Ion-Selective Electrocatalysis on Conducting Polymer Electrodes: Improving the Performance of Redox Flow Batteries

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The selective ion transport characteristics of a conducting polymer electrode, based on poly(3,4-ethylenedioxythiophene) (PEDOT), is evaluated with respect to its electrocatalytic performance, specifically targeting redox switching of quinone couples. Employing model organic redox quinones, here, the novel phenomenon of ion-selective electrocatalysis (ISEC) is conceptualized. The effect of ISEC is studied and evaluated using two forms of PEDOT electrodes, which differ in their ion-exchange characteristics, by comparing the redox transformations of catechol and tiron. It is rationalized that the choice of the specific redox couple and the ion selectivity characteristics of the conducting polymer electrode impacts the activation losses in aqueous organic redox-flow batteries. By carefully selecting and designing the conducting polymer electrodes, high conversion efficiency on acid-resistant electrodes is obtained. As far as it is known, this is the first redox flow battery to include conducting polymer electrodes operating in both the posolyte and negolyte configurations, thus the first “all-organic” RFBs.

1. Introduction

Redox flow batteries (RFBs) are promising energy storage solutions for large scale, stationary applications, for instance, combined with photovoltaics on buildings and power plants. The electrical energy is stored in molecules soluble in liquid electrolytes. The low self-discharge and good cyclability makes this technology attractive beside the lower energy density (≈50 Wh L⁻¹). Although there are various possible redox molecules, a recent focus has been toward organic molecules because of the abundance of their atomic elements and the versatility of organic synthesis for chemical design. Two main strategies to enhance the energy density for the RFBs has been to increase the solubility of the molecular reactants and the redox potential difference between the catholyte and anolyte. The later can be up to 3 V but organic solvent is thus required. Despite their lower operating voltage, water-based catholyte and anolyte are interesting because of their non-flammability and safety, which become crucial in large-scale battery systems.

A way to increase the energy density in water-based catholyte and anolyte is to consider multielectron transfer. The electron transfer reaction takes place between the porous electrode and the reactant in solution. Ideally, multielectron transfer should occur at the same potential. For instance, some viologens can undergo two discrete electron transfers but at two different redox potentials. Metal-free quinone molecules have been identified as interesting reactants for both aqueous catholytes (e.g., 4,5-dibenzoquione-1,3-benzenedisulfonate, also called tiron) and anolytes (e.g., anthraquinone-2,7-disulfonic acid AQDS) since they can store two electrons per molecule and charge-discharge at one single potential.

Organic redox-flow batteries (ORFBs) are traditionally optimized through the development of porous electrode of effective large specific interface between the electrode and the electrolyte components and that favor low-resistive electron transfer. While metal(-oxide) electrodes are known to display electrocatalytic effects in inorganic RFBs, little work has however performed to study the chemical nature of the electrodes in ORFBs. To the best of our knowledge, nobody has demonstrated organic conducting polymers (CPs) as electrocatalytic electrode in ORFBs.

Recently, there is a renewed interest in exploring conducting polymers as true electrocatalysts, which is evident from the targeted work on oxygen reduction reaction and carbon dioxide reduction. CPs are attractive material systems since they are composed of atoms of high natural abundance and the active electrocatalytic site can easily be chemically modified to promote specific desired reaction pathways. Moreover, there is no native insulating oxide layer formed along the CP
electrode–electrolyte interface, which then offers a “clean” interface for charge transfer and electrocatalysis.[12] Finally, CPs are typically also very stable in acid media.

A natural porosity at the molecular level distinguishes conducting polymers from traditional heterogeneous electrocatalysts. Indeed, a CP typically swells while in contact with an electrolyte,[13] which makes the CP bulk accessible to neutral and ionic reactants.[14] CPs are also known as mixed electron–ion conductors (MEICs),[15] a feature that is exploited in a vast array of different electrochemical devices. In those devices, the mode of operation is based on the electrochemical control over a property or material-related measure of the CP, e.g., color, volume, and conductivity of the CP, to define device functionality (e.g., electrochromics, electroactuators, and electrochemical transistors). The compensation and polarization of electrical and ionic charges within the CP bulk implies a bidirectional ion-to-electron transduction. This feature also resembles the fundamental concept utilized in various solid-state ion-selective electrodes.[16] The CP electrode can be designed to include a polymer blend or nanocomposite made of a conjugated polymer, ensuring electronic transport, and a polyelectrolyte phase, which provide charge compensation, ionic transport, and selectivity, with respect to charge and size.

