Negatively-Doped Conducting Polymers for Oxygen Reduction Reaction

Mikhail Vagin,* Viktor Gueskine, Evangelia Mitraka, Suhao Wang, Amritpal Singh, Igor Zozoulenko, Magnus Berggren, Simone Fabiano, and Xavier Crispin*

The oxygen reduction reaction (ORR) limits the efficiency of oxygen-associated energy conversion in fuel cells and air-metal batteries. Today, expensive noble metal catalysts are often utilized to enhance the ORR and the resulting conversion efficiency in those devices. Hence, there is an intensive research to find efficient electrodes, exhibiting a favorable electronic structure, for ORR based on abundant materials that can be manufactured using low cost processes. In that context, metal-free carbon-based nanostructures and conducting polymers have been actively investigated. The negatively doped poly(benzimidazobenzophenanthroline) (BBL) as an efficient and stable oxygen cathode material is reported here. Compared to the benchmark p-doped conducting polymer poly(3,4-ethylendioxythiophene) (PEDOT), the BBL provides electrocatalysis that fully reduces dioxygen into water, via a (2 + 2)-electron transfer pathway with hydrogen peroxide ($\text{H}_2\text{O}_2$) as an intermediate; while PEDOT limits the ORR to $\text{H}_2\text{O}_2$. It is demonstrated that n-doped BBL is a promising air electrode material for low-cost and ecofriendly model fuel cells, without the need of any co-catalysts, and its performance is found to be superior to p-doped PEDOT air electrodes.

1. Introduction

It is common wisdom that oxygen reduction reaction (ORR) is notoriously sluggish, which prompts extensive research for increasingly efficient electrocatalysts for this technologically important reaction in, e.g., fuel cells and metal–air batteries. It is, nevertheless, appropriate to briefly review the fundamental reasons for this sluggishness, which are of both thermodynamic and kinetic nature and can be traced back to peculiar properties of molecular oxygen.

The thermodynamic standard potential of $+1.23$ V (vs reversible hydrogen electrode (RHE)) for the 4-electron ORR pathway leading to water serves the reference for reporting overpotentials of its practical realizations, usually of a few hundred mV. The reverse, oxygen evolution reaction (OER) by water oxidation has, of course, the same standard potential, but completely different overpotentials at the same electrodes. This indicates that the mechanisms of ORR and OER are different: in practice, they follow a successive multielectronic pathway in opposite directions because the simultaneous transfer of four electrons is quite unlikely. The first electron transfer in ORR (Note S1; Equations (1) and (5), Supporting Information) is the most thermodynamically difficult of all the four and its standard potential is way more cathodic than that of the 4-electron pathway. This difficulty reflects a peculiar electronic structure of molecular oxygen, which, in spite of the high electronegativity of the oxygen atom, is a rather very weak oxidant. In this triplet diradical molecule, unpaired electrons occupy degenerate antibonding molecular orbitals, and further populating these is rather unfavorable.

The ORR overpotential has, in this sense, primarily a thermodynamic, and not kinetic, origin. By employing an electrocatalyst, that is an electrode material chemisorbing dioxygen, electron transfer to this adsorbate can be facilitated.

At electrodes chemically inactive toward molecular oxygen (e.g., gold and basal plane of highly oriented pyrolytic graphite), when their surface is in addition blocked by chemisorbed anions, the electron transfer to oxygen takes place without prior chemisorption, thus following an outer sphere mechanism. Among the various proofs of this mechanism one finds the detection of superoxide radical $\text{O}_2^\cdot-$, the product of the difficult and rate determining first electron transfer. Chemical inertness of defect-free organic structures, such as basal plane graphite, toward molecular oxygen diradical is primarily due to spin conservation restrictions, recently discussed by us in the ORR context. ORR in this case often does not go beyond two electrons, that is, it stops at $\text{H}_2\text{O}_2$.

