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Novel Conducting Polymer-Heteropoly Acid Hybrid Material for Artificial Photosynthetic Membranes

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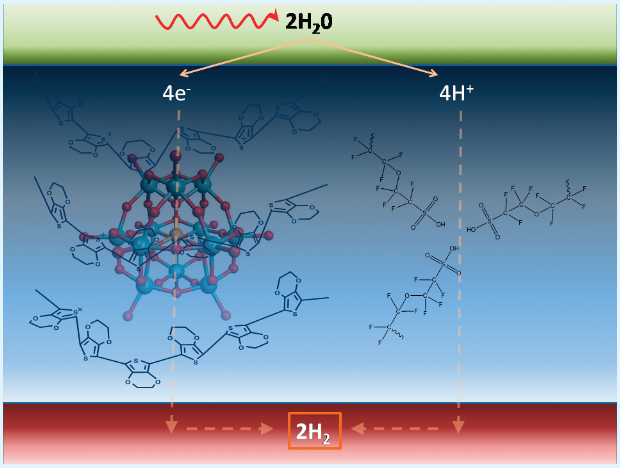
S Supporting Information



ABSTRACT: Artificial photosynthetic (AP) approaches to convert and store solar energy will require membranes capable of conducting both ions and electrons while remaining relatively transparent and chemically stable. A new approach is applied herein involving previously described in situ chemical polymerization of electronically conducting poly(3,4-ethylenedioxythiophene) (PEDOT) in the presence of proton conducting heteropoly acid (HPA) phosphomolybdic acid (PMA). The electrochemical behaviour of the PEDOT/PMA hybrid material was investigated and it was found that the conducting polymer (CP) is susceptible to irreversible oxidative processes at potentials where water is oxidized. This will be problematic in AP devices should the process occur in very close proximity to a conducting polymer-based membrane. It was found that PEDOT grants the system good electrical performance in terms of conductivity and stability over a large pH window; however, the presence of PMA was not found to provide sufficient proton conductivity. This was addressed in an additional study by tuning the ionic (and in turn, electronic) conductivity in creating composites with the proton-permselective polymer Nafion. It was found that a material of this nature with near-equal conductivity for optimal chemical conversion efficiency will consist of roughly three parts Nafion and one part PEDOT/PMA.

KEYWORDS: energy, photosynthesis, poly(3,4-ethylenedioxythiophene), phosphomolybdic acid, membranes

■ INTRODUCTION

Energy demands on the global scale are expected to reach 40 TW by 2050 from its current 15 TW.[1] Predicted increases in atmospheric carbon dioxide based on population growth and increased standard of living over the same time period have resulted in an increased urgency for the development of technologies capable of reducing reliance on nonrenewable fossil fuels. The most practical solution for addressing this will involve harnessing a possible 600 TW of power provided by the sun. In addition to producing photovoltaic technologies on that scale, there is the added challenge of storing energy for use in the dark. This has resulted in a research effort focused on artificial photosynthetic (AP) systems that can store energy in the form of chemical fuels.

Water splitting is one promising approach that may provide a means for a renewable AP system.[2] Figure 1 portrays a water splitting system including (a) photoelectrodes, (b) catalysts, and (c) a membrane capable of managing the flow of electrons and protons.[3] To date, relatively little work has been done on creating membranes optimized for artificial photosynthetic systems. Specifically, the challenge lies in the unique requirements including minimizing iR losses associated with proton and electron transport, maximizing transparency to reduce losses associated with absorption by the membrane, minimizing permeation and subsequent loss of fuels (O_2 and H_2 in this case), and avoiding reactivity with intermediates that may result in losses in electronic conductivity.[4]

The figures of merit for a membrane are dictated by the solar photon flux and the electronic and ionic current densities that will result. Under standard solar conditions, a system similar to that shown in Figure 1 would be expected to produce 10−20 mA cm^{-2} of current through a membrane. To keep iR losses in a membrane on the order of 1%, or about 10 mV given the driving force required for splitting water, conductivities for both protons and electrons through a mechanically stable 40 μm thick membrane would need to be ca. 8 mS cm^{-1}.[4] An additional consideration for membranes containing organic conductors is their stability in the presence of reactive intermediates of the half reactions involved in fuel generation as well as under various pH conditions required for operation.

