and its formation largely depends on the choice of electrolyte. To achieve all the desired properties, a mixture of different electrolyte solvents is often used.(38)

3.4.4 Water-in-salt electrolytes

To increase the stability window of aqueous electrolytes, a high salt concentration can be used. In lithium-ion batteries, Xu's group first described the use of a water-in-salt electrolyte. Here, LiTFSI was chosen as the salt due to its high solubility in water. Using a concentration of 21 M LiTFSI, an electrochemical window of 3 volts was achieved.(33) Later, several other water-in-salt concepts were shown. (39-41) Apart from using only LiTSFI as the salt, the electrochemical window can be further increased to over 4 volts by adding organic components that form an SEI layer on the anode, i.e., mixing LiTSFI (aq) with a highly fluorinated ether.(42) Another such concept uses a hybrid organic, aqueous electrolyte, 15 M LiTFSI water/dimethyl carbonate (DMC), which works well with a $Li_4Ti_5O_{12}$ (LTO) anode.(40) This concept inspired the work presented in **Paper II**.

4 Conducting redox polymer electrodes

As mentioned earlier, organic electrodes need to fulfil several requirements to work properly. The charge has to be stored, electron transfer between the redox-active group and the current collector has to be facilitated, and the dissolution of active material into the electrolyte has to be prohibited. Instead of addressing all these properties by different means, as done with conducting additives, binders and polymer electrodes, all can be achieved by using a conducting redox polymer (CRP) that is comprised of a conducting polymer backbone, which supplies electron transfer and inhibits dissolution, and a pendant group, which supplies the capacity in a battery. In the following chapter, I will discuss CRPs in more detail.

4.1 General considerations and methods of evaluating CRPs

4.2 Conducting polymers and their history

Normally, when one thinks of polymers, one imagines materials that are electrically insulating at room temperature. For a certain type of conjugated polymer, this is not entirely true, as they can be made to conduct under ambient conditions. Although both polyaniline and polypyrrole have been known as conducting polymers, a large breakthrough in the field of conducting polymers came in 1977 when Heeger, McDiarmid and Shirakawa showed that the conductivity of polyacetylene, a conjugated polymer, could be significantly increased by doping, i.e., oxidizing or reducing the material. Since this discovery, there has been considerable scientific progress, resulting in many different conducting polymers and visions for possible applications of this type of material in several fields. Soon though it became obvious that among most of the conducting polymers studied, polypyrrole, polythiophene and polyaniline, suffered from degradation and low conductivities over time, under both humid air and inert conditions. In the 1980s, an important step in the evolution of conducting polymers was achieved, in which thiophene moieties were substituted by oxygen at the 3- and 4-positions, giving rise to poly(3,4-ethylenedioxythiophene) (PEDOT). PEDOT is very stable in its doped form, resulting

in high conductivities, and this material can also be transparent, which is crucial for several envisioned applications that are mentioned below. Furthermore, by polymerizing in the presence of polystyrene sulfonate (PSS), PSS will act as a polyanion dopant forming PEDOT:PSS, which results in a stable suspension in water and enables easy industrial processing.(43) Today, conducting polymers, especially PEDOT:PSS, are used in a wide range of applications, ranging from energy storage(44, 45), sensors(46, 47), and OLEDS(48, 49) to neuromorphic devices(50, 51) and photovoltaics(52, 53).

Understanding doping using polyacetylene as a model (54)

To further understand why conducting polymers are only electrically conducting in their doped form, polyacetylene, the simplest conducting polymer, can be used as a model compound. Polyacetylene consists of CH units connected in a conjugated fashion. If one assumes equal bond lengths, polyacetylene is a quasi-1D metal with an electron band that is half filled (Figure 6a). Since this system is unstable due to the Peierls instability, CH groups move toward each other, thereby resulting in alternating double and single bonds and causing an energy gap at the Fermi level (Figure 6b). Importantly, the band gap is too large to allow thermal electron excitation at room temperature, thus yielding a nonconducting polymer under ambient conditions. Interestingly, polyacetylene can be doped, through the introduction of an anion (p-doping) or a cation (n-doping) that diffuses to the polymer chain. In the case of p-doping, the polymer acts as a polycation, whereas after n-doping, the polymer can be considered a polyanion. In both cases, doping introduces localized energy states within the energy gap created by the Peierls instability. Here, the difference in energy between the valance band and the doping-induced band is small enough to result in a conducting polymer at room temperature (Figure 6c). Importantly, doping affects only the π-electrons in the polymer, leaving σ-bonds intact, which are crucial for the structural integrity of the polymer.
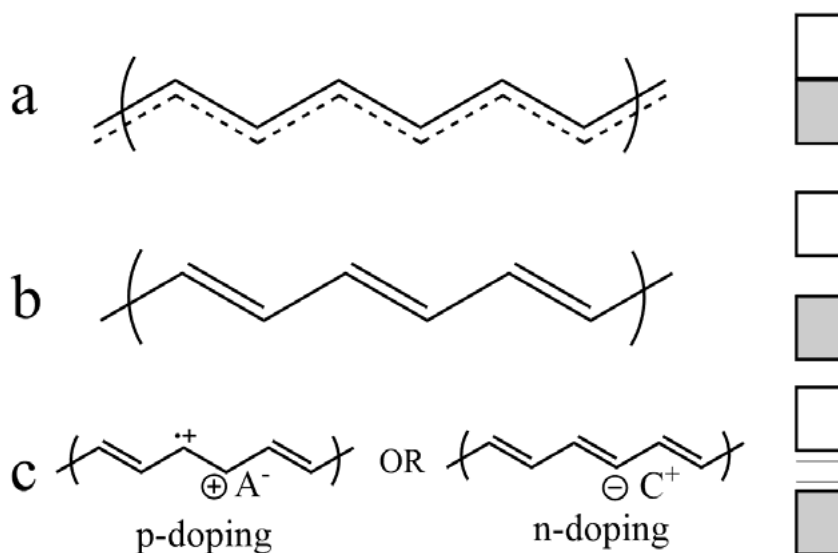
Figure 6. Polyacetylene model of conducting polymers. Assuming equal bond lengths (a). Alternating bonds due to the Peierls instability (b) and the resulting interbond states created from either p- or n-doping (c).

4.3 From conducting polymers to conducting redox polymers: The introduction of a pendant group

As mentioned earlier, the aim of this work is to study organic batteries. Since conducting polymers (CPs) in their "naked" form only result in a capacitive response, it is of interest to introduce and attach a high capacity pendent group to the CP backbone.

Potential matching

It is important to mention that although there is considerable freedom in changing the pendant group to tune the potential that will be achieved by individual electrodes, there is a limitation stemming from the conductivity region supplied by the CP backbone. If the CP backbone is outside its conducting region, i.e., is completely undoped, the crucial conductivity for charge transport through the material is lost. Therefore, the potential of the pendant group has to be matched with the conductivity region of the CP backbone, known as potential matching. Regarding p-doped PEDOT, the conductivity onset is approximately 0.05 V vs SHE (Figure 7); consequently, pendant groups with a potential higher than 0.05 V vs SHE can be used if p-doped PEDOT is utilized. However, it is important to mention, that the pendant group or the polymer mixed with PEDOT might influence the onset potential,

as shown in **Paper V**. Other influences on the onset potential, such as the electrolyte and length of the conducting polymer, also exist.
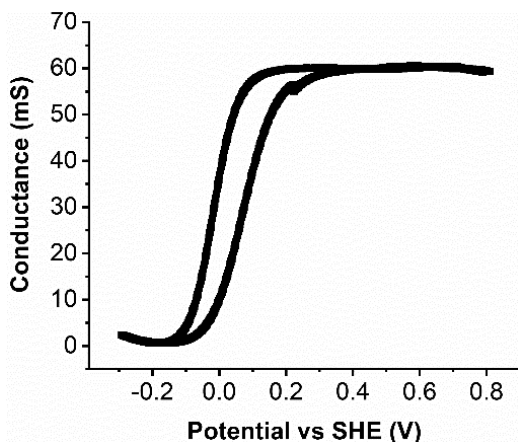

Figure 7. In situ conductance of PEDOT.