Organic metal-free oxygen-reducing molecular systems exist in vivo, namely, flavin cofactors. As direct sorption of molecular oxygen on the singlet organic cofactor prior to electron
transfer is spin-forbidden, the first step of ORR is the single outer-sphere electron transfer from the reduced deprotonated form of flavin, a closed-shell anion, to molecular oxygen with the formation of two radicals. Next, superoxide anion can be attached, or not, to the flavin radical, depending on the protein environment.[9]

The ORR pathway and its products largely depend on the electrode material. In the outer-sphere mechanism, O–O bond cleavage is not catalyzed, and this bond survives in the product, H₂O₂, which limits the two-electron reduction. In the inner sphere case, dioxygen chemisorption can be either associative, also conserving O–O bond in the adsorbate, or dissociative, by virtue of O–O bond breaking from the onset smoothly leading exclusively to the four-electron reduction product, H₂O. Not only the electrode material properties but also electrochemical conditions, such as pH and electrolyte composition influence the reaction path. However, this refers to the initial ORR, while the overall reaction yield is complicated by further reduction of H₂O₂ (2+2 electron mechanism) and its chemical exergonic disproportionation.

Conducting polymers are attracting considerable attention in the context of wide search for chemically and economically efficient ORR electrode materials. In this perspective, it is important to distinguish between more extensive research aimed at using conducting polymers just as an electronic and ionic conductive matrix for an already well established ORR catalysts[10] and that with the ambition to use a conducting polymer itself as transition metal-free, low-cost, and stable ORR electrocatalyst. We will exclusively concentrate on the latter.

Until now, the p-doped conjugated polymer poly(3,4-ethylenedioxythiophene) (PEDOT, inset to Figure 1A) has been considered as the benchmark for ORR organic electrocatalysts.[11] The efficient ORR on PEDOT electrodes, even without any metal layer underneath, has been confirmed experimentally.[12,13] Experimental evidence suggests that the reduction reaction follows a 2-electron transfer pathway that produces H₂O₂.[13,14] PEDOT is a p-type polymer with a high electrical conductivity that can reach 5000 S cm⁻¹ in its doped, oxidized state. However, ORR takes place at cathodic potentials, where PEDOT is at least partially reduced, and its conductivity demonstrably drops.

Increasing the conductivity of an electrocatalyst is recognized as an important objective allowing to attain larger catalytic currents otherwise limited by charge transport within the electrode coating.[26] Therefore, an n-type polymer stable within the potential window of the aqueous electrolytes and conductive in its reduced form available for the reaction with oxidant emerges as a logical choice for ORR. Recent advances allow to achieve high electrical conductivity, reaching a few S cm⁻¹, also for negatively doped conducting polymers, in particular poly(benzimidazobenzophenanthroline) (BBL, inset to Figure 1A). Synthesized already in the late 1960s,[27] BBL is a ladder-type redox polymer featuring a rigid linear π-conjugated backbone unit with integrated redox sites, together ensuring a high n-doping level that is typical for π-conjugated redox polymers[28] and high operational stability in water.[19] Also, BBL has a high thermal stability (up to 600 °C in air),[29] high tensile strength (115 MPa)[23] and is possible to process in water.[22] The BBL can be converted to a highly conducting state via reductive process (n-type doping).[23,24,25] The electronic structure of BBL has also recently been theoretically investigated.[26] The high conducting state for a n-doped conducting polymers makes BBL attractive to new applications such as thermoelectric polymers,[26] and adding its stability in aqueous electrolyte made it promising as an electrode in asymmetric supercapacitor,[27] channel in an electrochemical transistor.[19] Recently, the blend of BBL with a p-type polymer leads to the first polymer charge transfer salt.[26] However, to the best of our knowledge, n-doped conducting polymers have not been investigated in ORR or in any associated applications.