A benchmark MEIC electrode material is poly(3,4-ethylenedioxythiophene) (PEDOT) doped with an anionic system. It is the most widely used intrinsically CP in electrochemical devices and setups, in part owing to its favorable processability and high electronic conductivity value (reaching up to a few thousand S cm⁻¹).[17] The high density of positive charge carriers within the PEDOT phase, which is necessary for electronic conductivity, is made possible by charge compensation from the anions. These so-called primary dopants are distributed throughout the PEDOT electrode to ensure high conductivity of the entire bulk. The mobility of the primary dopants depends on the molecular architecture and its size and defines the rate of ion transport as the doping level changes. Maintaining electroneutrality of the PEDOT film upon increasing the charge density is ensured by the insertion of anions or by the expulsion of cations. If the primary dopant is immobile, such as the case for linear polyanions (e.g., polystyrenesulfonate (PSS)), the compensating ionic charge, as the hole concentration is changed, is then primarily provided by mobile cations from the electrolyte. The ingress of anions is here to a large extent hindered due to the Donnan’s effect,[18] which makes cation transport dominant in PEDOT:PSS during reduction–oxidation switching[19] (vertical arrow in Scheme 1A). In contrast, for PEDOT films fabricated using small and exchangeable anions (e.g., tosylate (Tos)) as the primary dopant, then result in an electrode favoring anion transport to balance charge compensation (vertical arrow in Scheme 1B).

Here, we demonstrate that CPs are promising electrode materials for ORFBs because they can be chemically designed to control/prevent the diffusion of the molecular reactants within their bulk, thus adding another dimension to control the current density. We twin the concept of electrocatalysis at CP electrodes with the phenomenon of ionic selectivity of the CP bulk to demonstrate the phenomenon of ion-selective electrocatalysis (ISEC). We explore the impact of the counterions, of the CP electrodes, on the rate of electron transfer to and from reactants of the electrolyte solution. We focus on complex electrocatalytic reactions, such as the two proton-coupled electron charge transfer of organic quinones. Those reactions are often poorly reversible at planar inorganic electrocatalytic electrodes because the reversibility requires two protons and one quinone molecule be present at the same site of the electrode; a phenomenon that is kinetically not favorable. But, we have recently demonstrated that PEDOT:PSS provides reversible reactions for quinones, thanks to the high proton mobility and concentration within the CP electrode bulk.[14]

Scheme 1. A,B) The ion-selective electrocatalysis.
2. Results and Discussion

2.1. Voltammetry

Two types of PEDOT electrode materials have been explored and investigated for the operation in ISEC and aqueous organic redox-flow battery (AORFB) setups: 1) PEDOT:PSS thus containing a nonexchangeable polyanionic primary dopant and PEDOT:Tos including a small anionic primary dopant that is mobile and exchangeable. First, these MIEC electrodes were characterized in the absence of electroactive components in the solution. To quantify the intrinsic electrode phenomena, without any contribution from the underlying current collector, the voltammograms were recorded on uncoated glass substrates. The crosslinking[20] and casting from the nonaqueous solvent[21] were utilized for the stabilization of PSS- and Tos-based films of PEDOT in aqueous media, respectively. For both PEDOT:PSS and PEDOT:Tos, capacitive currents scale linearly with the film thickness. A four times increase of polymer film thickness results in a fourfold and fivefold higher capacitive currents for PEDOT:PSS and PEDOT:Tos, respectively (Figure 1B,C). Therefore, the electrochemically active surface area (EASA) scales linearly with the film volume, thus confirming that the entire bulk of both electrodes is accessible to small counter-ions. For the same film thickness, PEDOT:Tos exhibit higher capacitance values while comparing with PEDOT:PSS. This is in agreement with that a higher PEDOT content is reached in the former electrode system: the thiophene-to-dopant (sulfonate) ratio is 3.3 in PEDOT:Tos[22] and only 0.4 in PEDOT:PSS.[23]

In the presence of catechol within the background electrolyte, well-defined peak pairs in the current–voltage characteristics manifest a reversible redox process in both the PEDOT:PSS and PEDOT:Tos electrodes (Figure 1A). The peak-to-peak separation is smallest in the PEDOT:PSS electrode (20 mV for PEDOT:PSS and 65 mV for PEDOT:Tos films; Table S1, Supporting Information), thus indicating a faster kinetics of the heterogeneous electron transfer between the reactant and PEDOT:PSS compared to PEDOT:Tos. The peak currents of catechol on both PEDOT:PSS and PEDOT:Tos are weakly dependent on the film thickness (Figure 1B,C). This implies that the penetration of the neutral redox component inside the film is rather limited. There is apparently no electrostatic urge for the neutral reactant to penetrate deep into the bulk, at least at the time scales of the experiment, here reported. The performance of both PEDOT:PSS and PEDOT:Tos with respect to catechol is thus very similar.