4.4 *In situ* conductance measurements using an interdigitated array(55)

There are several ways of measuring conductance. When studying conducting polymers to be used in electrochemical applications, their *in situ* conductance response at different applied potentials, along with other responses, are of interest to match the potential of the pendant group to the conductivity region of the CP backbone, which I will explain later. In principle, regarding *in situ* conductance measurements, the CP covers two WEs connected to a bipotentiostat. By applying a voltage bias (E_{bias}) and recording the current difference (Δi) between the two WEs, the conductance can be recorded according to Equation 8.

$$G = \frac{\Delta i}{2 \times E_{bias}} \tag{8}$$

To increase the signal-to-noise ratio during the measurement, a so-called interdigitated array (IDA) electrode is used, which has many bands in a comb-like structure. Figure 8 shows a schematic of the experimental setup for an *in situ* conductance measurement using a bipotentiostat and an IDA electrode. Below, I will briefly explain how Equation 8 is derived from the experimental setup.

The conductance (G) is inversely proportional to the resistance (R); furthermore, using Ohm's law, the bias current (i_{bias}) can be related to the voltage

bias (E_{bias}) and the resistance in the polymer film between WE1 and WE2 (R_p) according to Equation 9:

$$G = \frac{1}{R} = \frac{i_{bias}}{E_{bias}} \tag{9}$$

E_{bias} is known from the experimental setup, and i_{bias} can be calculated in the following way. Since the sum of all currents in a point is zero according to Kirchhoff's law, for points A and B in *Figure 8*, the following equations can be written:

$$0 = i_1 - i_{bias} - i_{c1} \tag{10}$$

$$0 = i_2 - i_{c2} + i_{bias} \tag{11}$$

where i_{c1} and i_{c2} are the currents generated by the redox reaction. By subtracting Equation 11 from Equation 10 and converting $\Delta i = i_1 - i_2$ and $\Delta i_c = i_{c1} - i_{c2}$, the following expression is obtained:

$$\Delta i = 2 i_{bias} + \Delta i_c \tag{12}$$

Assuming that Δi_c is close to 0, i.e., i_{c1} and i_{c2} are identical or $i_{bias} \gg i_{tot}$, which is achieved by a small scan rate, the bias current can be calculated by:

$$i_{bias} = \frac{\Delta i}{2} \tag{13}$$

Inserting Equation 13 into Equation 9 results in Equation 8, i.e., the expression for the conductance of the polymer coated on an IDA.
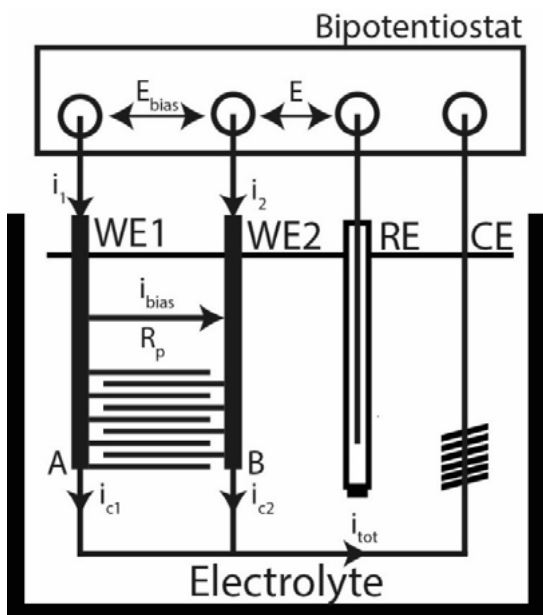
Figure 8. Biopotentiostat setup. Here, 2 working electrodes are used (WE1, WE2) along with an RE and a CE.

4.5 Processing of CRPs

Conducting polymers in general and conducting redox polymers in particular are known for their insolubility in common solvents when being processed. Although this insolubility is an advantage in regard to electrode stability, as CRPs will not dissolve in an electrolyte, this insolubility is a major drawback during the processing of electrode materials. In the following section, different means of processing and depositing active material on electrodes are discussed.

Electrochemical polymerization
During electrochemical polymerization, a potential is applied so that the precursor is oxidized and thus polymerized. (Schematic 2) In this way, the polymer slowly builds on the electrode surface. This method for processing the electrode material is used in **Paper I** and **Paper II**. Although this method provides good control over the polymerization process, it has several drawbacks. First, the exact amount of material polymerized is difficult, if not impossible to determine. Second, and more importantly, when polymerizing electrodes to be used in batteries, the amount of material that can be coated on the surface by this method is rather limited.
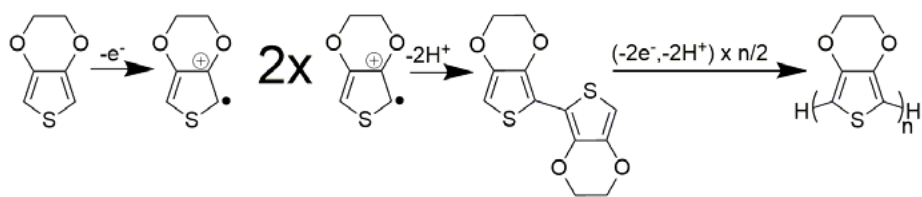
Schematic 2. Oxidative polymerization of EDOT. Once oxidized, a radical is formed, which together with another radical forms a dimer. This process is repeated until a polymer (PEDOT) is formed.

Chemical oxidation forming a suspension

Another common way to supply an oxidative environment that results in the polymerization of EDOT forming PEDOT is to use a chemical oxidant such as iron(III) salts. One drawback with this method of polymerization is that the oxidant has to be washed out. This can be circumvented by using an oxidant that will evaporate along with the solvent of the suspension. For example, in **Paper IV,** we showed that when an oxoammonium cation (TEMPO$^+$) was used as an oxidant, no washing step was necessary. In principle, the TEMPO-oxidation process has three steps: (1) the trimer precursor and oxidant are dissolved, and subsequently, CRP is formed by adding the oxidant solution to the trimer solution. (2). This forms a stable suspension containing redox-active black polymer particles, which can easily be cast onto a current collector (3). Finally, the drop-cast film is dried (*Figure 9*). It is important to note, however, that the oxidation potential of TEMPO$^+$ is 0.84 V vs SHE(11), which is too low to oxidize EDOT-based precursors. Instead, a trimeric precursor, EEE or EPE, has to be used.
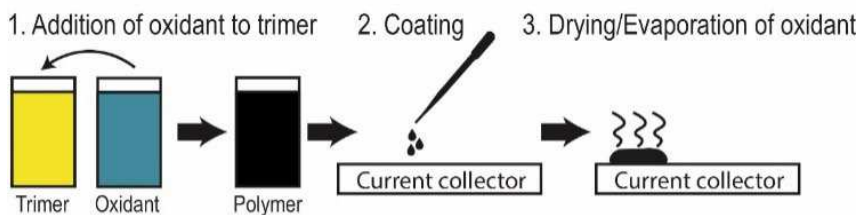

Figure 9. Chemical oxidation using TEMPO+. First, the trimer and oxidant are dissolved, and then the oxidant is added to the trimer solution, which forms a stable suspension of CRP; subsequently, the suspension can be coated onto a current collector. In the third and last step, the coated material is dried. Reproduced from Paper IV © 2020 Wiley-VCH GmbH.

Postdeposition polymerization

Postdeposition polymerization is a processing method designed to address the drawbacks of both electrochemical polymerization and chemical oxidation for polymerization. In this process, a terthiophene trimer is dissolved in a solvent, for example, N-methyl-2-pyrrolidone, then drop-cast and dried, followed by electrochemical polymerization or oxidative polymerization (Figure 10). This method works since the drop-cast and dried trimer is not soluble in the solvent, which is chosen during polymerization. Since the exact drop-cast amount is known, the exact amount of material that is applied to the electrode is also known. As we show in **Paper III**, this method allows for rather high mass loadings of several mg/cm^2.
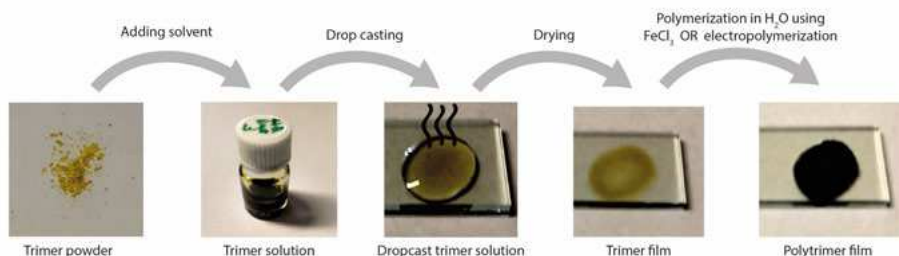
Figure 10. Postdeposition procedure with all steps from the trimer powder to a finished polymer film. Reproduced from Paper III © 2020 Wiley-VCH GmbH.