Figure 1. The effect of polymer conductivity on the efficiency of ORR electrocatalysis. Voltammetric curves (5 mV s⁻¹) acquired on BBL-, PEDOT-, and P3HT-modified electrodes in 0.1 m KCl are presented as brown, blue, and green curves. In situ resistometry A) background-subtracted linear sweep voltammograms obtained on film-modified interdigitated arrays, 5 mV s⁻¹, 50 mV bias; Inset: the electronic energy levels and the molecular structures of polymers and cyclic voltammetry B) film-modified GCE, 5 mV s⁻¹ in argon- and oxygen-saturated electrolyte (solid and dashed curves, respectively); C) linear sweep voltammograms in oxygen-saturated electrolyte (2500 rpm, 5 mV s⁻¹, 10 mC PEDOT film).
In this work, we focused on investigating ORR at n-doped BBL experimentally and theoretically. We pinpoint the importance of the electronic structure of the conducting polymer for the design of a polymer electrode promoting ORR by comparing n-doped BBL with p-doped conducting polymers of different ionization potentials (poly(3-hexyl thiophene) P3HT and PEDOT, inset in Figure 1A). We formulate a hypothesis regarding the mechanism for the ORR at the BBL electrode for different pH and its difference with the benchmark p-doped PEDOT electrode. Finally, we developed for the first time, model conducting polymer-based cathode-limited H₂/air fuel cells.

Note that in some synthesis pathways of conducting polymers (e.g., PEDOT), residual transition metal ions can significantly affect the ORR electrocatalysis efficiency. Here, we have chosen a synthetic pathway that is not involving any such metal ions: our process is based on a polycondensation of the BBL monomer and an electrochemical polymerization pathway of PEDOT in a metal-free environment. Hence, we believe that the results, here presented, exclusively are due to the conducting organic materials themselves.

2. Results

2.1. Insulating-to-Conducting Transition in Polymer Electrodes

In order to relate the ORR activity to the conductivity regions of the polymers, we performed in situ resistometry on microelectrochemical electrode setups (Figure 1A), the configuration similar to an electrochemical transistor, in combination with cyclic voltammetry on electrodes modified by three polymers BBL, P3HT, and PEDOT (Figure 1B). At 0.7 V, we observe that the resistance of the P3HT film drops abruptly (green curve). This is attributed to a simultaneous injection of holes, from the source metal terminal, into the valence band, i.e., oxidative doping, and the penetration of anions from the electrolyte into the P3HT layer. The resulting P3HT film is positively doped and has become electrically conducting. The other thiophene derivative investigated is PEDOT (blue curve), which is a low ionization potential polymer compared to P3HT due to its ethoxy electron-withdrawing groups. For this reason, PEDOT increases drastically since its oxidation level becomes low enough so that PEDOT reduces to its neutral state, characterized by the high resistance of the film (≈100 kΩ, Figure 1A). Comparing now Figure 1A,B for BBL, we observe that at the first reduction peak (≈0.25 V) there is a three-orders of magnitude decrease of the channel resistance, while measured in the microelectrochemical device. At negative electrode potentials, the electron energy increases, which gives that electrons are added (n-doping) into the lowest unoccupied molecular orbital of BBL. This causes the polymer to switch from its pristine neutral and low conducting state to the n-doped and highly conducting state. At even more negative potentials subsequent faradaic processes occur (Figure 1B). This is observed at −0.9 V with a corresponding transition from metallic to a second insulating state of the material, which is due to over-reduction accommodated of two electrons per repeat unit.

The “p-type” polymer of low ionization potential, which is positively doped at positive potentials, becomes insulating at elevated negative potentials. Conversely, the “n-type” polymer with high electron affinity is insulating at positive potentials and becomes highly conducting at negative potentials. Having different potential windows and energetics for charge transport (i.e., n-type redox, p-type, and metallic p-type for BBL, P3HT, and PEDOT, respectively), all the three conducting polymers revealed the same order of magnitude in conductivity in their highly conducting state, as illustrated by the values of the channel resistance measured on films of similar thickness and width. The doping level of BBL is neutral aqueous electrolytes reaches 1.3 electron per monomer unit, which is higher than for PEDOT (≈0.3 electron per monomer unit).

The interaction between BBL and oxygen is reflected in a more than 4 times increase of the channel resistance compared to argon exposure (dashed line vs full line in Figure 1A, 0.12 V), resulting from the partial dedoping (oxidation) of BBL due to ORR. Interestingly, the onset of the channel resistance increase is clearly visible at higher positive potentials (0.3 V, Figure 2B) than the onset of steady-state currents (0 V, Figure S2, Supporting Information). This indicates that dedoping of n-type polymer precedes the appearance of the visible ORR currents. In the same vein, ORR induces doping at p-type PEDOT. This might illustrate, first, a nonsteady-state character of the in situ resistometry measurements. Second, ohmic current changes through the conducting polymer might have a higher sensitivity to the Faradaic phenomena in comparison with steady-state voltammetry.