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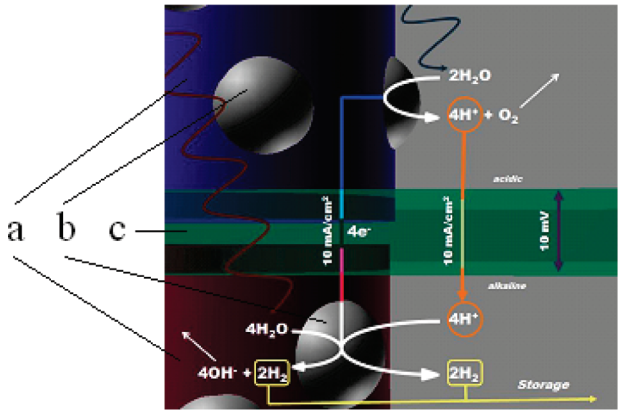

Figure 1. General diagram of (a) an AP device with micrometer-scale cylindrical electrodes (anode-top, cathode-bottom) assembled on (c) a membrane. Solar irradiance provides energy to split water on (b) surface-decorated catalysts on both sides; that occurring at the anode generates electrons and protons, which must combine to hydrogen at the cathode by passing through the barrier membrane at estimated currents of 10 mA cm^{-2} each and be met with minimal resistance (<10 mV drop).

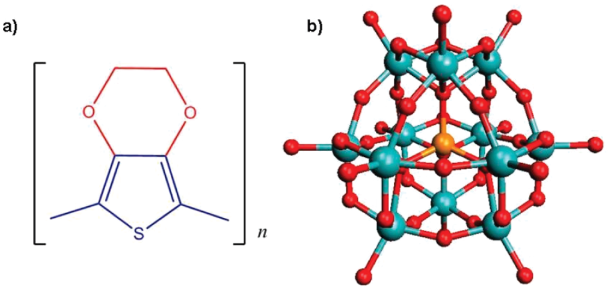

Figure 2. (a) Structure of PEDOT. The 3,4- functional group (red) stabilizes the conjugated thiophene (blue) backbone where charge conduction occurs as well as improves transparency; (b) proposed structure of PMA[11] with a central phosphorous atom (orange) caged by a network of molybdenum (blue) and electron-rich surface oxygen (red), which possess acid-base chemistry with free protons and hydrogen-bonding interactions with water.

In this work, we explore a conducting polymer-heteropoly acid hybrid material as a potential membrane. These materials are particularly attractive since the heteropoly acid can be used to induce polymerization[5−7] and can serve as the proton conductor.[8] For this application poly(3,4-ethylenedioxythiophene) (PEDOT) (Figure 2a), was chosen for its stability and optical transparency. This chemical resilience, such as stability over a wide pH range,[9] is attributed to the 3,4 functional group which may protect the conjugated thiophene backbone from chemical attack. The oxygen groups donate electron density to the conjugated backbone resulting in a shift of the absorbance to the near-IR, making it the most transparent conducting polymer currently available.[10]

Phosphomolybdic acid (PMA) (Figure 2b) was chosen as oxidant and proton conductor because of its favorable redox potential,[12] enabling it to induce polymerization and to become immobilized in the polymer matrix as a dopant. HPAs are known to exhibit high proton conductivity as a result of their large molecular surface of oxygen groups, which loosely bind solvent (water) molecules and/or protons, thus acting as a strong Brønsted acid.[11]

Here we describe an approach for creating PEDOT/PMA membranes and composites for use in AP systems. The electrochemical properties, electronic conductivity and ionic conductivity as a function of electrochemical potential and pH are investigated to determine the limits of operation and figures of merit.