Apart from using CRP-precursors such as EP(NQ)E, one can also use the post-deposition method with a trimeric CP precursor, EPE, and mix it with a redox polymer with naphthoquinone (NQ) redox-active groups to form PNQ@pEPE upon postdeposition polymerization of the trimeric precursor (*Figure 11*). This method was explored in **Paper V**. As we show in this paper, this method provides a simple synthesis method for a variety of redox polymers that can be paired with pEPE as conducting and binder additives.

Figure 11. Postdeposition polymerization of EPE together with a redox polymer (PNQ), resulting in PNQ@pEPE. Reproduced from Paper V © 2021 American Chemical Society.

5 Design criteria for quinone organic batteries

The aims of this thesis have been to study different quinone organic battery materials and, to some extent, to formulate design criteria for this type of electrode material, which is important when moving forward toward designing application-specific batteries. Below are several important aspects that have been addressed throughout this thesis.
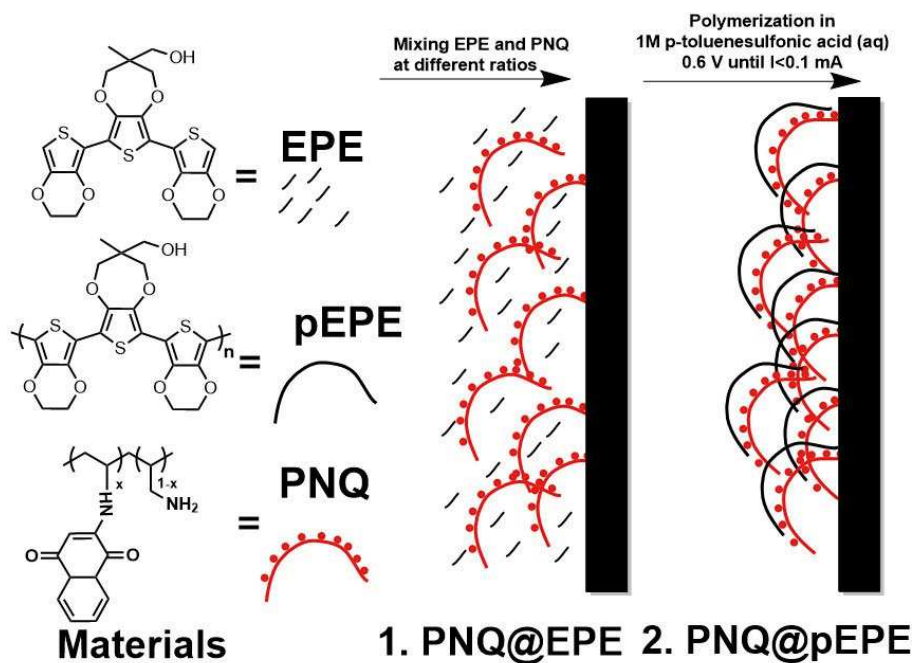
The quinone redox-active groups provides a well-defined potential
For a redox-active group to be used as a battery material, it preferably provides a well-defined potential. In this way, the potential of the battery itself will be well defined as opposed to being dependent on the state of charge of the battery, which is undesirable as a device characteristic.

The quinone redox-active group is well matched with the potential window of the solvent
As previously mentioned, the potential stability window of the solvent governs which material can be used in the battery so that no side reactions occur because the electrolyte is degraded. Therefore, the quinone redox potential has to be within the stability window of the electrolyte.

Efficient charge transport
For the material to be accessed efficiently, charge transport to the redox sites has to be effective. In many organic battery designs, this transport can be facilitated by mixing with a carbon-based additive, such as carbon black or carbon nanotubes. The focus of this thesis has been to utilize CPs for charge transport. Regarding this type of material, it is important that the pendant group is *potential matched*, i.e., the potential of the redox reaction is within the potential region where the CP is oxidized and thus conductive.

Processability

The electrode material has to be easy to process, especially in an industrial setting. Regarding the methods used in this thesis, it entails that the CRP or redox polymer and CP are sufficiently soluble in an available solvent and that it can be applied to the electrode as one would apply a paint.

Efficient ion transport

Apart from electron transport, ion transport must also be efficient to counterbalance the redox reaction. For example, the hydrophobicity of the quinone pendant group in aqueous battery systems is one parameter to keep in mind. This parameter has not been studied as extensively in this thesis as other aspects, but it is nevertheless important and further exploration of this topic might be of interest.

Easy synthesis

Another aspect that has not been discussed in this thesis, but which is also important for a battery to be commercialized, is that the synthesis of the materials is fairly easy. The synthesis does not require many steps and can be accomplished with green solvents.

6 Characteristics of quinone-based organic batteries

In the course of my research for this thesis, I have designed several organic batteries based on quinone redox-active groups. The full manuscripts describing these batteries can be found at the end of this thesis. In this chapter, I want to provide a short overview of the key characteristics of these battery designs, which in principle are represented in one paper each. (Table 4)

Table 4. Overview of the different batteries designed in this study.

Paper	Anode material	Cathode material	Electrolyte	Cell voltage (V)
I	pE(NQ)	pE(HQ)	MeTriHTFSI	0.45
II	LTO	pE(HQ)	15 M LiTFSI	1.35
III	pEP(NQ)E	pEP(QH$_2$)E	0.5 M H$_2$SO$_4$(aq)	0.4
IV	pEP(NQ)E	Oxygen catalyst	0.5 M H$_2$SO$_4$(aq)	0.5
V	PNQ@pEPE	MnO$_2$	0.05 M H$_2$SO$_4$(aq) + 1 M MnSO$_4$	0.95

6.1 All-organic battery using a nonstoichiometric ionic liquid, **Paper I**

In this study, an all-organic battery was designed. Monomeric precursors (EDOT with functionalized quinone groups) were used, which were electro-polymerized on small glassy carbon electrodes and resulted in pE(NQ) as the anode and pE(QH$_2$) as the cathode; these results were in accordance with an earlier work by this group.(55, 56) This design was similar to an all-organic battery design with pE(QH$_2$) as the cathode and EDOT, with an anthraquinone pendent group, as the anode, resulting in a battery that cycled protons in a rocking chair fashion.(57) By choosing pE(NQ), it could be ensured that the redox reaction of the anode was within the electrochemical stability window of the electrolyte, which had been an issue in the previous design. Further-more, the electrolyte was changed from the previous design to consist of a nonstoichiometric protic ionic liquid (NSPIL). Earlier, a pyridine-pyridinium slurry was used as the electrolyte, which was both toxic and very aggressive chemically. The NSPIL was designed with a low melting point to yield a high conductivity even at room temperature (58), which was reflected by the high C-rates that could be achieved (*Figure 12*a). Importantly, the pKa of the elec-trolyte was tuned to 2.45 to enable potential matching, as previously discussed in this thesis. The battery had a cell voltage of approximately 0.45 V, as pre-viously mentioned, fast rate capabilities and moderate cycling stability (Figure 12). Since electropolymerization was used as a means of coating the elec-trodes, no exact mass loading could be calculated. While there were many limitations of this approach, especially resulting from the use of electropoly-merization as the method for making the electrodes, the study was an im-portant step for building an all-organic proton battery.
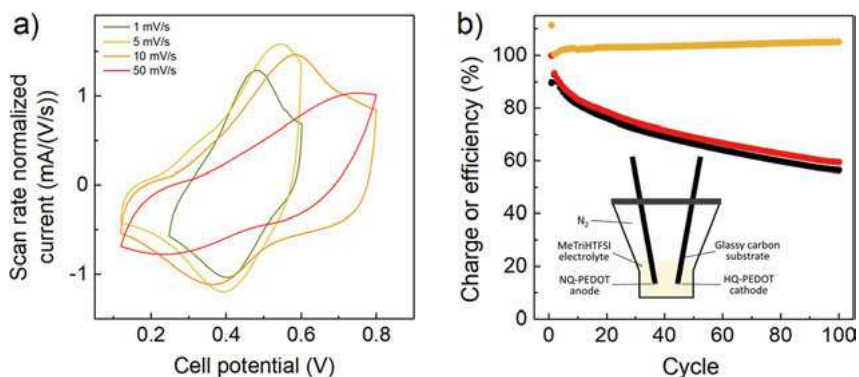

Figure 12. Electrochemical performance of an all-organic proton battery with an electropolymerized CRP electrode material. (a) CVs at different scan rates, 14C (green) to 700C (red) and the (b) cycling stability for the first 100 cycles. Repro-duced from Paper I © 2018 American Chemical Society.

