The activity for an electrocatalyst for the oxygen reduction reaction (ORR) is most often assessed using bare metal electrodes in direct contact with an aqueous electrolyte. This architecture allows all reactants and products to have equivalent geometric access to the catalyst surface, but this does not always lead to an optimal reaction environment. By adding an intermediate phase as a layer between the catalyst and the electrolyte, diffusive driving forces can be engineered into the system to force reactants to the catalyst and products away from it, increasing the overall system activity. For instance, previous research explored nanoporous Ni/Pt electrodes encapsulated with the ionic liquid [MTBD][beti]. The high oxygen solubility in this ionic liquid was thought to explain the nearly doubled increase in the composite electrocatalyst activity, but it is possible that other ionic liquid properties (water solubility, oxygen diffusivity, ionic conductivity, viscosity) might also be affecting ORR activity. In this work, we surveyed a number of ionic liquids in nanoporous Ni/Pt/ionic liquid composite catalysts with an eye toward clarifying to what extent the physical properties of the IL have on the activity of the composite ORR catalyst. Overall, we find the oxygen solubility and water solubility most strongly affect the decrease in ORR overpotential.
Figure 1. Schematic representation of electrolyte/IL/metal interface employed, with a diagram illustrating the oxygen concentrations in each layer, in equilibrium (solid line) and under kinetic control (small dashed line).

Figure 2. Chemical structure of IL anions and cations used in this study.

- [HNC(dma)]: this protic cation also led to ILs with low melting points. It is significantly less “bulky” than MTBD, suggesting higher proton conductivity.
- [M3BN]: this quaternary ammonium cation is one of the simplest aprotic cations.
- [bmim]: this aprotic cation contains a bulkier charge holding group, suggesting a significantly different proton conductivity compared to [M3BN].
- [beti]: This bis-perfluorethyl sulfonamide was used in Refs. 5, 6, 9, and with [MTBD] led to an IL with approximately two times higher oxygen solubility than the aqueous electrolyte.
- [bfpi]: Similar to [beti], this anion has slightly longer perfluorethyl sidechains.

In this work, we focused primarily on the [beti] anion. The reason for this is that except for the one bfpi-based IL we also report here, no other ILs have been discovered that enhance ORR activity in composite catalysts with np-NiPt. The requirements for such ILs are stringent: hydrophobic, a higher oxygen solubility than the aqueous electrolyte, conductive, and viscous enough to resist washing away from the composite, yet still liquid at room temperature. Other ILs have been examined by our group in the past, e.g., [TBP][TMDP], that clearly inhibited oxygen reduction and therefore were not examined further. We also examined ILs with the widely used, shorter side chain anion [Tf2N] (bis(trifluoromethylsulfonyl)imide), but in all cases, their relatively higher solubility in the aqueous electrolyte and lower viscosities meant these composites were not durable in np-NiPt composite catalysts, and the IL easily flowed away from the porous metal. Hypothesizing that longer chains would add more stability, and potentially higher oxygen solubility, we explored using [bfpi] as an anion. Yet, except for [HNC(dma)], the listed cations resulted in ILs that are solid at room temperature when combined with bfpi, and were hence excluded from detailed analysis.

The experimental plan was to vary the properties of the IL by varying its composition, keeping the catalyst (bulk np-NiPt) fixed. On one hand, our notion was to identify what properties of the IL are required to optimize ORR activity in the composite catalyst; on the other hand, our goal was to confirm (or not) that the primary physical property of the IL that controlled the increase in ORR activity was oxygen solubility. While we ultimately found that oxygen solubility is the primary determinant for good ORR activity, the activity was also found to have a strong inverse correlation to the solubility of water in the IL.
Synthesis.— Nanoporous NiPt (np-NiPt) was formed through electrochemical dealloying of 77 at.% NiPt precursor alloys by cycling the potential repeatedly from 0.0–1.2 V vs. RHE (reversible hydrogen electrode) in 0.1 M H₂SO₄ (J.T. Baker, 95–98%), similar to the recipe in Ref. 9. This process results in a np-NiPt catalyst disk with ligaments 3–5 nm in diameter, passivated with a layer of Pt, but with an average bulk composition containing 25 at.% Ni. For each IL composite tested, the surface of the NiPt disk was polished and dealloyed to approximate the same depth, measured using hydrogen under potential deposition (Hupd) to the same effective surface area. This effective surface area was normalized by the geometric surface area, yielding the roughness factor \( R_f \). In all examples here, the roughness factor was typically near \( R_f \sim 120 \), corresponding to a dealloyed depth of approximately 850 nm, which is deeper than the depth to which reactants during ORR would be expected to penetrate.