2.2. ORR at Polymer Electrodes

We report the use of the three different polymers, namely, n-type BBL and p-type P3HT and PEDOT for ORR electrode applications (Figure 1C). The efficiency of ORR was studied with a rotating disk electrode in an oxygen saturated neutral aqueous electrolyte. As the reference system, we choose the GCE, which displays a rise of current at a potential of −0.33 V, that evolves up to −1.7 mA cm⁻² (at −0.7 V) in neutral media. A P3HT film coated on the GCE led to a suppression of the currents from ORR since P3HT is not conducting in that potential range. Conversely, a clear enhancement of current...
Pronounced ORR electrocatalysis been reported for the ladder redox polymers poly(o-phenylenediamine)[46] and poly(2,3-diaminonaphthalene),[47] and characterized by at least 5 times smaller current densities than those observed on BBL. Both materials are poor redox conductors in neutral aqueous electrolytes,[48] stipulating their low-level ORR activities in comparison with BBL. These facts allow us to formulate the following phenomenological hypothesis of the design of organic electrocatalysts for ORR: the combination of i) redox moiety with high electronic conductivity along with ii) a rigid ladder polymer structure, composed of four interconnected bonds, and iii) the presence of both N- and O-heteroatoms.

2.3. Mechanistic Evaluation of ORR on BBL and PEDOT

The mechanistic evaluation of the possible electrocatalytic performance of BBL and PEDOT, toward ORR, was carried out using voltammetry on a rotating disk electrode. In contrast to PEDOT-modified electrode, the increase of the rotation speed of BBL-modified electrode in a H₂O₂-containing deoxygenated electrolyte led to the increase of the recorded currents (Figure 2) illustrating the control by reactant diffusion. This manifests the existence of the of hydrogen peroxide reduction reaction (HPRR) on BBL (Figure 4A). Considering H₂O₂-terminated ORR on PEDOT (Figure 4B)[31,44] HPRR on BBL enables the further conversion of H₂O₂ to water in a course of a complete 2+2-electron ORR.[45]

Modulating the rotation speed of the disk electrode allows us to define the kinetic currents of ORR and HPRR (Figure 3A) manifested by the emergence and the independence of the rotation. These currents correspond to the charge transfer and are unaffected by reactant/product mass transport. Describing the rate-determining step, the Tafel slope of 90 mV dec⁻¹ obtained for HPRR on BBL is smaller than reported values for metals.[46,47] This illustrates the inherently different surface state of organic catalyst in comparison with metals. The first order of HPRR on BBL, as concluded from the potential independence of the slope in J⁻¹ vs ω¹/² plots (Figure S3, Supporting Information),[47] excludes disproportionation of H₂O₂ to water and oxygen, which is typical for metal-based catalysts.[46,48]

The potential region of kinetic currents of ORR on BBL in alkaline media overlaid with the standard electrode potential of O₂/H₂O₂ couple (0.695 V (vs RHE),[49] Figure 4A) illustrating the achievement of the equilibrium between oxygen and H₂O₂. This manifests the absence of the thermodynamic loss (overpotential) for the first 2-electron part (Figure 4A) of the complete 2+2-electron ORR on BBL.

Being a proton-coupled multielectron transfer reaction, the ORR-on-BBL showed both a rise of the overpotential and an increase of the Tafel slope with the acidity increase of the electrolyte solution (Figure 3A), manifesting the change of the rate-determining step of the whole process. Illustrating the kinetic loss, the Tafel slope of 58 mV dec⁻¹ observed in acidic electrolyte is close to the values reported for numerous ORR catalysts (60 mV dec⁻¹)[50] and illustrative to EC*E (i.e., the chemical step as rate determining step preceded and followed by the two single electron transfers).[51] In contrast, the Tafel slope of 30 mV dec⁻¹ observed in alkaline media is atypical and might increase up to ~3 mA cm⁻² for PEDOT and ~5.4 mA cm⁻² for BBL (at ~0.7 V) as well as a positive shift of the onset potential compared to the naked GCE: to ~0.2 V for PEDOT and 0 V for BBL. The low ionization potential of PEDOT and high electron affinity of BBL enable those polymer films to remain p-doped PEDOT and n-doped BBL, i.e., electrically conducting, in the electrochemical potential region necessary for the ORR. From steady-state measurements (Figure S2A, Supporting Information), we find that a purely Faradaic electrode phenomenon provides up to a 14-fold increase (at ~0.2 V) of the ORR currents acquired on BBL electrodes of smaller film thicknesses as compared to those acquired for PEDOT. The decrease of the overpotential in combination with a relatively higher ORR current observed on the BBL electrodes, suggest a clear electrocatalytic phenomenon for ORR from this material. The n-type BBL clearly outperforms the two p-type polymers.