■ MATERIALS AND METHODS

Materials Preparation. Thin films of PEDOT/PMA were prepared in a 3:2 molar ratio of oxidant and monomer by separately dissolving EDOT and PMA (purchased from Aldrich and used without further purification) in an acetonitrile-based metastable solution. Upon mixing, the solution appears orange-green and then becomes dark green with time as PMA oxidizes EDOT. The mixture was immediately dropped onto glass substrates, glassy carbon (GC) electrodes (0.07 cm^2, CH Instruments), fluorine-doped tin oxide (FTO)-on glass electrodes (sectioned to 1 cm^2) and gold interdigitated array (IDA) electrodes lithographically printed on glass (129−2 mm parallel digits; 5 μm spacing, BioAnalytical Systems) and spin-coated at 2000 rpm for 20 s. Spin coating allows for control of formation of thin, uniform films by evenly spreading the solution over the substrate and accelerating solvent evaporation. The visible color change from light to dark as the electrodes were spun indicated complete polymerization.[5] Films were typically on the order of a few hundred nanometers thick.

Beforehand, the GC electrodes were cleaned by polishing with progressively smaller particle size alumina suspension and rinsed with water and acetone while the glass substrate electrodes were gently rinsed with a test tube brush and soapy water then rinsed with distilled water followed by isopropyl alcohol. Immediately following polymerization, the films could be rinsed by immersion into dichloromethane (in which PMA is insoluble) followed by adding isopropanol drop-wise until blue material (incompletely reacted material, excess reduced PMA) began entering the solution. After several minutes, the polymer electrodes were exposed to pure isopropanol to be sure all excess unreacted material was removed.

The thickness of polymers was determined by constructing capacitance-volume calibration curves in a similar method previously described[13] involving sample standards directly measured by an Alpha Step Profilometer. See SI-1 in the Supporting Information.

As control materials for the voltammetric studies, PEDOT/ClO_4^-[14] and poly(pyrrole) (PPy)/ClO_4^-[15] films were deposited on GC electrode substrates electrochemically at a constant potential of 1.0 V until 120 mC of charge was passed. PEDOT was prepared in an acetonitrile-based solution of 0.02 M EDOT and 0.1 M $LiClO_4^-$ while PPy in an aqueous solution of 0.1 M pyrrole and 0.1 M $LiClO_4^-$. Samples of GC, PEDOT/PMA and PEDOT/ClO_4^- were also decorated with Pt particles by electrodeposition at −0.14 V until 10 mC of charge was passed (10 μg cm^{-2} loading level[16]) in a 0.1 M H_2SO_4 solution with 2 mM K_2PtCl_4 dissolved.

PEDOT/PMA/Nafion thin films were prepared similarly except using ethanol instead of acetonitrile as the primary solvent so as not to cause water miscibility issues with Nafion solution. Nafion was purchased as a 5 wt % dispersed resin in a mixture of lower aliphatic alcohols and water. The weight percent (wt %) of Nafion was controlled by keeping the amount of EDOT constant and gradually increasing the amount of Nafion solution. Because the parent solutions are relatively dilute, polymerization conditions were kept constant by topping up each one to the same volume with EtOH. The dimensions of these materials were resolved similarly to pure PEDOT/PMA only corrected for the amount and density contribution of Nafion because it is insulative and the dimensions from a CV would presumably reflect only the electroactive PEDOT and PMA components.