6.2 Hybrid-organic battery using LTO as the anode and HQ-PEDOT as the cathode, **Paper II**

Recently, in the lithium-ion battery field, there was a push to create batteries using an aqueous electrolyte, which would make these batteries both fast and safe.(59) Inspired by this development, we aimed to build a hybrid-organic battery, which would cycle lithium ions and result in a substantially higher cell voltage than our all-organic battery discussed in **Paper I**. From previous work (60), we hypothesized that the quinone pendent group could cycle lithium if the concentration of lithium ions in the electrolyte was high enough. A water-in-salt electrolyte (15 M LiTFSI water/DMC) was therefore chosen, which was similar to inorganic battery concepts, and $Li_4Ti_5O_{12}$ (LTO) was used as the anode material, which had been studied with this electrolyte.(40) This electrolyte did indeed exhibit lithium-ion cycling, as shown in **Paper II**. Similar to the study in **Paper I**, in this study, a monomeric CRP precursor (EQH_2) was electropolymerized on an electrode and used as the cathode. Importantly, the resulting CRP was potential matched, although the potential of the redox reaction with lithium ions was downshifted compared to a proton cycling analog under acidic conditions. Together, these two-electrode materials resulted in a cell voltage of 1.35 V, which was much higher than that in the all-organic battery designs. This cell voltage was lower than other inorganic water-in-salt concepts, which, for example, reported 3.2 V using an LTO anode and lithium manganese nickel oxide as the cathode.(40) Unfortunately, the cycling stability was rather poor (*Figure 13*), which we attributed to self-discharge on the LTO anode and resulted in a shift in potential that was cycled at the cathode. This result was in contrast to data previously reported, where the LTO anode could provide a stable potential over time, but which we were not able to reproduce.(40) Importantly, this study showed how versatile quinone materials could be when used as electrode materials; in this case, these quinone materials successfully cycling lithium in a hybrid-organic battery.
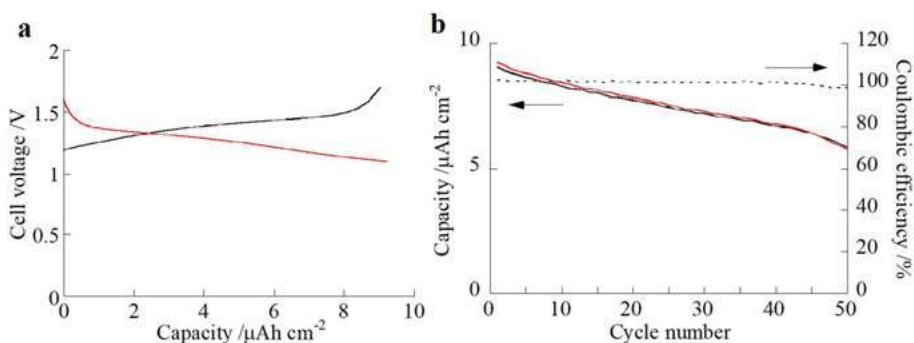

Figure 13. Battery performance of a HQ-PEDOT, LTO hybrid-organic battery using 15 M LiTFSI water/DMC as the electrolyte. Charge (black) and discharge (red) curves (a) and cycling stability (b). Both were measured at 30C. Reproduced from Paper II © 2019 Elsevier

6.3 All-organic aqueous proton battery, **Paper III**

This study was in several aspects different from previous studies. For processing, we used a trimeric precursor, EP(NQ)E and EP(QH$_2$)E, instead of monomeric precursors. It was established that longer oligomer chains resulted in a lower oxidation potential, (61, 62) which we envisioned would result in milder polymerization conditions resulting in a better polymer. We further developed a method, postdeposition polymerization, as previously described in this thesis, which allowed the trimer to be deposited on the electrode and polymerized after drying. In this way, a precise mass loading of up to 10 mg/cm^2 could be achieved, and specific capacities could be calculated, which was in stark contrast to previous work where only rough estimates of the amount of deposited material could be made. Furthermore, this method yielded thicker layers and shows promise for large-scale processing. When evaluating the battery, two different types of charging were used. Constant-potential charging followed by constant-current discharge and traditional galvanostatic cycling, i.e., constant-current charge and discharge. As shown in Figure 14, a battery with a voltage of 0.4 V was realized. During the potential step, 50% of the battery was charged in less than 10 s (Figure 14a), and after a full charge, an initial capacity of 60 mAh/g was realized (Figure 14b), which was approximately 80% of the theoretical capacity (75 mAh/g). Considering the cycling stability of this battery, 85% of the initial capacity was retained after 500 cycles. (Figure 14b). When cycling galvanostatically, a similar initial capacity was achieved, 60 mAh/g (Figure 14d); however, only 50% of the initial capacity was retained after 500 cycles (Figure 14d). We also tested the battery at subzero temperatures, i.e., -24 °C. The battery retained almost all of its capacity and rate capabilities (Figure 14e and Figure 14f) and, interestingly, was much more stable, retaining approximately 95% of its initial capacity after 500 cycles (Figure 14f).
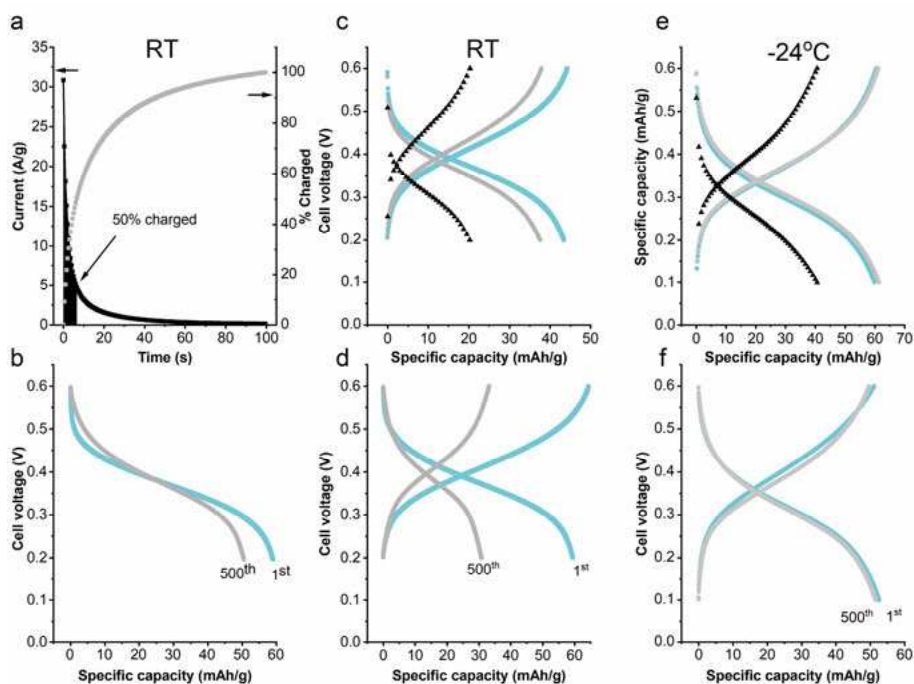
Figure 14. Evaluation of the all-organic battery at room temperature (RT) (a-d) and at -24 °C (e-f). Current profile (a) resulting from constant-voltage charging. Here, 50% of the capacity is reached after approximately 6.5 s; voltage profiles with the same charging type for the first (cyan) and 500th (gray) cycles (b). Study of the rate capability at RT (c) with C-rates corresponding to 0.6 A/g (cyan) and 5.5 A/g (black). Voltage profile (d) for the first cycle (cyan) and 500th cycle (gray) using galvanostatic charging and discharging. Similarly, rate capabilities (e) and voltage profiles for the first cycle (cyan) and 500th cycle (gray) at -24 °C. Reproduced from Paper III © 2020 Wiley-VCH GmbH.