The half-wave potential calculated from the steady-state voltammetry data and estimated maximum kinetic current of ORR on BBL (Figure S2A, Supporting Information) were 0.3 V (vs RHE) and 2 mA cm⁻², respectively, which is humble in comparison with the characteristics of state of the art platinum group metal-free ORR electrocatalysts.[40]
be assigned to EEC* (i.e., the two consecutive single electron transfers followed by the chemical step as rate-determining). Accordingly, the mechanism of ORR on BBL in alkaline media might be identified as series peroxo-pathway, which proceed via H$_2$O$_2$ as an intermediate (Figure 4A). ORR on PEDOT in neutral electrolytes reveals a Tafel slope that is close to that observed on BBL (Figure S4, Supporting Information), which suggests the similarity of rate-determining step. However, PEDOT shows a larger overpotential comparing to BBL, leading to an efficiency loss in chemical-to-electrical energy conversion.
Furthermore, the absence of HPRR on PEDOT (Figure 2B) results in 2-electron ORR pathway\cite{1,4} with $\text{H}_2\text{O}_2$ as a terminal product. In contrast to PEDOT,\cite{53} the aromatic ladder character of BBL defines the dense film behavior inhibiting the ionic transport to the bulk of the polymer.\cite{25} This could influence the reactivity of ORR intermediates yielding the pathway elongation.

The change in pH of the electrolyte media in contact with the BBL electrode alters the adsorptive properties of $\text{H}_2\text{O}_2$. We utilized voltammetry on BBL-modified rotating disk electrode surrounded with an independent ring electrode to quantify $\text{H}_2\text{O}_2$ (Note S3, Supporting Information). The potential of the ring electrode is set to detect $\text{H}_2\text{O}_2$ formed at the disc electrode. The adsorption/desorption equilibrium of $\text{H}_2\text{O}_2$ on BBL is decisive for the ratio of the products coming from both 2-electron and 2+2-electron pathways. In the alkaline medium (pH 12.5), the largest peroxide yield detected on the ring electrode (Figure 3C) indicates that the desorption of the $\text{H}_2\text{O}_2$ is enhanced, apparently due to the repulsion between the negatively-doped BBL and deprotonated hydrogen peroxide-anion $\text{HO}_2^-$ (pKa 11.7). This is the illustration of the 2-electron pathway prevalence due to the HPRR reactant desorption from BBL surface. In a more acidic solution (pH 3.8), the adsorption of neutral $\text{H}_2\text{O}_2$ is stronger at the BBL-coated disc, as evidenced by lower peroxide yield (Figure 3C), which favors HPRR in a course of the complete (2+2)-electron ORR (Figure 4A). Coherently, the number of electrons transferred per oxygen molecule (Note S3, Supporting Information) increases up to almost 4 (Figure 3D). Further decrease of pH down to 1.8 decreases the peroxide yield, while peculiarly the number of electrons decreases to 2. This might illustrate the alteration of the BBL state at highly acidic pH, presumably via protonation of nitrogen atoms, resulting in lower ORR activity, as evidenced by both the largest overpotential and a decline of peroxide yield (Figure 3C).

The highest ORR activity of BBL in the alkaline media is depicted by the combination of the largest values of the heterogeneous rate constant (Note S3, Figure S5, Supporting Information), the achievement of a zero overpotential for $\text{O}_2$/H$_2\text{O}_2$ part and the smallest kinetic loss.