Experimental Methods and Electrochemistry. Electrical and electrochemical measurements were performed using a CH Instruments®

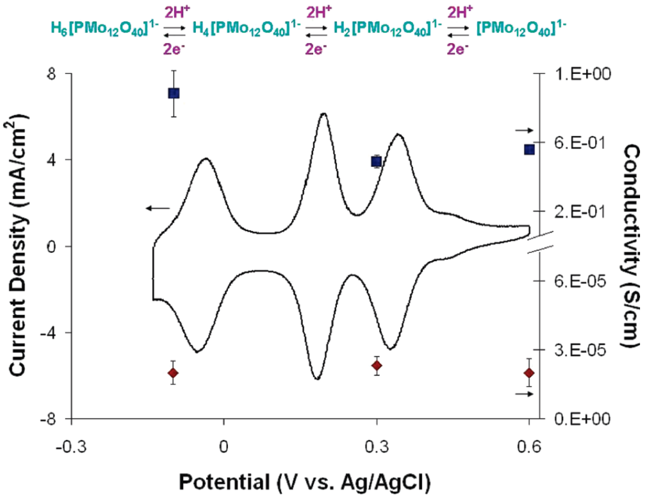

Figure 3. Electronic conductivity (σ_e, squares) and ionic conductivity (σ_i, rhombuses) of PEDOT/PMA as a function of degree of oxidation in 0.025 M H_2SO_4 (pH 1.6) with a cyclic voltammagram (CV) in the same electrochemical conditions depicting the redox states of PMA throughout the potential range studied. Above reaction shows the protonation/deprotonation electrochemically indicated by each redox peak observed in the CV.

model 760 potentiostat in a three-electrode cell set-up involving the working electrodes described above interfaced with a Pt wire (0.2 mm diameter) auxiliary electrode and Ag/AgCl reference electrode (against which all potentials are reported). Aqueous solutions were made with 18.2 MΩ cm distilled, ion-exchanged water from a Milli-Q-Academic model A10 instrument (Millipore Corp.). General CVs were performed in 0.2 M Na_2SO_4 (supporting electrolyte) tuned to pH 1 with H_2SO_4 in order to observe the redox chemistry of PMA-containing materials. Electrochemical impedance spectroscopy (EIS) measurements were made using a Solartron 1287 electrochemical interface and 1255B frequency response analyzer. Frequencies in the range of 100 kHz to 0.1 Hz (10 points/decade) with an AC perturbation amplitude of 5 mV were applied to a PEDOT/PMA-coated FTO working electrode in solutions of various pH (0.025 M H_2SO_4, Na_2SO_4, and NaOH). Similar anions were used to control ionic strength and a low concentration was used so as to not interpret conductivities exaggerated by electrolyte in the "pore phase" of the polymer.[17] Ionic conductivities were analyzed with ZPLOT and Excel software and interpreted with a transmission line model previously described[18] and applied,[19] which allows for the calculation of ionic conductivities σ_i by

$$\sigma_{\mathrm{i}} = \frac{1}{(Z_{\infty} - Z_0)A} \tag{1}$$

where *l* is the thickness of the material, *A* is the area of the electrode material, and the term $(Z_{\infty} - Z_0)$ is the ionic resistance from impedance plots.

Electronic conductivities in solution (pH dependence) were determined by applying a current equivalent to 10 mA cm^{-2} across a polymer-coated IDA electrode. The area dimension is defined as the overall thickness of polymer material deposited multiplied by the length of the bars (2 mm); multiplied by the number of spacings to give a total area through which charge may be transported. The films were exposed to the same solutions as those used for impedance experiments. Voltages were monitored and recorded as a function of time and run until the mean reached a stable current. Knowing the dimensions (*l*, the digit distance; *A*, the area of the interdigit material through which charge passes), voltage applied (*V*) and current monitored (*i*), the conductivity can be calculated by