The cyclic voltammetry characteristics for the PEDOT:PSS and the PEDOT:Tos electrodes, when tiron is included in the electrolyte solution, is instead very different. For the case of the PEDOT:PSS electrode, the tiron-associated redox process is significantly suppressed (Figure 1A). We attribute this result to the noncongruence of selective ionic transport and reactant diffusion within the electrode bulk. Indeed, the access to the bulk of the film is primarily restricted to cations, due to the presence of PSS (immobile polyanions). The tiron anion reactant is thus excluded from the PEDOT:PSS bulk. This is also evident from the fact that the peak currents of tiron, while using a PEDOT:PSS electrode, are weakly dependent on the film thickness (Figure 1B) thus confirming that the redox process is restricted to the electrode surface. On PEDOT:Tos, the tiron-associated redox process is instead rather prominent.
Its formal potential is anodically shifted by ≈100 mV versus that of catechol due to the effect of electron density withdrawing of sulfonic acid groups. Also, importantly, the intensity of its current peak currents scale linearly versus the film thickness (Figure 1C) (2.8 times increase in thickness leads to 2.5 times increase in oxidation peak current) or its capacitance (Figure S2, Supporting Information), which implies that the entire CP electrode bulk is accessible for the tiron-associated redox process. At the same time, its redox peak currents are diffusion controlled (proportional to the square root of the scan rate; Figure S3, Supporting Information), which further signifies that this negatively charged reactant is driven into the bulk of the electrode. Tiron is thus involved in the congruent ionic transport along with the transferable dopant anions of the conducting polymer PEDOT:Tos while it is repelled from the bulk of PEDOT:PSS. This is a first indication that the electrochemical process can be classified as ion-selective electrocatalysis ISEC. Interestingly, the ISEC phenomenon with those quinones is controlled by the chemical design of the conducting polymer electrode.

2.2. Kinetic Analysis

To substantiate our claims for electrocatalysis of the quinone reactant, we need to characterize the kinetics of the faradaic processes on our CP electrodes. For this, we utilize hydrodynamic electrode voltammetry on films coated onto glassy carbon (GC) disk electrode. By modulating its rotation speed, we determine the electrocatalytic kinetic control regions of applied potentials (Tafel regions) (Figure 2). Current density in the Tafel region at the formal potentials (as estimated from cyclic voltammetry on stagnant electrodes) equals the rate of the overpotential-free oxidation and reduction reactions at equilibrium, that is, the exchange current density. Note, the rate of catechol oxidation that we observe on bare GC is within the range of reported values.[24] Importantly, the kinetics of catechol redox process on blank GC is sluggish (Figure S4, Supporting Information), thus confirming the absence of GC surface contamination with alumina used for GC recovery.[25] This motivates us to consider GC as being an “inert” current collector.

Let us first consider exchange currents per geometric area of the electrode (Table 1). For catechol (the neutral reactant), the exchange current densities on both PEDOT:PSS- and PEDOT:Tos-modified electrodes are, remarkably, about two orders of magnitude higher than those recorded on bare GC. Furthermore, on PEDOT:PSS this redox process is about 45% faster than on PEDOT:Tos, which is consistent with the results we have observed previously for hydroquinone,[14] which is attributed to a faster proton transport supported by the polyanion. However, the difference between PEDOT:PSS and PEDOT:Tos electrodes in the case of neutral catechol can be considered relatively weak. In contrast, for the anionic tiron the contrast between the performance on these electrode materials is considerable. On PEDOT:PSS, the reaction of tiron is practically as sluggish as on the bare GC, while on PEDOT:Tos its redox interconversion is the fastest value recorded in our experiment (Table 1), which is in accordance with the data recorded from cyclic voltammetry on stagnant film-coated glass electrodes, showing an almost 400-fold increase with respect to the blank GC electrode.