Since an aqueous electrolyte based on sulfuric acid was used in the battery, an important step to a more sustainable organic battery was taken, which is in line with other aqueous organic batteries that are currently developed.(16, 25) This study and battery clearly showed how an all-organic aqueous battery was designed and its favorable characteristics in regard to its rate capability and low-temperature operation. As we showed in this study, powering a small sensor or direct charging from solar cells without typically required charging electronics (*Figure 15*) could make for interesting applications. However, it is important to mention that the energy content of this battery would need to be improved for commercial viability, which could be done by replacing the cathode material with material having a higher redox potential that is closer to the oxygen evolution potential.
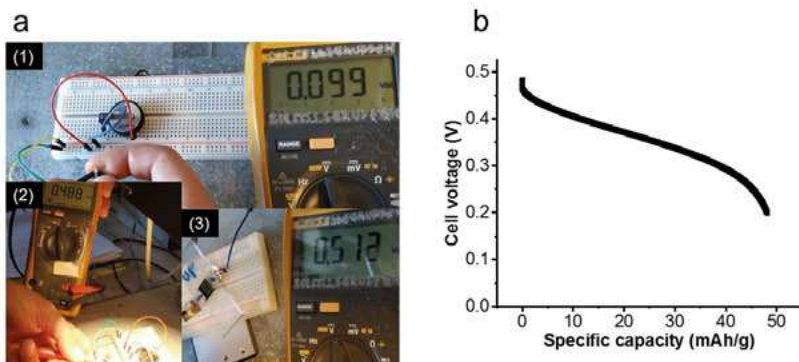
Figure 15. (a) Charging the all-organic battery with a solar cell. (b) Discharge curve after the charging step. Reproduced from Paper III © 2020 Wiley-VCH GmbH

6.4 Hybrid-organic battery with pEP(NQ)E as the anode and an oxygen catalyst as the cathode, **Paper IV**

In this work, we focused on building an organic-air battery. There is considerable research concerning secondary metal-air batteries (63), and primary zinc-air batteries are widely used in hearing aids.(64) Recently, an organic-air battery using a hydroquinone redox group was reported (65), and we were curious whether CRPs could provide equal performance with a better cell voltage by choosing an NQ redox group, i.e., pEP(NQ)E. We further aimed to improve the polymerization and electrode coating method used in **Paper III**. Here, we designed a process where the trimer was oxidized by TEMPO$^+$ instead of undergoing postdeposition polymerization, which might be difficult to conduct as a large-scale industrial process. This oxidation process yielded a suspension that could enable printing of the electrode material and thus marked another method for coating electrodes, as previously discussed in this thesis. TEMPO$^+$ was especially interesting as an oxidant since the product, TEMPO, sublimated at low temperatures (66); consequently, no washing step was necessary to remove the oxidation product. We further showed that the trimer precursor was pivotal for the oxidation by TEMPO$^+$ since a monomer, e.g., E(NQ), would not be polymerized by this mild oxidant. The resulting battery, with pEP(NQ)E as the anode and an oxygen catalyst as the cathode, showed a stable discharge voltage of 0.5 V and exhibited very good rate capabilities (Figure 16). In regard to the cell voltage, there was still considerable potential for improvement. However, this had to occur at the oxygen catalyst cathode since pEP(NQ)E was already close to the hydrogen reduction potential discussed earlier, and most of the overpotentials, as shown in the voltage profile of *Figure 16*a, stemmed from the cathode.
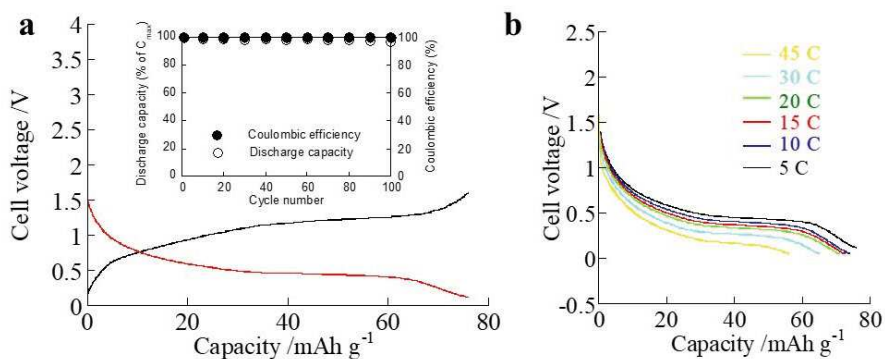

Figure 16. Operation of an organic-air battery. (a) Charge (black) and discharge (red) potential profile curves at 5C with the cycling stability as an inset. (b) Rate capability at different C-rates. Reproduced from Paper IV © 2020 Wiley-VCH GmbH.

6.5 Hybrid-organic battery with PNQ@pEPE as the anode and MnO$_2$ as the cathode, **Paper V**

The aim of this study was twofold. First, we wanted to evaluate how a trimer, EPE, could be a soluble precursor to form a conducting and binder additive in organic batteries. Here, we chose a nonconducting redox polymer (PNQ) as the redox material, which would provide a good comparison to our well-established pEP(NQ)E. Second, we wanted to create a battery close to the maximum voltage that could be achieved within the water stability window. Since we lacked an organic cathode with a potential close to the oxygen evolution potential, we chose carbon felt coated with MnO$_2$, as demonstrated earlier in an inorganic aqueous battery design.(67)

Previously, the mixing of a conducting polymer with a redox polymer was extensively studied by Inganäs et al.(68-70) However, importantly, the conducting polymer or its precursor could not be solution processed with the dissolved redox-active material. We aimed to solve this problem by using EPE as a precursor and forming a composite, NQ@pEPE, after polymerization. We further envisioned this method as a way to easily screen redox polymers, since mixing and polymerization are easy and provide initial information on the performances of redox polymers. In this study, we also found that when using pEPE as a conducting additive, wetting of the redox polymer improved, which could be a challenge in regard to hydrophobic redox polymers. The use of hydrophobic anthraquinone as a redox group on a polyvinyl polymer, for example, cycling under acidic conditions, had previously been reported to be challenging.(26) In our study, pEPE as a conducting additive outperformed both the hydrophobic carbon BP2000 and its hydrophilic analog PBX51, which is used in aqueous lead acid batteries when used with PNQ.

The battery was nearly optimal in regard to its utilization of the electrochemical stability window of water, yielding a potential of 0.95 V with a specific capacity of 63 mAh/g (Figure 17a). The capacity was retained well, with a value of 93% during the first 500 cycles at 1C. (Figure 17b). Furthermore, the rate capabilities were favorable, and even at 10C, a specific capacity close to 50 mAh/g was achieved (Figure 17). This study demonstrated my view quite nicely, i.e., the potential of an aqueous organic battery. In future work, a suitable candidate to exchange the MnO$_2$ cathode with organic redox materials should be identified. This exchange would result in a similar battery as the one presented here in regard to performance, which is crucial for commercial relevance, but with all-organic electrode materials.

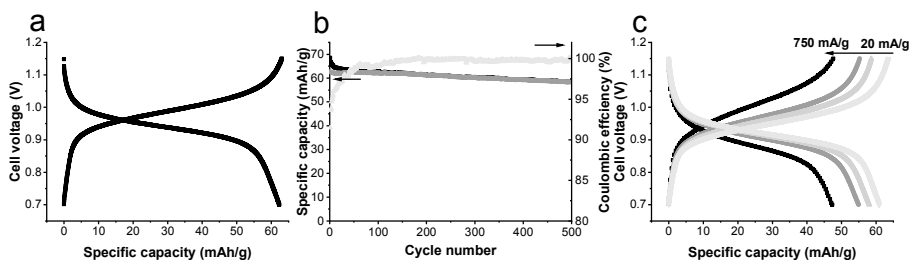*Figure 17. Electrochemical performance of the PNQ@pEPE MnO₂ battery. Voltage profile with charge and discharge curves (a). Cycling stability at 1C for the first 500 cycles (b) including the coulombic efficiency (light gray) and voltage profiles, thereby showing the rate capabilities of this battery from 0.3C (20 mA/g) to 10C (corresponding to 750 mA/g). Reproduced from Paper V © 2021 American Chemical Society.*

7 Concluding remarks and future work

In this work, I have shown different types of quinone-based organic batteries. Special emphasis has been placed on using CRPs as active materials in different battery designs. Using these different designs, I have shown the versatility of these types of materials in regard to creating innovative batteries. For example, I have shown how all-organic quinone batteries can withstand fast charging, which would enable their direct integration with an organic solar cell, and how, by adjusting the electrolyte, quinone organic batteries are well suited for operation at low temperature.