$$\sigma_{\mathrm{e}} = \frac{i}{V}\frac{1}{A} \tag{2}$$

The potential (oxidation state) during impedance measurements was controlled directly by the potentiostat while for electronic measurements, the IDAs were constantly electrochemically polarised by a second potentiostat connected to the polymer and interfaced with a counter and reference electrode. Electronic conductivities for Nafion-containing PEDOT/PMA on glass substrates were calculated from the slope of *I*−*V* plots from four point probe measurements. Films were physically characterized using a JEOL 5900 IVAN-LV scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Polymer Synthesis and Electrochemical Characterization. The synthesis of PEDOT/PMA films resulted in a dark grey film, which upon rinsing resulted in a light blue color consistent with PEDOT in its oxidized conducting state.[10] In order to determine the thickness of spin coated polymer films on IDAs using capacitance measurements, all electrode samples were subjected to cyclic voltammetry. In acid, the redox chemistry associated with PEDOT and PMA is observed, as shown in Figure 3. At 0.6 V, both PEDOT and PMA are fully oxidized. Scanning cathodically, PMA becomes reduced while PEDOT remains in its conducting state. As a result, the negative charge added to the PMA must be balanced by the influx of protons entering the polymer from the acid solution. This is reversible, as shown in the figure, where each peak in the voltammogram corresponds to a two-proton, two-electron transfer[20] to and from the PMA.

Oxidation State Dependence of Conductivities. The precise electrochemical potential of the membrane in a functioning device is unknown and may vary. Therefore, considering the potential dependence of both the ionic and electronic conductivity is necessary. Since PEDOT remains electronically conducting throughout the potential window, the conductivity remains relatively constant and close to the reported value of ca. 0.5 S cm^{-1}. Somewhat surprisingly, the change in oxidation state of PMA and the accompanying change in protonation does not have a dramatic impact on the ionic conductivity which remains relatively constant near 20 μS cm^{-1}. This is approximately an order of magnitude lower than previously reported under similar conditions for PEDOT/PSS,[17] which also contains an immobilized dopant (polystyrenesulfonate).

The absence of potential dependence suggests that any change in the electrochemical potential of the membrane will not significantly alter its ability to pass charge generated by the photoelectrodes. However, the low ionic conductivity relative to the electronic conductivity indicates that it will be the limiting factor in the performance of this material and suggests that additional steps to increase ionic conductivity will need to be considered.

pH Dependence of Electronic Conductivity. The pH conditions present in an artificial photosynthetic system based on water splitting will likely be dictated by the semiconductors and catalysts used which will oxidize water to generate protons on the anodic side. Conversely, they can direct the one-step reduction of water on the cathode side (Figure 1) producing hydroxide ions as well. As a result, the performance of any potential membrane should be investigated over a wide range of pH values.

To investigate the pH dependence of electronic conductivity, experiments were performed on IDAs which allow for the in situ

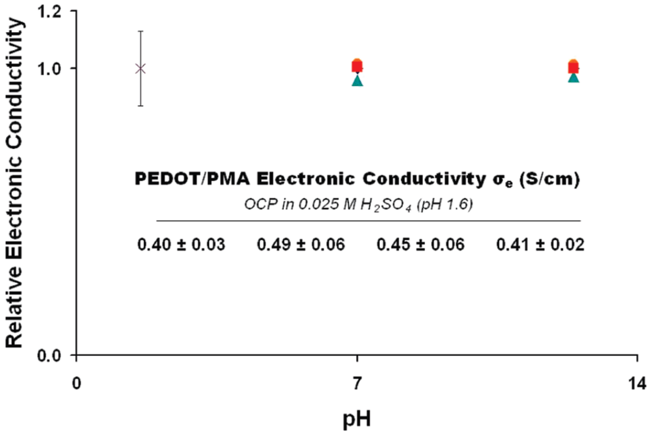

Figure 4. Electronic conductivities (σ_e) of several films in neutral and basic solution relative to their combined average conductivity in acid (x, pH 1.6). The error shown only for the acidic point represents total (sample-to-sample) variability. Inset: σ_e magnitudes of some samples in the acid solution when the film is at its open circuit potential (OCP) (approx. 0.1 V vs Ag/AgCl).