To synthesize aprotic ILs, aprotic cations (in their chloride salt form) \([\text{bmim}]^+\) (1-Butyl-3-methyl-imidazolium chloride, Sigma Aldrich, 95%) and \([\text{M3BN}]^+\) (Methyltributylammonium chloride, Sigma Aldrich, 95%) and \([\text{M3BN}]^-\) (Methyltributylammonium chloride, Sigma Aldrich, 75 wt% solution in water) were added in an aqueous solution to an equimolar solution of Li [beti] (Lithium bis(pentafluoroethanesulfonyl)imide, Oakwood Chemical). This was rinsed several times with deionized water and allowed to fully dry under reduced pressure at 75 °C for 24 hours, to form ILs \([\text{bmim}][\text{beti}]\) and \([\text{M3BN}][\text{beti}]\).

To synthesize protic ILs, the method outlined by Luo et al.\(^{11}\) was employed. Equimolar amounts of cation, \([\text{MTBD}]^-\) (7-Methyl-1,5,7-triazacylclo[4.4.0]dec-5-ene, Sigma Aldrich, 98%) or \([\text{HNC(dma)}]^-\) (Hundertmark, 95%) and \([\text{M3BN}]^-\) (Methyltributylammonium chloride, Sigma Aldrich, 75 wt% solution in water) were added in an aqueous solution. An equimolar solution of Li [beti] (Lithium bis(pentafluoroethanesulfonyl)imide, Oakwood Chemical) was dissolved in a deionized water and cooled in an ice bath. The cation solution was neutralized by adding concentrated nitric acid (BDH) dropwise and subsequently mixed with the anion solution. Similar protocols to the aprotic ILs were used to wash and dry the resulting IL.

Electrochemical measurements.— A variable rate flow cell apparatus was used to measure electrochemical behavior instead of the more common rotating disk electrode (RDE) configuration, because ILs of any greater than nominal thickness spin off of electrodes in the RDE, and even for thin layers, depending on the viscosity of the IL used, the thickness of this layer would vary. Therefore, to maintain a planar electrolyte/IL interface, and an IL with controlled volume, a channel flow cell was fabricated similar to that outlined by Heller-Ling et al.,\(^{12}\) using a Pine Instruments RDE sample holder for the working electrode, pressure fitted into the channel; a Pt wire as a counter electrode; and a secondary beaker housing an Hg/Hg₂SO₄ (Hach) reference electrode. The channel has a height of 1 mm, width of 30 mm, and is 100 mm in length. A variable flow rate peristaltic pump (Fisher-Scientific) allowed a range of flow rates, from 5–75 ml/min, monitored by a flowmeter (Gilmore). A schematic of the flow cell is shown in Figure 3.

Oxygen reduction activity was measured using a Gamry Interface 1000 Potentiostat and a solution of 0.25 M perchloric acid (Sigma Aldrich, 70%) using glassware cleaned by soaking in a solution of NoChromix (Godax Laboratories, Inc.) and sulfuric acid overnight. In an effort to limit non-faradaic currents commonly found with highly porous metals, ORR was measured potentiostatically. That is, data points were taken by holding the samples at fixed potentials, and then recording the steady state current. Data intervals were taken every 100 mV in the diffusion limited regime and 15 mV in the mixed kinetic-diffusion region, once the current stabilized for each point.