Importantly, I have formulated several design criteria for quinone organic batteries in general and CRP-based batteries in particular. Here, the right choice of electrolyte, together with the right redox-active pendant groups, is paramount.

Furthermore, in regard to using CRPs as electrode materials, I have studied and developed different methods of processing these types of materials, which is especially important if these types of batteries are to be commercialized. Here, the development from electropolymerized electrode materials to post-deposition polymerization and the TEMPO oxidation of trimeric precursors has provided important results to enable the further application of these types of materials.

In future development, there are three major research questions to be answered. First, one could explore the fundamental aspects of the postdeposition method and its interaction with the pendent group or redox polymer that the CP is blended with. It would also be interesting to further understand how the polymerization occurs and what governs the limiting aspects, such as mass loading. Second, one could further explore different battery designs with new pendant groups or new redox polymers. Furthermore, different types of hybrid-organic battery designs could be researched. These studies could open up new designs and batteries with improved capabilities in regard to capacity, cycling stability and cycling rate. Third, one could look beyond batteries and employ conducting polymers and the postdeposition method for other applications, such as catalysis.

8 Sammanfattning på svenska

En av vår tids stora utmaningar är att uppnå de globala hållbarhetsmålen som har definierats av FN. Dessa mål är viktiga i vår strävan att minska koldioxidutsläpp och bekämpa den globala uppvärmningen som vår ekonomiska välfärd resulterat i.

För att skapa ett koldioxidneutralt samhälle krävs nya teknologier både för produktion av energi och dess lagring. Många av de förnybara energislagen, så som solel eller vindkraft, är så kallad intermittent energi. Det betyder att energin bara är tillgänglig vissa tider på dygnet och inte alltid samtidigt som elförbrukningen är som högst. Detta är ett av skälen till att energilagrings krävs och ett bra sätt att lagra energin på är i batterier. En annan sektor som är i stort behov av billig energilagring är fordonssektorn som till följd av den ökade elektrifieringen kräver både effektiv och billig energilagring.

En av de mognaste teknologierna när det gäller energilagring är Litium jon batterier. Dessa har en hög energitäthet och priset för denna typ av energilagring har minskat stort de senaste åren. Tyvärr har denna typ av energilagring sina nackdelar när det gäller hållbarhet. Tillverkning kräver mycket energi, teknologi för återvinning finns endast på konceptstadiet och mycket av de metaller som krävs för batteriet framställs på etiska och miljömässigt tveksamma sätt. Kobolt används ofta som del i katodmaterialet i Litium-jonbatterier och bryts till exempel under väldigt enkla förhållanden i Kongo.

En ny typ av batterier, baserad på organiska material, försöker att adressera dessa problem. Genom organisk syntes kan en uppsjö av molekyler skapas av grundämnen som är lättillgängliga. Inom forskningen har ett stort antal av olika batterikoncept baserat på organiska molekyler och polymerer undersökts. Fokus för denna avhandling har varit batterier som använder sig av molekylgruppen kinoner för att lagra energi. Förutom själva redoxgruppen som lagrar energi krävs också ett sätt att leda elektronerna som frigörs eller konsumeras av redoxreaktionen genom materialet och ut i batteriets poler. I de flesta batterikoncept som har presenterats i forskningen hittills har kol eller kolliknande tillsatser använts. Fokus i denna avhandling har däremot varit att använda så kallade ledande polymer som laddningsbärare. Redoxgruppen har antingen direkt fästs på den ledande polymeren, vilket ger en ledande redoxpolymer, eller en redoxpolymer som blandats med en ledande polymer.

På detta sätt har viktiga aspekter när det gäller kinonbaserade organiska batterier undersökts.

Elektrolyten, som innehåller jonerna som balanserar redox reaktionen på elektroden har varierats från vattenbaserade elektrolyter, till jonvätskor och en så kallad "water-in-salt" elektrolyt, där saltkoncentrationen är så hög att oönskade sidoreaktioner inte sker. Kinoner cyklade beroende på elektrolyt både protoner (vattenbaserad och jonvätska) eller lithiumjoner ("water-in-salt"). Detta visar hur versatilt kinoner som redoxgrupp är när det gäller elektrolyt och cyklingsjon.

Material på anod och katod har varierats för att dels skapa hel-organiska (både anod och katod består av kinoner som redoxgrupp) och dels hybrid-organiska batterier (en elektrod är organisk, den andra är metallbaserad). Här är det viktigt att framhäva de önskade egenskaper hos kinonen som redoxgrupp. Det är önskvärd att kinonen ger en tydlig redoxpotential vilket i sin tur ger en väldefinierad potential i batteriet. Det är också viktigt att redoxgruppen är vad som kallas för "redox-matched". Detta krav är ett resultat av att den ledande polymeren endast är ledande inom vissa potentialintervall. Det är således viktigt att redoxgruppen befinner sig inom detta intervall för att elektroden ska fungera som den ska.

I detta arbete har även processbarheten av elektrodmaterialen undersökts. Elektropolymerisering, där man applicerar en oxidativ potential i en lösning av monomerer för den ledande redoxpolymeren man vill belägga, för att på så sätt belägga elektroden har använts i två av de studier som presenteras i denna avhandling. Denna metod tillåter bra kontroll över polymeriseringsförhållanden. Samtidigt är det svårt att exakt kunna bestämma mängden material som har belagds och att belägga mycket material. Metoden är därför inte industriellt gångbart. I ramen för denna avhandling har det därför utvecklats en ny metod där man istället för en monomer som polymeriseras använder sig av en oligomer, till exempel en trimer. Detta möjliggör att ett lager av trimer beläggs på elektroden som sedan polymeriseras. På så sätt har man väldigt bra kontroll över polymeriseringsförhållanden och det går att belägga relativ mycket material på elektroden. Intressant nog kan denna metod inte bara användas på ledande redoxpolymerer utan det går också att blanda en redoxpolymer med ett utgångsmaterial till en ledande polymer, vilket efter polymerisering skapar en redoxpolymer som är ihopblandat med en ledande polymer.

Sammanfattningsvis presenterar materialet i denna avhandling hur kinoner kan användas som aktivt material i batterier och hur dessa kan utformas på olika sätt. Utöver att vidare undersöka de grundläggande mekanismer bakom dessa batterier kan arbetet som beskrivs i denna avhandling utgöra en bra grund för att undersöka andra tillämpningar som exempelvis material för katalys eller organiska sensorer.

9 Acknowledgments

First, I want to thank and express my humblest gratitude to my main supervisor Prof. Martin Sjödin for providing me the opportunity to pursue a Ph.D. and patiently advising me along the way. Similarly, my cosupervisor Dr. Rikard Emanuelsson has been an excellent mentor on how to become a researcher, with all that implies. You two have been a great team in nudging me to excel at my research.

I would also like to thank Prof. Maria Strømme, my second cosupervisor, for inspiring the whole NFM team and providing valuable feedback on all of my writings. Furthermore, I have to mention that outside of research, running together with Maria has been fun and motivating.

I was fortunate to be able to collaborate with excellent researchers, which has been a great learning experience: The team at Lund University, Sweden, Dr. Christoffer Karlsson and Prof. Patric Jannasch and the team at Waseda University, Japan, Prof. Kenichi Oyaizu, Prof. Hiroyuki Nishide and Kouki Oka. I want to especially thank Oka for valuable discussions about science and your synthetic help to realize some of my scientific ideas. It was truly enjoyable working with you.

Research is to some extent a team effort, and this thesis would not have been possible without the effort of other members of the battery team at NFM.

Lisa, it has been entertaining working with you and sharing the office with you was one of my best decisions during my time here. You always have good advice, both scientific and about life in general.

Huan, your hard work is very inspiring, and you contribute very interesting results to the group. I wish you all the luck whether you decide to stay in Sweden or move back to China.

Mia, thanks for valuable discussions, especially nonscientific discussions. It was also enjoyable traveling to conferences with you, and my only disappointment is that we could not do the Freedom Trail together.

Rebecka and Felicia, I am very much looking forward to your future contribution to the battery group. I would also like to thank the temporary members of the team - the project students I have been fortunate to supervise, namely, Adrian, Elin and Josep. It has been fun and instructive to teach you electrochemistry. Furthermore, your work has been a valuable contribution to my research topic.