2.4. Computational study

To shed light on the interaction between BBL and molecular oxygen, we performed density-functional theory calculations to assess the possibility of chemical bond formation between various possible sites of a representative BBL oligomer and molecular oxygen. The radical anion $^2\text{BBL}^-\text{O}_2$ revealed unfavorable energetics for the chemisorption of molecular oxygen, which may appear as a surprise for a reaction involving radicals. However, this is in consistency with previous reports stating an absence of adsorbed species on BBL for a wide range of pH values,\cite{54} as well as the fact that n-doped BBL exhibits high degree of ambient stability. On the other hand, the electron transfer from $^2\text{BBL}^-$ to oxygen leading to either $^2\text{O}_2$ or $^2\text{HO}_2$, depending on the availability of protons, is found to be thermodynamically favorable. Therefore, n-doped BBL can be considered as an outer-sphere electron donor for molecular oxygen in water following both neutral and acidic pathways (Note S1; Equations (1) and (5), respectively, Supporting Information). Note that in the region of negative applied potentials, where the outer-sphere single electron transfer to molecular oxygen takes place, the remaining electron transfer is thermodynamically more facile.

The absence of the first chemical step in the ORR on BBL is in accord with the EEC$^*$ mechanism, without chemisorption preceding the transfer of electron, as revealed by electrochemical analysis. This implies an outer-sphere mechanism which is contrary to the ORR mechanism found on platinum group metal electrocatalysts, where the chemisorption of molecular oxygen precedes any electrochemical reduction steps. The absence of oxygen attachment to BBL preceding the first electron transfer implies the absence of catalysis for the first step in a strict chemical sense. The stability of n-doped BBL in the oxygenated aqueous media finds its explanation: no oxygen adduct is formed because the oxygen adduct could lead to irreversible degradation of the polymer backbone. Hence the behavior of BBL is similar to that of flavin-based ORR biosystems (see the Introduction).

2.5. Fuel Cells

Among the various pH conditions, the largest value of the heterogeneous rate constant in half-cell measurements (Figure S5, Supporting Information) in combination with the smallest overpotential (and the smallest Tafel slope) result in the highest ORR activity when BBL is in the alkaline media. This suggests that the use of BBL in a fuel cell could be best in alkaline medium and would thus require an anion-exchange membrane. To further elaborate on this we explored polymer-based air-breathing electrodes applied into model proton- or anion-exchange membrane fuel cells (PEMFC or AEMFC, respectively) using standard graphite gas diffusion electrodes. We utilized a hydrogen anode of high platinum load to achieve an ORR-limited fuel cell. We functionalize the graphite gas diffusion electrode by coating its surface with a certain load of conducting polymers, either BBL or PEDOT. Both devices showed a significant activation loss ($\approx$0.7–0.3 V, Figure 4C). This might be due to the need to achieve a certain state of polymer having ORR activity. Importantly, BBL-based model fuel cells (loaded with 0.5 mg of BBL) reveals both a lower degree of activation loss and a larger slope of ohmic overpotential, when comparing with PEDOT-based PEMFC (loaded with 12 mg of PEDOT). In coherence with kinetic analysis, BBL-based AEMFC shows the largest maximum power density (0.034 mW cm$^{-2}$; Figure 4D), while the use of proton-exchange membrane led to a 25% lowering of the maximum power density. The PEDOT-based PEMFC shows the lowest maximum power (0.018 mW cm$^{-2}$).

Coherently with half-cell measurements, BBL outperforms PEDOT in air-breathing cathodes of model fuel cells. Also in agreement with the half-cell results, basic anion-exchange membrane favors ORR at BBL.