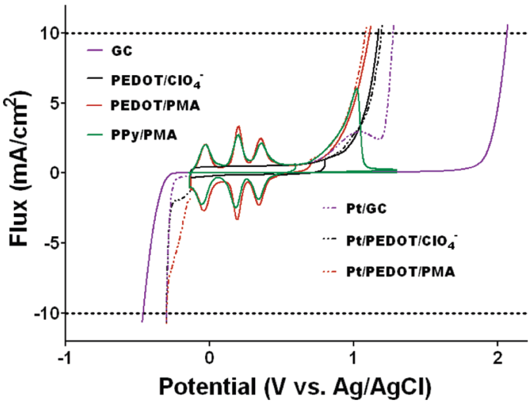

Figure 5. Voltammetric study in pH 1 aqueous solution of PEDOT/PMA vs. other materials including the bare glassy carbon (GC) electrode substrate, PEDOT without PMA incorporated, electrodes with surface-deposited platinum particles (dashed), and PPy.

measurement of conductivity under various solution conditions. In this case a current density of 10 mA cm^{-2} was applied across the film and the voltage measured while immersed in solutions of various pH.

Figure 4 demonstrates that the electronic conductivity of the film is relatively insensitive to pH as reported.[9] Additionally, it shows the system can support relatively high current densities during exposure, which is expected in solar applications.

Electrochemical O_2/H_2 Evolution Studies. To explore the compatibility of PEDOT/PMA with the half reactions associated with water splitting, voltammetry was used to assess overpotentials and reversibility under water splitting conditions. A potential window was chosen where the oxygen and hydrogen evolution reactions approached a charge flux consistent with that expected for solar photon irradiation (~10 mA cm^{-2}). Ultimately the effects of H_2 and O_2 evolution on the material is important to gage its usefulness in AP applications. By exploring films containing PEDOT, PEDOT/PMA and Pt catalyst, it is possible to separate the contributions of each component and the expected thermodynamic driving forces expected. Figure 5 shows the charge flux (current density) through the various films deposited on GC electrodes, where the reversible redox behavior of PMA is observed in the potential window of −0.1 to 0.6 V. At potentials more positive than 0.6 V the current increases to the point where oxygen evolution is observed on the electrode surface, and at potentials more negative than −0.1 V, hydrogen evolution is observed.

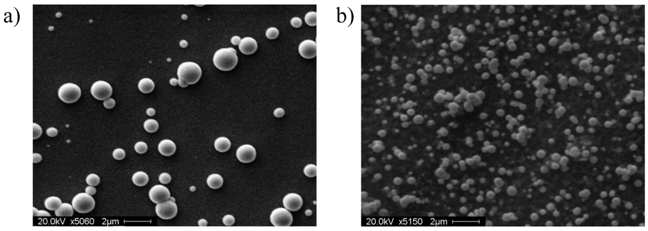

Figure 6. SEM images of platinum microparticles (Pt MPs) electrochemically deposited on GC and PEDOT/PMA electrode surfaces. They are ca. 1 μm and spherical in shape.

GC electrodes, upon which polymer materials were deposited for voltammetry experiments, were used as a control where oxygen and hydrogen evolution were observed at 2.0 and −0.4 V, respectively.

PPy was also examined to compare to the performance of PEDOT as it is known to be a less stable CP.[21] On the positive side, Figure 5 shows a PEDOT electrode reaching 10 mA cm^{-2} at much lower overpotential (1.1 V) than the GC electrode, indicating electrocatalysis which is consistent with literature reports.[22] Furthermore, there is a clear shift to lower overpotential (1.0 V) for the PMA-containing PEDOT, which is expected for HPAs as they are studied heavily in catalysis.[8] On the cathodic side, the catalytic impact of PEDOT and PMA has no obvious effect (not shown).

The PPy/PMA electrode reveals a current spike beginning at the same potential as PEDOT/PMA, only peaking before reaching 10 mA cm^{-2}. The current instantly drops to very low values and remains low in the reverse scan, where the redox chemistry of neither the polymer nor the PMA is observable. This phenomena is widely associated with over-oxidation[21] and occurs at extreme positive potentials. This is consistent with chemical deterioration to the conjugated system in conducting polymers. In the case of PPy, the reactant responsible is the hydroxyl radical which is an intermediate in water oxidation.[23] Conducting polymers in general will therefore be prone to over-oxidation under conditions where water is being electrolyzed. Indeed, in experiments where a 10 mA cm^{-2} current density is passed through a PEDOT/PMA electrode, the resistance of the circuit dramatically increases after less than 60 s indicating a chemical change to the electrode.