Physicochemical properties of ILs.— A fixed volume of IL (2.5–10 μl) was added to the porous metal sample to form the composite catalyst—any smaller volume is difficult to accurately measure and be uniformly distributed. Then, the composite was placed under reduced pressure to encourage the IL to penetrate into the pores of the metal catalyst. This step was necessary because pre-saturating the IL with water changed the surface tension, and ILs did not pull into the porous electrode. Geometrically, the volume of IL can be used to estimate the thickness of the layer, assuming the volume penetrating into the porous structure is negligible. Under this assumption, a 5 μl volume corresponds to a thickness of 255 μm. To more exactly determine the thickness of IL above the np-NiPt electrode outer geometric surface, an IL that is solid at room temperature was added to the porous metal at a temperature above its melting point, allowed to penetrate into the porous structure and then cooled. The thickness was simply measured in cross-section using an optical microscope (Olympus PMG 3). This, combined with a SEM (JEOL JSM-6700F) cross section to determine the depth of porosity, allows a more precise measurement of the IL thickness. Typical IL thicknesses were employed ranged from 40–420 μm, the majority of experiments using a 250 μm layer. We note that these are significantly thicker IL layers than those used in Refs. 5, 6, 9, which by design tends to exacerbate the effects of different IL properties on the ORR activity.

The viscosity of each IL was measured using a capillary viscometer (Semi-Micro Extra Low Charge Viscometer, Cannon Instruments). Densities were determined using a Mettler Toledo Analytical Balance with a precision of ±0.01 mg to weigh a known volume of IL. Water content was measured using Karl Fischer Titration (Mettler Toledo C20 Coulometric KF Titrator) and determined to be less than 1000 ppm for each dry sample. Conductivity was calculated through potentiostatic electrical impedance spectroscopy measurements\(^{13}\) using a Gamry Reference 3000 potentiostat and self-made conductivity cell, calibrated using NaCl solutions (Sigma Aldrich).
Oxygen solubility and diffusivity were measured using a Pt microdisc electrode, following the procedure outlined in Evans et al. Briefly, a small drop of IL (10 μl) is placed in contact with a working electrode composed of an encapsulated 10 μm Pt wire, the area of which is calibrated using ferrocene redox couple. The IL is fully saturated with oxygen and held at a potential of zero current, relative to an Ag silver wire reference electrode. The potential is then stepped to one where oxygen is fully reduced with no kinetic limitations, and the current decays as oxygen gets reduced. The resulting current versus time data is modeled by the equation

\[ I = -4nFDO_2[O_2]r_d f(\tau), \]  

where \( f(\tau) = 0.7854 + 0.88863\tau^{-1/2} + 0.2146e^{-0.7823\tau^{-1/2}} \)  

and

\[ \tau = \frac{4D_{O_2}t}{r_d^2}. \]  

where \( I \) is the measured current, \( n \) is the number of electrons involved in the reaction, \( F \) is Faraday’s constant, \( r_d \) is the radius of the disk, \( \tau \) is the time constant dependent on time \( t \). The diffusivity and solubility of oxygen, \( D_{O_2} \) and \([O_2]\) respectively, are simultaneously fit to the potential decay vs. time. A nuance to this measurement is that the fits are sensitive to the time offset, i.e., when one sets \( t = 0 \). There is a systematic error introduced due to the few milliseconds it takes to step to the desired potential. During this time period, some oxygen within the IL is being reduced while within the kinetically limited regime, so choosing a point for the onset time incorporating the entire potential ramp overestimates the oxygen solubility. Yet, waiting until the potential reaches the desired point results in some oxygen being prematurely reduced and underestimating the quantity. For our reported values, we selected a midpoint offset time that minimizes these effects.

We explored materials other than ILs as well, but there are simply few materials discovered to date that simultaneously show enough of the necessary properties – i.e., reasonably high oxygen solubility, hydrophobicity, viscosity, etc. For instance, we used perfluorodecalin, which as mentioned, has an ideally high oxygen solubility, but this material has no ionic conductivity and easily washes away. We have also perfactorily tried blending perfluoroalkanes with ILs, but they are not miscible.