2.3. AORFB

Encouraged by our new understanding and favorable characteristics of the influence of ISEC on the rate of redox half-reactions, we decided to explore the ISEC concept in an AORFB setup. The model battery (Figure S6, Supporting Information) was assembled utilizing symmetric carbon electrodes modified with Tos- or PSS-doped PEDOT films as electrocatalyst layers. As tiron exhibits distinct ISEC characteristics on the PEDOT-electrodes, it is the ideal choice as the posolyte redox material in an AORFB device and to evaluate the impact of ISEC on the charge storage performance.

| Reactant | Charge | PEDOT film | Primary dopant | Charge of transported ionic species | \( J_0 \) [mA cm\(^{-2}\)] | \( J_{0,\text{capacitive}} \) |
|----------|--------|------------|----------------|-----------------------------------|------------------|----------------------------|
| Tiron    | Negative | PSS        | Positive       | 0.06                             | 0.55              |
|          |         |            | TOS            | 3.90                             | 144.71            |
| Catechol | Neutral | PSS        | Positive       | 1.30                             | 9.00              |
|          |         |            | TOS            | 0.89                             | 45.99             |
|          |         |            |                | Blank GC                         | 0.01              | 3.34                      |

Figure 2. The quantification of the exchange current densities of A) catechol-associated and B) tiron-associated redox processes on PEDOT:PSS (black and blue) and PEDOT:Tos films (red and green). The linear sweep voltammograms were acquired on film-modified GC RDE (pH 2; 20 mV s\(^{-1}\); 1200, 1600, 2000, and 2500 rpm).
As the negolyte counterpart, we choose ARS, a sulfonated anthraquinone derivative that becomes anionic in aqueous solution.[26] By testing the behavior of ARS on PEDOT, we observe that the ARS redox currents scales with the PEDOT film thickness, both for the PSS and Tos dopants (Note S2, Supporting Information). This is coherent to the results obtained for the tiron-based system. The exchange current density of the ARS-associated process (estimated in this case on stagnant electrodes from the initial rising portion of the cyclic voltammogram, where kinetic limitation can safely be assumed) on PEDOT:Tos, is more than two times higher than on the PEDOT:PSS (Table S3, Supporting Information). This result is in consistent with the dopant anion mobility. The ISEC effect is thus present for ARS redox interconversion, though its amplitude turns out to be smaller in comparison with tiron. This might be due to the following reasons: i) monoanion ARS has a lower negative charge density than the dianion tiron; ii) ARS has higher hydrophobicity than tiron, which might affect its mobility within the polymer electrode; iii) the experimental conditions are different (stagnant and planar layout, larger film thickness, and higher supporting electrolyte concentration).

The significant effect of ISEC on AORFB performance was manifested in the galvanostatic charge–discharge measurements (Figure 3). Essentially, the congruent ionic transport at the interfaces, assured by the electrode modification with PEDOT:Tos films, yields a 96% decrease of activation loss in comparison with blank graphite paper, while noncongruent ionic transport on PEDOT:PSS shows only a 25% decrease. The use of ten times smaller amount of ion-selective catalyst leads to a more than 40% increase of the charge capacity of the AORFB while comparing with the polymer interface with noncongruent ionic transport: 21.5 mA h on 13.4 mg PEDOT:Tos load versus 15.2 mA h on 141 mg PEDOT:PSS load.

The decrease of cell voltage achieved by the use of ISEC mitigated the crossover of redox components thought the Nafion membrane driven by the electro-osmotic drag.[27] This resulted in the general performance improvement. For instance, the decrease of charge capacity after 45 cycles illustrated by the discharge time reduction was 60% on PEDOT:PSS (Figure 3C), while it only reached 28% in the PEDOT:Tos-based AORFB (Figure 3D). Finally, the use of ISEC led to increase of Coulombic efficiency for PEDOT:Tos-based AORFB (Figure S7, Supporting Information) in comparison with PEDOT:PSS with noncongruent ionic transport and bare graphite.

In conclusion, we report a comparative study of redox flow battery reactions including organic neutral and charged species on two types of conducting polymers serving as electrodes that provides opposite characteristics with respect to ion selectivity. The results allow us to introduce the concept of ion selective electrocatalysis, an electrode-bulk and -roughness phenomenon offering an increase of the rate of electrode processes, by the means of selective ionic transport of the reactant/product. We believe that the ISEC phenomenon is of a general interest for the area of chemical-to-electrical energy conversion relying on mixed ion electron conduction of porous electrodes. From voltammetry and analysis of the kinetics, we conclude the fundamental mechanism and prerequisites of ISEC. We then apply this novel ISEC phenomenon to a redox flow battery system using the conducting polymer electrodes along with selected quinones, operating in both the negolyte and posolyte configurations. The control of ion transport on acid resistant electrodes yields an overall improvement of the redox flow battery performance. Since both electrode, membrane and reactants are organic-based, we can truly claim the first “all-organic” redox flow batteries.