In an attempt to mitigate damage by chemical intermediates and enhance stability, an effort to remove the water oxidation reaction directly from the polymer surface has been made by adding some Pt catalyst[24] to the electrode interface. This is somewhat analogous to the scheme depicted in Figure 1 whereas the reactions occur on catalysts and not directly on the membrane. The dashed lines data in Figure 5 represent the same materials examined only with Pt electrodeposited on their surface as depicted in Figure 6. On the oxygen-evolving side, there appears to be no discernable difference between the overpotentials at the flux level of interest for polymers with and without Pt. Over time, there appears to be no significant improvement to the stability as well. The electrolytic nature of carbon was however

Figure 7. Thin films of PEDOT/PMA containing 0, 16, 80, 90, and 100 wt % Nafion, from left to right, spin-coated and permanently bound to FTO-on-glass electrodes.

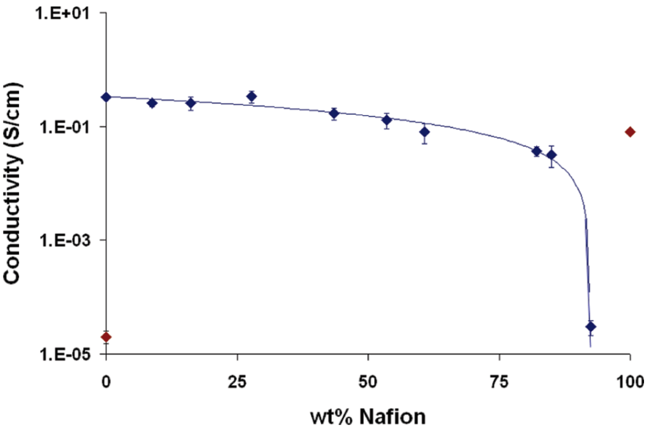

Figure 8. Linear fit of σ_e (from four point probe) as a function of wt% Nafion on a logarithmic *y* axis.

greatly enhanced with the Pt presence on the positive side. On the hydrogen-evolving side, the influence of the catalyst is dominant. The flux of all materials tested shift from other, more extreme potentials to diverge at approximately −0.3 V. This reaction occurring on Pt is obvious because its surface is active for proton reduction.

Because of the complications from chemically reactive intermediates and the extreme potentials which must be sustained during water-splitting in a practical device, it is desirable to avoid both oxidation and reduction directly on a CP-based membrane. This is already theoretically accomplished by the design of the AP device with reactions occurring on catalysts on rod structures not directly in the membrane vicinity. However, it is apparent from this electrochemical study that PEDOT/PMA is electrocatalytic and more stable than PPy at the flux needed to drive H_2O electrolysis.

PEDOT/PMA/Nafion Composite Membranes. In a previous section, we showed the stable and reasonable values for σ_e and subsequently σ_i values four orders of magnitude lower, which is insufficient for AP applications. To address this issue, we have incorporated a known ionically conductive polymer component.

Nafion is the central material for all proton exchange membranes (PEMs) with application in fuel cell technology involving the role of a barrier and highly conductive, permselective proton pathway.[25] This material is available in an alcohol/water dispersion and so can be cast with various fractions of the EDOT/PMA metastable solution to tune the electronic and ionic conductivity. Polymerized and rinsed films are shown in Figure 7.