**Results**

**Performance of the flow cell.**— Figure 4 displays the ORR curves obtained using the flow cell apparatus for np-NiPt at varying flow rates, from 10–50 ml/min. A monotonic increase in the diffusion-limited current density magnitude \( i_{DL} \) on volumetric flow rate \( v_f \) is observed, analogous to the diffusion-limited current density vs. rotation rate using an RDE. Similar behavior was also observed with IL-impregnated composites, albeit with lower magnitude diffusion-limited current densities. In all cases, the IL layer appeared undisturbed during flow of the electrolyte composite catalyst, and laminar flow was confirmed by the uniform distribution of a dye fed into the input electrolyte stream as it flowed over the catalyst electrode. In addition, the hydrophobic ILs used in this study always balled up when directly dropped into aqueous solution, i.e., it is very easy to see them, and we observed no evidence of IL ever leaving electrode, with one caveat. When a planar, non-porous electrode was used, the IL tended to wash away, illustrating the importance of capillary forces within the porous network being important to keep the IL in place.

Theoretical analysis of \( i_{DL} \) over a catalytic electrode in a flow cell predicts a dependence of the form

\[ i_{DL} \propto v_f^{1/3}. \]  

The inset of Figure 4 shows that this dependence holds well for bare np-NiPt in our flow cell. The composite catalyst has an IL/metal interface nearly 0.25 mm below the IL/electrolyte interface. This secondary barrier makes for a significantly more complex analysis of \( i_{DL} \) vs. \( v_f \). Nonetheless as shown in the inset for np-NiPt + [MTBD][beti] (5 μl), \( i_{DL} \) still increases with \( v_f \).

**Physiochemical properties of ILs.**— Measured properties of the ILs used in this study are listed in Table I. There is an order of magnitude difference in the viscosities of ILs tested, although this did not correlate with either ionic conductivity or oxygen diffusivity. While viscosity played a role in experimental setup, i.e. measuring out a precise volume or forming the composite, little effect on ORR activity (half-wave position) was noticed.
The ionic conductivities for the [HNC]-based ILs are noticeably higher than the other ILs, and coincides with a significantly higher magnitude for the diffusion limited current in the ORR when using this cation.

Oxygen solubility is thought to be dictated by the anion, our data proving relatively consistent with this idea. The bulk of our composite systems employ the [beti] anion, so while different cations led to modest variations in oxygen solubility, there were no large orders of magnitude difference among our values.

**Oxygen reduction reaction activity.**— After an IL-dependent break-in period, potentiostatic ORR currents versus potential for each IL-composite at a constant IL volume of 5 µl and flow rate of 15 ml/min were measured. Results are shown in Figure 5, comparing each composite with the bare np-NiPt sample as a baseline. The diffusion limited current density and half-wave potentials for each IL are summarized in Table II. All the composite catalysts here improved the half-wave relative to that of bare np-NiPt.

Furthermore, we confirmed that the shifts in half-wave are independent of the thickness of the IL layer, and that the diffusion-limited current density approaches the value for bare np-NiPt as the IL thickness decreased. However, reliably controlling the IL volume between samples and composites is considerably more difficult from a practical standpoint for the smaller volumes of IL, because measuring such small volumes of highly viscous fluids is problematic. Our “standard” condition, 5 µl of IL, represents a compromise between the achieving the desired current density magnitudes and exact repeatability between composites.

**Discussion**

**Oxygen reduction in the diffusion limited regime.**— In the diffusion limited regime (0.6–0.8 V in Figure 5), there is no obvious correlation between $i_{DL}$ and oxygen solubility. In order to explore our system in greater detail, consider the hydrodynamic equation governing the flow cell geometry

$$i_{DL} = 0.925nF[O_2]D_{O_2}^{1/3}\left(\frac{v}{H}d\right)^{1/3}w C^{2/3}$$  \[6\]

where $n$ is the number of electrons, $F$ is Faraday’s constant, $h$, $d$, $w$, and $x$ are geometric parameters of the flow cell, assuming a planar geometry, and the other parameters are defined, above.\[12\] The interface between IL and metal catalyst is below the level of the IL/flowing electrolyte interface, so this equation doesn’t exactly describe our situation. However, if the product ($i_{DL}$ $D_{O_2}^{1/3}$)electrolyte were greater than ($[O_2]D_{O_2}^{1/3})_{IL}$, we would expect that oxygen be diffusion limited in the IL, and not the aqueous electrolyte, considerably complicating any conclusions. In our case, the independent measurements of these parameters confirmed that in all cases this product is greater in the IL than in the aqueous electrolyte, so that the presence of the IL only affects ORR activity in the kinetically controlled potential regime.