In general, I would like to thank all my other colleagues at NFM both past and present, there have always been interesting discussions with you during lunch and with some of you I could share various sport activities: running, skiing, bowling and, the most fun of all, laser-tag.

I would like to provide some special thanks to some old colleagues, who over time have become an important part of my life outside of research.

Dr. Hao, I am very grateful for your friendship. What began with discussing my synthesis ideas and scientific questions now has moved on to the large questions of life.

Dr. Maria, both studying with you and working with you, has been fun. You always have good advice and hanging out with you (and Hao) can truly lighten up my day.

Dr. Simon, there is a lot to be said about you, from being the most efficient laboratory partner during our study years to a fun person to share an apartment with. I am so grateful for your unshakable friendship.

Furthermore, outside of the research community, I am very grateful for the support of all my friends in various settings. You have truly provided me the energy to balance all the effort I invested this research. At this point, I want to extend a special thanks to Cassandra. The time you have been in my life has been filled with joy, fun and very interesting discussions about life and reality.

Importantly, I also extend my deepest gratitude to my family, including not only my parents Dorothea and Carsten and my sisters Elisabeth and Friedericke but also the whole Demke and Strietzel family. You have followed me most of my life and are all large contributors to where I stand today. For that I am very thankful.

10 References

1. Gunderson J. Romanticism: Creative Education; 2008.
2. Pirsig RM. Zen and the art of motorcycle maintenance : an inquiry into values1974.
3. UN. 17 Goals to Transform Our World 2020 [Available from: https://www.un.org/sustainabledevelopment/.
4. Majeau-Bettez G, Hawkins TR, Strømman AH. Life Cycle Environmental Assessment of Lithium-Ion and Nickel Metal Hydride Batteries for Plug-In Hybrid and Battery Electric Vehicles. Environmental Science & Technology. 2011;45(10):4548-54.
5. Poizot P, Dolhem F. Clean energy new deal for a sustainable world: from non-CO2 generating energy sources to greener electrochemical storage devices. Energy & Environmental Science. 2011;4(6):2003-19.
6. Ispas A, Bund A. Electrochemical Quartz Crystal Microbalance. In: Kreysa G, Ota K-i, Savinell RF, editors. Encyclopedia of Applied Electrochemistry. New York, NY: Springer New York; 2014. p. 554-68.
7. Sauerbrey G. Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung. Zeitschrift für Physik. 1959;155(2):206-22.
8. Armand M, Grugeon S, Vezin H, Laruelle S, Ribière P, Poizot P, et al. Conjugated dicarboxylate anodes for Li-ion batteries. Nature Materials. 2009;8(2):120-5.
9. Muench S, Wild A, Friebe C, Häupler B, Janoschka T, Schubert US. Polymer-Based Organic Batteries. Chemical Reviews. 2016;116(16):9438-84.
10. Kentaro N, Kenichi O, Hiroyuki N. Organic Radical Battery Approaching Practical Use. Chemistry Letters. 2011;40(3):222-7.
11. Nishide H, Iwasa S, Pu Y-J, Suga T, Nakahara K, Satoh M. Organic radical battery: nitroxide polymers as a cathode-active material. Electrochimica Acta. 2004;50(2):827-31.
12. Suga T, Ohshiro H, Sugita S, Oyaizu K, Nishide H. Emerging N-Type Redox-Active Radical Polymer for a Totally Organic Polymer-Based Rechargeable Battery. Advanced Materials. 2009;21(16):1627-30.
13. Liu K, Zheng J, Zhong G, Yang Y. Poly(2,5-dihydroxy-1,4-benzoquinonyl sulfide) (PDBS) as a cathode material for lithium ion batteries. Journal of Materials Chemistry. 2011;21(12):4125-31.
14. Jin L, Wang G, Li X, Li L. Poly(2,5-dimercapto-1,3,4-thiadiazole)/sulfonated graphene composite as cathode material for rechargeable lithium batteries. Journal of Applied Electrochemistry. 2011;41(4):377-82.
15. Sukegawa T, Sato K, Oyaizu K, Nishide H. Efficient charge transport of a radical polyether/SWCNT composite electrode for an organic radical battery with high charge-storage density. RSC Advances. 2015;5(20):15448-52.
16. Perticarari S, Sayed-Ahmad-Baraza Y, Ewels C, Moreau P, Guyomard D, Poizot P, et al. Dual Anion–Cation Reversible Insertion in a Bipyridinium–Diamide Triad as the Negative Electrode for Aqueous Batteries. Advanced Energy Materials. 2018;8(8):1701988.

17. Wild A, Strumpf M, Häupler B, Hager MD, Schubert US. All-Organic Battery Composed of Thianthrene- and TCAQ-Based Polymers. Advanced Energy Materials. 2017;7(5):1601415.

18. Kassam A, Burnell DJ, Dahn J. Lithiated 1, 4, 5, 8-naphthalenetetraol formaldehyde polymer, an organic cathode material. Electrochemical and Solid State Letters. 2010;14(2):A22.

19. Nokami T, Matsuo T, Inatomi Y, Hojo N, Tsukagoshi T, Yoshizawa H, et al. Polymer-Bound Pyrene-4,5,9,10-tetraone for Fast-Charge and -Discharge Lithium-Ion Batteries with High Capacity. Journal of the American Chemical Society. 2012;134(48):19694-700.

20. Xiang J, Chang C, Li M, Wu S, Yuan L, Sun J. A Novel Coordination Polymer as Positive Electrode Material for Lithium Ion Battery. Crystal Growth & Design. 2008;8(1):280-2.

21. Geng J, Bonnet J-P, Renault S, Dolhem F, Poizot P. Evaluation of polyketones with N-cyclic structure as electrode material for electrochemical energy storage: case of tetraketopiperazine unit. Energy & Environmental Science. 2010;3(12):1929-33.

22. Liang Y, Jing Y, Gheytani S, Lee K-Y, Liu P, Facchetti A, et al. Universal quinone electrodes for long cycle life aqueous rechargeable batteries. Nature Materials. 2017;16(8):841-8.

23. Guo Z, Huang J, Dong X, Xia Y, Yan L, Wang Z, et al. An organic/inorganic electrode-based hydronium-ion battery. Nature Communications. 2020;11(1):959.

24. Guo Z, Ma Y, Dong X, Huang J, Wang Y, Xia Y. An Environmentally Friendly and Flexible Aqueous Zinc Battery Using an Organic Cathode. Angewandte Chemie International Edition. 2018;57(36):11737-41.

25. Tong L, Jing Y, Gordon RG, Aziz MJ. Symmetric All-Quinone Aqueous Battery. ACS Applied Energy Materials. 2019;2(6):4016-21.

26. Choi W, Harada D, Oyaizu K, Nishide H. Aqueous Electrochemistry of Poly(vinylanthraquinone) for Anode-Active Materials in High-Density and Rechargeable Polymer/Air Batteries. Journal of the American Chemical Society. 2011;133(49):19839-43.

27. Deng W, Liang X, Wu X, Qian J, Cao Y, Ai X, et al. A low cost, all-organic Na-ion Battery Based on Polymeric Cathode and Anode. Scientific Reports. 2013;3(1):2671.

28. Liu C, Ma T, Xia K, Hou X, Nian Q, Cai Y, et al. High performance polyanthraquinone/Co–Ni(OH)2 aqueous batteries based on hydroxyl and potassium insertion/extraction reactions. Sustainable Energy & Fuels. 2020;4(1):132-7.

29. Jian Z, Liang Y, Rodríguez-Pérez IA, Yao Y, Ji X. Poly(anthraquinonyl sulfide) cathode for potassium-ion batteries. Electrochemistry Communications. 2016;71:5-8.

30. Wang H, Emanuelsson R, Banerjee A, Ahuja R, Strømme M, Sjödin M. Effect of Cycling Ion and Solvent on the Redox Chemistry of Substituted Quinones and Solvent-Induced Breakdown of the Correlation between Redox Potential and Electron-Withdrawing Power of Substituents. The Journal of Physical Chemistry C. 2020;124(25):13609-17.

31. Huynh MT, Anson CW, Cavell AC, Stahl SS, Hammes-Schiffer S. Quinone 1 e– and 2 e–/2 H+ Reduction Potentials: Identification and Analysis of Deviations from Systematic Scaling Relationships. Journal of the American Chemical Society. 2016;138(49):15903-10.