As the weight percent (wt %) of Nafion increases in each composite, PEDOT content decreases and thus does σ_e. This can clearly be seen in Figure 8. Up to 90 wt % Nafion there is a linear decrease in σ_e within one order of magnitude. Beyond this, there is a sudden drop of three to four orders of magnitude. We are interested in this point because it means the composite follows pseudo-percolative behavior,[4] whereas the electronically conductive domains are within physical contact up to a point, the percolation threshold, and then conduct through a mechanism that involves travel through insulator domain barriers at lower weigth percent of conductor.[26] The percolation threshold is observed at approximately 10 wt % PEDOT loading (90 wt % Nafion), similar to other subsequent work.[4] The σ_e value of PEDOT/PMA by four point probe is 0.33 S cm^{-1} which is consistent with values reported previously[7] as well as from IDAs in solution (Figure 4), but two orders of magnitude lower than this value for PEDOT/PSS. This is in good agreement with literature because when doped with PSS, PEDOT is reported to have higher conductivity.[27]

The equal conductivity of AP membranes is stressed because the arrival of one proton at the cathode must be met with the arrival of one electron (see Figure 1). The limiting conductivity of one species becomes an inefficiency in the system. For reasons discussed in SI-2 in the Supporting Information, σ_i was not involved in estimating the ideal Nafion loading (Figure 8). Instead, the σ_i value of 1×10^{-5} S cm^{-1} for PEDOT from Figure 3 was used as a starting point. It is presumed this value will increase and approach the literature value of 1×10^{-2} S cm^{-1} [28] for Nafion as wt % loading of Nafion increases. Thus, to construct a membrane of equal conductivities given the data included in Figure 8, a fraction of 3:1 Nafion-to-PEDOT can be assigned. Here, both σ_i and σ_e would be ca. 0.05 S cm^{-1}.

■ CONCLUSION

For the first time, the application of electrode materials comprised of both a highly processable electron conductor PEDOT and immobilized dopant PMA were prepared in a one-step facile synthesis and were directly deposited onto various substrates. The functionality of the PEDOT/PMA hybrid material was characterized both electrically and electrochemically to justify its use as a membrane in an artificial photosynthetic device.

Membranes will require electron and proton conducting properties under various conditions of oxidation state and pH. The electronic conductivity σ_e was found to be stable with reasonable values as a function of both these variables, confirming PEDOT as a suitable electron conductor for AP applications. Ionic conductivity σ_i was found to be relatively similar for the various oxidation states; however the value is up to four orders of magnitude lower than σ_e. PMA as the CP dopant in this case is not a sufficient proton conductor.

In electrochemical conditions where water splitting occurs, it was found that both PEDOT and PMA were electrocatalytic for water oxidation while known catalyst Pt dominated on the H_2-evolving side. However, CPs in general were shown to be prone to over-oxidation and other harmful processes when exposed to potentials associated with water electrolysis. We propose that in a working AP device this may not present a problem as long as the reactions do not take place on the membrane surface.

Lastly, we have successfully demonstrated that our system is not limited by the low σ_i values as composites of other H^+ conductors such as Nafion can easily be incorporated. Given the σ_i value for Nafion of ca. 0.01 S cm^{-1}, it will need to comprise three quarters of the material by weight to have the sufficient, equal electronic and ionic conductivities necessary for AP membranes.

Future work will involve recognizing figures of merit that were not addressed in this work. Particularly, mechanical strength, absorbance and gas management.[4] The materials examined here are electrode-bound thin films but practical devices would require free-standing structures. Nafion is not only promising for its ionic permselectivity but also its robust structure and transparency. If Nafion is to be relied upon as the main component in AP membranes, it will be the electron conductor which must be modified to achieve the required figures of merit. PEDOT as a material was proven an excellent candidate; however, its microstructure may be manipulated to increase its conductivity in composites, which will reduce the amount required to achieve sufficient electron transport. Thus less absorbing material will exist in the Nafion-based composite which will increase transparency. Additionally, if there are lower iR drops associated per thickness of material, thicker membranes can be manufactured which will ultimately reduce losses due to gas diffusion and recombination.

ASSOCIATED CONTENT

Supporting Information. Methods of determining polymer thicknesses on electrodes with complicated surfaces. EIS (ionic conductivity) data with an explanation of context in this research. This material is available free of charge via the Internet at http://pubs.acs.org.

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