**Kinetically controlled regime.**— Our explanation that the increased activity in IL + np-NiPt composites is dependent upon the increased oxygen solubility is rooted in the extensive previous work to determine the reaction pathways and rates for oxygen reduction. The kinetic ORR current are generally described by an expression of the form\[6,13\]

$$i = nFE[O_2](1 - \theta_{ad})\exp(-\beta FE/RT) \exp(-\gamma r_{ad})/RT$$  \[7\]

where $n$ is number of electrons transferred ($n = 4$ here), $K$ is a chemical rate constant, $\theta_{ad}$ is the surface coverage of adsorbed species, $v$ depends on site requirements of adsorbates (a value of 1 for $O_2$), $\beta$ and $\gamma$ are symmetry factors, $F$ is the applied potential, and $r_{ad}$ describes the rate of change of the free energy of adsorption with the surface coverage by adsorbing species. Details aside, Eq. 8 indicates that the ORR current is first order in the concentration of oxygen at the catalyst surface – doubling the concentration there via the IL intermediate phase should double the current.

All composites tested in this study improved the kinetic activity over that of neat np-NiPt, assessed by the shift in the half-wave potential. Comparing the ILs amongst themselves, [MTBD][beti] has the greatest increase in oxygen solubility, with a concentration of 3.2 mM, while [HNC(dma)][bfpi] has the lowest of the ILs tested at 0.8 mM, corresponding to the highest and lowest shifts in the half-wave respectively. Both ILs are protic, in addition to having similar viscosities and densities, so our initial hypothesis regarding oxygen solubility dependence being the only vital factor seems accurate in this respect. However, we measured the oxygen solubility of the electrolyte, 0.25 M perchloric acid, to be 1.55 mM, a solubility higher than that of the majority of ILs we tested in our composites, requiring us to nuance our working model.

One factor that straightforwardly could be impacted by the addition of an IL is the adsorption behavior on the Pt surface. Assuming reaction intermediates have minimal coverage and there is no significant contamination of halides or sulfides within the electrolyte, the adsorbed species of interest is $\text{OH}^-$. If the IL were to disrupt an ordered water or oxide layer forming at the surface of the metal interface, perhaps more open active sites would be available and thus increase activity.\[17\] To examine this, we examined the cyclic voltammetry of each composite, shown in Figure 6, specifically looking for a shift in the onset of Pt oxidation.

Examining the hydrogen adsorption/desorption region of the curves, between 0.0–0.4 V vs. RHE in Figure 6, it becomes apparent the magnitude of the currents for each composite compared to the bulk np-NiPt are reduced. However, when correlated to the double layer region (0.4–0.6 V vs. RHE), the currents scale accordingly, implying the area under the curve would remain fairly consistent between samples and is likely an effect due to the decreased proton mobility through the thick IL layer. For instance, np-NiPt + [M3BN][beti] appears the most diminished, but also has the highest viscosity. These transport issues are not as readily noticed in the ORR curves since those measurements are steady state, as opposed to the sweep that is performed for cyclic voltammetry. Upon examining the Pt

| Ion Liquid      | $\rho$ (g/ml) | $\eta$ (mPa·s) | $\sigma_{C}$ (ms/cm) | $[O_2]$ (mM) | $D_{O_2}$ ($10^{-6}$ cm$^2$/s) | $[H_2O]$ (M) |
|-----------------|---------------|----------------|----------------------|--------------|-------------------------------|--------------|
| [MTBD][beti]   | 1.54 ± 0.05   | 392.3 ± 1.4    | 1.96 ± 0.50          | 3.19 ± 0.01  | 4.84 ± 0.16                   | 1.33 ± 0.01  |
| [HNC(dma)][beti] | 1.56 ± 0.02   | 232.7 ± 1.8    | 13.1 ± 2.15          | 1.91 ± 0.16  | 8.70 ± 0.92                   | 3.53 ± 0.01  |
| [HNC(dma)][bfpi] | 1.51 ± 0.07   | 434.9 ± 1.6    | 7.35 ± 3.12          | 0.80 ± 0.03  | 40.3 ± 2.22                   | 1.56 ± 0.01  |
| [bmim][beti]   | 1.52 ± 0.03   | 112.0 ± 0.5    | 4.22 ± 1.11          | 1.50 ± 0.49  | 10.1 ± 4.38                   | 0.62 ± 0.01  |
| [M3BN][beti]   | 1.26 ± 0.05   | 1184.3 ± 9.4   | 2.77 ± 0.59          | 0.90 ± 0.37  | 6.72 ± 2.84                   | 0.31 ± 0.01  |
| 0.25M HClO$_4$ | –             | –              | –                    | –            | –                            | –            |