3. Conclusions

To conclude, we demonstrate that an n-doped conjugated polymer of high electron affinity and high electrical
conductivity, here represented by BBL, is excellent as the negative electrode in reduction processes. BBL exhibits a true electrocatalytic activity on oxygen reduction reaction (low overpotential and high currents) superior to the benchmark p-doped conducting polymer electrode PEDOT. BBL is a versatile ORR electrode material as it is active in a wide pH range. By varying pH, the reaction pathway can be altered to produce either H$_2$O$_2$ predominantly in highly basic media (due to the repulsion of ionized H$_2$O$_2$ (HO$_2^-$)), or switch to deeper reduction favoring water. The possibility to attain at BBL the complete reduction of molecular oxygen to water is worth emphasizing and not found with PEDOT, neither any other known conducting polymers. This four-electron reduction at BBL follows a sequential (2+2) electron transfer mechanism implying the formation of H$_2$O$_2$ as an intermediate, which can be reduced further to water in a separate step. Indeed, a direct-four-electron reduction bypassing H$_2$O$_2$ is indicative of a dissociative chemisorption pathway observed at active electrocatalysts based on platinum group metals. At BBL, on the contrary, the initial step of molecular oxygen reduction is outer sphere electron transfer, not preceded by chemisorption. This mechanism is coherently confirmed by our electrochemical studies and theoretical modeling. Based on the knowledge accumulated in this study, we were able to integrate BBL and PEDOT in a model fuel cells. We demonstrated the first direct hydrogen fuel cell operated in alkali medium with a polymer air electrode and shows it superior performance compared to the fuel cells working in acidic medium with a PEDOT-based air electrode.

4. Experimental Section

Electrochemical Experiments: All electrochemical experiments were performed with an Autolab type III bi-potentiostat (Metrohm Autolab, Netherlands) in a conventional three-electrode electrochemical cell using a platinum wire as the auxiliary electrode and an Ag/AgCl (3 M KCl) as the reference electrode in aqueous media. A GCE (5 mm diameter) was utilized as a working electrode. Prior to use, GCE was successively polished with 1.0 and 0.05 µm Al$_2$O$_3$ powders, and sonicated in Milli-Q water. The rotating disk ring electrode setup (5 mm OD GCE, 320 µm gap, platinum ring 6.25 mm ID, 7.92 mm OD, Pine Research Instrumentation Inc.) has been utilized for the control of rotation speed. The potentials of platinum ring electrode were 0.5, 0.8, and 1 V (vs Ag/AgCl, 3 M KCl) for alkaline (0.1 M NaOH, pH 12.5), semi-acidic (0.1 M KCl, pH 3.8), and acidic (0.05 M KCl, 0.05 M HCl, pH 3.8) electrolytes, respectively.

Electrode Modification with PEDOT: A two-terminal gold interdigitated microelectrode array on glass (15 µm gap (channel); MicruX Technologies, Spain) was utilized as two independent working electrodes controlled by bi-potentiostat in combination with a common counter and reference electrodes. The channel current was calculated as a difference between the currents recorded on first working electrode biased by 0 and 50 mV with respect to the second working electrode. The apparent film resistance was calculated as a quotient of 50 mV bias to channel current. The array modification with PEDOT has been done by in situ electrosynthesis on biased array in a monomer solution (Note S4, Supporting Information). The previously mentioned procedure was utilized for the array modification by BBL and P3HT films. The resistometry data were acquired by voltammetry (5 mV s$^{-1}$) in aqueous 0.1 M KCl using a common electrochemical setup.

Supporting Information

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

Acknowledgements

The authors would like to acknowledge the Knut and Alice Wallenberg Foundation (H$_2$O$_2$ project, Scholars) and the Swedish Research Council (VR 2019-05577, Flexible metal-air primary batteries). M.V. thanked Olga Pavlova for valuable discussions. S.F. acknowledged financial support from the Swedish Research Council (2016-02979), ÅForskn (18-312), and the Advanced Functional Materials Center at Linköping University (2009-00971). M.B. acknowledged support the Karl Erik Önnesjö Foundation.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

conducting polymers, electrocatalysis, N-type polymers, oxygen reduction reaction

Received: August 18, 2020
Revised: November 6, 2020
Published online: December 13, 2020

[1] E. Yeager, Electrochim. Acta 1984, 29, 1527.
[2] W. T. Borden, R. Hoffmann, T. Stuyver, B. Chen, J. Am. Chem. Soc. 2017, 139, 9010.
[3] S. Fallab, Angew. Chem., Int. Ed. 1967, 6, 496.
[4] H. Dau, C. Limberg, T. Reier, M. Risch, S. Roggan, P. Strasser, ChemCatChem 2010, 2, 724.