32. Darling HE. Conductivity of Sulfuric Acid Solutions. Journal of Chemical & Engineering Data. 1964;9(3):421-6.

33. Suo L, Borodin O, Gao T, Olguin M, Ho J, Fan X, et al. "Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries. Science. 2015;350(6263):938.

34. Karlsson C, Strietzel C, Huang H, Sjödin M, Jannasch P. Nonstoichiometric Triazolium Protic Ionic Liquids for All-Organic Batteries. ACS Applied Energy Materials. 2018;1(11):6451-62.

35. Aylward GFT. SI Chemical Data: Wiley & Sons Australia; 2002.

36. Greaves TL, Drummond CJ. Protic Ionic Liquids: Evolving Structure–Property Relationships and Expanding Applications. Chemical Reviews. 2015;115(20):11379-448.

37. Galiński M, Lewandowski A, Stępniak I. Ionic liquids as electrolytes. Electrochimica Acta. 2006;51(26):5567-80.

38. Xu K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. Chemical Reviews. 2004;104(10):4303-418.

39. Zhao J, Li Y, Peng X, Dong S, Ma J, Cui G, et al. High-voltage Zn/LiMn0.8Fe0.2PO4 aqueous rechargeable battery by virtue of "water-in-salt" electrolyte. Electrochemistry Communications. 2016;69:6-10.

40. Wang F, Borodin O, Ding MS, Gobet M, Vatamanu J, Fan X, et al. Hybrid Aqueous/Non-aqueous Electrolyte for Safe and High-Energy Li-Ion Batteries. Joule. 2018;2(5):927-37.

41. Suo L, Han F, Fan X, Liu H, Xu K, Wang C. "Water-in-Salt" electrolytes enable green and safe Li-ion batteries for large scale electric energy storage applications. Journal of Materials Chemistry A. 2016;4(17):6639-44.

42. Yang C, Chen J, Qing T, Fan X, Sun W, von Cresce A, et al. 4.0 V Aqueous Li-Ion Batteries. Joule. 2017;1(1):122-32.

43. Elschner A, Kirchmeyer S, Lovenich W, Merker U, Reuter K. PEDOT: principles and applications of an intrinsically conductive polymer: CRC Press; 2010.

44. Liu Y, Weng B, Razal JM, Xu Q, Zhao C, Hou Y, et al. High-Performance Flexible All-Solid-State Supercapacitor from Large Free-Standing Graphene-PEDOT/PSS Films. Scientific Reports. 2015;5(1):17045.

45. Cheng T, Zhang Y-Z, Zhang J-D, Lai W-Y, Huang W. High-performance free-standing PEDOT:PSS electrodes for flexible and transparent all-solid-state supercapacitors. Journal of Materials Chemistry A. 2016;4(27):10493-9.

46. Bai H, Shi G. Gas Sensors Based on Conducting Polymers. Sensors. 2007;7(3):267-307.

47. Jang J, Chang M, Yoon H. Chemical Sensors Based on Highly Conductive Poly(3,4-ethylenedioxythiophene) Nanorods. Advanced Materials. 2005;17(13):1616-20.

48. Tung Y-L, Chen L-S, Chi Y, Chou P-T, Cheng Y-M, Li EY, et al. Orange and Red Organic Light-Emitting Devices Employing Neutral Ru(II) Emitters: Rational Design and Prospects for Color Tuning. Advanced Functional Materials. 2006;16(12):1615-26.

49. Kim WH, Mäkinen AJ, Nikolov N, Shashidhar R, Kim H, Kafafi ZH. Molecular organic light-emitting diodes using highly conducting polymers as anodes. Applied Physics Letters. 2002;80(20):3844-6.

50. Keene ST, Melianas A, van de Burgt Y, Salleo A. Mechanisms for Enhanced State Retention and Stability in Redox-Gated Organic Neuromorphic Devices. Advanced Electronic Materials. 2019;5(2):1800686.

51. van de Burgt Y, Melianas A, Keene ST, Malliaras G, Salleo A. Organic electronics for neuromorphic computing. Nature Electronics. 2018;1(7):386-97.

52. Tan Z-K, Moghaddam RS, Lai ML, Docampo P, Higler R, Deschler F, et al. Bright light-emitting diodes based on organometal halide perovskite. Nature Nanotechnology. 2014;9(9):687-92.

53. Krebs FC, Gevorgyan SA, Alstrup J. A roll-to-roll process to flexible polymer solar cells: model studies, manufacture and operational stability studies. Journal of Materials Chemistry. 2009;19(30):5442-51.

54. Etemad S, Heeger A. Polyacetylene,(CH) x: The prototype conducting polymer. Annual Review of Physical Chemistry. 1982;33(1):443-69.

55. Karlsson C, Huang H, Strømme M, Gogoll A, Sjödin M. Ion- and Electron Transport in Pyrrole/Quinone Conducting Redox Polymers Investigated by In Situ Conductivity Methods. Electrochimica Acta. 2015;179:336-42.

56. Emanuelsson R, Karlsson C, Huang H, Kosgei C, Strømme M, Sjödin M. Quinone based conducting redox polymers for electrical energy storage. Russian Journal of Electrochemistry. 2017;53(1):8-15.

57. Emanuelsson R, Sterby M, Strømme M, Sjödin M. An All-Organic Proton Battery. Journal of the American Chemical Society. 2017;139(13):4828-34.

58. Greaves TL, Drummond CJ. Protic Ionic Liquids: Properties and Applications. Chemical Reviews. 2008;108(1):206-37.

59. Suo L, Borodin O, Sun W, Fan X, Yang C, Wang F, et al. Advanced High-Voltage Aqueous Lithium-Ion Battery Enabled by "Water-in-Bisalt" Electrolyte. Angewandte Chemie International Edition. 2016;55(25):7136-41.

60. Wang H, Emanuelsson R, Liu H, Edström K, Mamedov F, Strømme M, et al. Redox-State-Dependent Interplay between Pendant Group and Conducting Polymer Backbone in Quinone-Based Conducting Redox Polymers for Lithium Ion Batteries. ACS Applied Energy Materials. 2019;2(10):7162-70.

61. Oka K, Tsujimura O, Suga T, Nishide H, Winther-Jensen B. Light-assisted electrochemical water-splitting at very low bias voltage using metal-free polythiophene as photocathode at high pH in a full-cell setup. Energy & Environmental Science. 2018;11(5):1335-42.

62. Jamal R, Zhang L, Wang M, Zhao Q, Abdiryim T. Synthesis of poly(3,4-propylenedioxythiophene)/MnO_2 composites and their applications in the adsorptive removal of methylene blue. Progress in Natural Science: Materials International. 2016;26(1):32-40.

63. Li Y, Lu J. Metal–Air Batteries: Will They Be the Future Electrochemical Energy Storage Device of Choice? ACS Energy Letters. 2017;2(6):1370-7.

64. Pei P, Wang K, Ma Z. Technologies for extending zinc–air battery's cyclelife: A review. Applied Energy. 2014;128:315-24.

65. Oka K, Furukawa S, Murao S, Oka T, Nishide H, Oyaizu K. Poly(dihydroxybenzoquinone): its high-density and robust charge storage capability in rechargeable acidic polymer–air batteries. Chemical Communications. 2020;56(29):4055-8.

66. Maruo H, Tanaka S, Takamura M, Oyaizu K, Segawa H, Nishide H. Oxoammonium cation of 2,2,6,6-tetramethylpiperidin-1-oxyl: a very efficient dopant for hole-transporting triaryl amines in a perovskite solar cell. MRS Communications. 2018;8(1):122-6.

67. Chen W, Li G, Pei A, Li Y, Liao L, Wang H, et al. A manganese–hydrogen battery with potential for grid-scale energy storage. Nature Energy. 2018;3(5):428-35.

68. Milczarek G, Inganäs O. Renewable Cathode Materials from Biopolymer/Conjugated Polymer Interpenetrating Networks. Science. 2012;335(6075):1468.

69. Admassie S, Elfwing A, Jager EWH, Bao Q, Inganäs O. A renewable biopolymer cathode with multivalent metal ions for enhanced charge storage. Journal of Materials Chemistry A. 2014;2(6):1974-9.

70. Nilsson TY, Wagner M, Inganäs O. Lignin Modification for Biopolymer/Conjugated Polymer Hybrids as Renewable Energy Storage Materials. ChemSusChem. 2015;8(23):4081-5.

Acta Universitatis Upsaliensis

Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 2023

Editor: The Dean of the Faculty of Science and Technology