**Table II. Electrochemical properties of ILs taken from Figure 5.**

Sample | Half-wave (V) | $I_D$ (mA/cm$^2$) |
|--------|---------------|------------------|
| np-NiPt | 0.9605        | –0.7590          |
| np-NiPt + [MTBD][beti] | 1.0114        | –0.5228          |
| np-NiPt + [HNC(dma)][beti] | 0.9956        | –0.6460          |
| np-NiPt + [HNC(dma)][bfpi] | 0.9860        | –0.5134          |
| np-NiPt + [bmim][beti] | 0.0035        | –0.4854          |
| np-NiPt + [M3BN][beti] | 1.0052        | –0.4511          |
oxidation/reduction portion of the curve from 0.6 to 1.2 V vs. RHE, there is no significant change in the onset potential for Pt oxidation relative to the bulk np-NiPt, so it is unlikely we are disturbing any ordered layer at this interface.

A second factor that can impact the oxygen reduction reaction in our system, apart from oxygen solubility and adsorption behavior, is the water concentration at the metal/IL interface. This concept was not incorporated into any prior modeling because the metal electrode is typically in direct contact with an aqueous electrolyte so the activity of water is always unity. But when adding an intermediate IL layer, we control how much water is soluble in the layer and hence present at the metal/IL interface. While the ILs we used are “hydrophobic”, they are known to have some degree of water solubility. As made, these ILs are fully dried to have a water content too low to be accurately measured. Yet, a notable feature of all the measurements performed in this study was that prior to the ability to take a potentiostatic ORR measurement, it was found that the IL layer must first be “broken in.” This issue was noted for the thin IL layers used in Refs. 5, 6, 9, but with the thicker IL layers used here, the “break-in” period was more pronounced. Furthermore, it was found here that there are two distinct ways to break-in the composite catalyst, each leading to the same reproducible potentiostatic ORR behavior. First, one can either cycle the potential multiple times in de-aerated electrolyte, or run ORR cycles until the voltammograms become stable.

As there is clearly no removal of the IL nor any evidence that the IL itself is becoming chemically modified, the dynamic nature of the break-in period suggests that the IL layer and/or IL-metal interface is structurally or compositionally changing after initial catalyst impregnation. The two most plausible explanations are the IL is becoming saturated with water or the structure of the adsorbed water/oxide layer on the catalyst is different here than in non-IL containing catalysts. We see no evidence of the latter, as described above, so we measured the water solubility in each IL using Karl Fischer titration. To do so, we allowed each IL to equilibrate with deionized water at room temperature.

Figure 5. Potentiostatic ORR current density versus potential for np-NiPt (solid line) and (a) np-NiPt+[MTBD]([beti], (b) np-NiPt+[HNC (dma)][beti], (c) np-NiPt+[HNC(dma)][bfpi], (d) np-NiPt+[bmim][beti], and (e) np-NiPt+[M3BN][beti].
Figure 6. Cyclic voltammograms of np-NiPt/IL composites, conducted in a deoxygenated solution of 0.25 M HClO₄ at a flow rate of 15 ml/min with a 5 mV/s sweep rate, after break-in for np-NiPt (solid line) and (a) np-NiPt+[MTBD][beti], (b) np-NiPt+[HNC(dma)][beti], (c) np-NiPt+[HNC(dma)][bfpii], (d) np-NiPt+[bmim][beti], and (e) np-NiPt+[M3BN][beti].

for several days, before removing the excess water and measuring the water content (solubility). Results (Table II) show substantial water solubility in all the ILs, as well as a clear variation among them.