3. Experimental Section

Reagents: All inorganic salts, 3,4-ethylenedioxythiophene (EDOT), ethanol pyridine, glycerol, dimethyl sulfoxide (DMSO), iron (III) chloride, sodium persulfate, and (3-glycidyloxypropyl) trimethoxysilane (GOPS) were purchased from Sigma (Sweden) and used as received. PEDOT:PSS

![Graph showing cell voltage and capacity](image-url)
(Clevios, PH1000) and iron (III) tosylate (54 wt% in butanol, Clevios CB-54) were purchased from Heraeus Holding GmbH. Experiments were carried out with deionized water.

**Procedures:** Conducting polymer film electrodes on microscopic glass slides were fabricated with the following procedure. First, the ends of the glass slides were sequentially covered by a layer of chromium (10 nm) and gold (50 nm) to ensure a better electric contact with polymer films. Importantly, the contacts between the conducting polymer films and metal layers remained dry during all electrochemical measurements to ensure the absence of metal electrode contribution in the registered currents. Then, metal-modified glass slides were cleaned with soap and rinsed with acetone, distilled water, and isopropanol. Then, the slides were treated with UV-ozone in Ozone cleaning device (Model: PSD-UV8) for 15 min before film coating.

PEDOT:PSS film on the modified glass electrodes were prepared by drop-casting of the blend (PH1000, DMСO, 10 × 10⁻³ m glycerol, GOPS (94, 4, 1.5, and 0.5 wt%), respectively) on to the glass, and then the slides were heated up to 140 °C for 30 min for drying.

PEDOT:Tos films on GC were prepared by vapor phase polymerization.1,2,3 First, 5 mL of iron(III) p-toluenesulfonate (40% solution in n-butanol) and 0.2 mL of pyridine were mixed and stirred for 1 h. Next, the oxidant solution was spin-coated onto the metal-modified glass described above and then heated up for 30 s at 60 °C before putting in the vacuum chamber, and three drops of EDOT monomer were added onto two glass slides and placed in the hotplate by the side of sample. The polymerization was completed in a vacuum condition of 60 mmHg for 1 h followed by heating for 2 min at 60 °C.

Rotating disk electrode (RDE, GC disk 5 mm diam., Pine Research Instrumentation Inc., USA) was used for kinetics study. The RDE was modified with PEDOT:PSS films via drop-casting 5 μL of the above blend solution followed by the heating (60 °C for 30 min). PEDOT:Tos films were prepared first as described above followed by gentle transfer onto the RDE in water. Then, RDE was dried with nitrogen flow followed by heating (60 °C for 30 min).

Biologic SP200 potentiostat was used for all the electrochemical measurements. Ag/AgCl electrode in 3 m KCl and a Pt mesh were used as reference electrode and counter electrode, respectively. 85% of ohmic drop correction (determined by a high frequency impedance measurement on film working electrodes).

**AORFB:** The AORFB hardware C-flow 5 × 5 (active area of 25 cm²; Figure S5, Supporting Information) was purchased from C-Tech Innovation Ltd. (UK). The carbon paper (Toray O60, FuelCellStore (TX, USA)) was used as blank or PEDOT-modified electrodes. The graphite felt (AvCarb G200, FuelCellStore (TX, USA)) used as diffusion layer of the cell was hydrophilized by immersing in concentrated H₂SO₄ for about 5 s followed by washing with an excess of water. Nafion membranes (Nafion 115, Sigma-Aldrich) were pretreated by the following procedure: 1 h in 80 °C in 3% H₂O₂ followed by water rinsing, 1 h in 80 °C in water, and 1 h in 80 °C in 0.5 m H₂SO₄, and in the end, followed by final water rinsing. The hydrophilized felt and activated Nafion membranes were stored separately in water and directly used in AORFB assembly.

In order to load the system with PEDOT:PSS, the polymer sheet was fabricated first by overnight drying of optimized blend (PH1000, DMСO, 10 × 10⁻³ m glycerol, GOPS as 94, 4, 1.5, and 0.5 wt%, respectively) on a Petri dish. The cut of polymer sheet (5 × 5 cm, 141 mg) was transferred onto activated Nafion membrane followed by coverage by the blank graphite paper (5 × 5 cm).

The loading by the PEDOT:Tos layer (13.4 mg) was done by direct drop casting of the polymerization mixture of oxidizer (5 mL solution of iron(III) p-toluenesulfonate (40% solution in n-butanol) and 0.2 mL of pyridine) and monomer (EDOT) as 20:1 volume ratio on the blank graphite paper followed by annealing for 10 min at 100 °C.

The posolylte (30 mL) was 0.025 m tiron solution in 1 m H₂SO₄ while the negolyte (30 mL) was 0.025 m ARS solution in nitrogen-saturated 1 m H₂SO₄. The flow rates controlled by two peristaltic pumps were 15 mL min⁻¹.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

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