Our results suggest that reducing the water solubility also results in significant improvement in the half-wave. For instance, while the [M3BN][beti] composite has an oxygen solubility below that of the surrounding electrolyte, it still yielded the second greatest improvement in half-wave position due to an appreciably lower water solubility. The next greatest improvement is from the [bmim][beti] composite, which has a moderate oxygen solubility, but again a very low water solubility. [HNC(dma)][beti] increases the oxygen concentration relative to the electrolyte, yet absorbs water easily, thus reducing its kinetic control and improvement making it among the worst composite systems tested. We can understand these results from simple chemical kinetics arguments. Increasing the oxygen solubility at the interface pushes reactants into the interface, biasing the reaction to completion; similarly, pulling products away from the interface via hydrophobicity also biases the reaction to completion.

The driving forces that lead to oxygen and water solubility as the primary determinants for increased oxygen reduction activity can be discussed in more detail by examining the diffusion of water within the system. Referring back to Figure 1, let $C_{PL}^{P}$ be the concentration of water at the np-NiPt interface with the IL. Let $C_{IL}$ be the concentration at the interface between the electrolyte and IL, which we assume to be the solubility of water in the IL. At any current density, we can assume that $C_{PL}^{P}$ is in steady-state, i.e.,

$$\frac{dC_{PL}^{P}}{dt} = 0 = \alpha (J_{form} - J_{diff})$$

where $J_{form}$ is the formation rate of water due to the reduction of oxygen and $J_{diff}$ is the magnitude of the flux away from the interface due to diffusion in the IL; under steady state, $J_{form} = J_{diff}$. The diffusive flux is simple Fickian diffusion away from the interface, assuming that the concentration at the interface never rises much higher.
than background solubility. With this assumption, we can express

$$J^{\text{diff}} = -D \nabla C = \frac{D}{h} (C_{\text{Pt}} - C_{\text{IL}}). \quad [9]$$

where $D$ is the diffusion coefficient of water in the IL, and $h$ is the IL thickness. At a particular current density, the driving force for pulling water away from the interface is increased if the IL has lower water thickness. We also know that $J^{\text{form}}$ is proportional to the current passed during the ORR, which is 1st order in the concentration of oxygen at the interface. That is, following Eq. 8

$$J^{\text{form}} \propto i_{\text{ORR}} = \beta C_{O_2}, \quad [10]$$

where $\beta$ is a constant of proportionality that can be found by measuring $i_{\text{ORR}}$ in the kinetic regime. This relation once again illustrates the importance of a higher oxygen solubility. Therefore, under steady-state conditions, we can find the concentration of water at the Pt/IL interface:

$$\frac{D}{h} (C_{\text{Pt}} - C_{\text{IL}}) = \beta C_{O_2} \rightarrow C_{\text{Pt}} = \frac{h \beta}{D} C_{O_2} + C_{\text{IL}} \quad [11]$$

To our knowledge, there have been no measurements of the diffusion coefficients of water in ionic liquids, but is reasonable to assume that $D$ will be of similar order to the oxygen diffusivities in the IL, which is turn is not much smaller than water self-diffusivity. Using our measured values of current density to determine values for $\beta$, we find that for our range of overpotential and ionic liquids, $C_{\text{Pt}}$ typically rises only to 0.01 M to 0.03 M. This confirms the assumption that the excess water at the interface is small. It also quantitatively bolsters the suggestion in Ref. 9 that there is no water layer at the Pt/IL interface.

Conclusions

We have examined multiple np-NiPt/IL composite systems to determine the ideal properties for ILs that can be used to improve the catalytic activity for the oxygen reduction reaction. Analysis of various physical parameters such as oxygen and water solubility, viscosity, conductivity, and adsorption behavior showed that in the absence of any specific chemical interaction with the catalyst surface, the greatest reduction in ORR overpotential correlates to those materials that combine high oxygen solubility and low water solubility, due to a straightforward kinetic diffusion analysis. To date, the IL leading to the greatest reduction in half-wave remains [MTBD][beti] in np-NiPt.

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