Enhancing Pt/C Catalysts for the Oxygen Reduction Reaction with Proton Ionic Liquids: The Effect of Anion Structure

Kan Huang, a,∗ Tangqiumei Song, b Oscar Morales-Collazo, b,e Hongfei Jia, a,u,z and Joan F. Brenneckeb,c,z

aToyota Research Institute of North America, Ann Arbor, Michigan 48105, USA
bDepartment of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, USA

Protonic ionic liquids (ILs) have been recently studied as a potential approach to enhance oxygen reduction reaction (ORR) activity of carbon supported platinum catalysts (Pt/C) for application in polymer electrolyte membrane fuel cells. The high oxygen solubility in the ILs was suggested as one of the main reasons for the accelerated reaction rates. Because the nature of the anion of the IL has been associated with increased oxygen solubility, in this work we survey a number of ionic liquids with various anions to study this effect. While the search for direct correlation between the ORR activities and the oxygen solubilities does not produce any conclusive results, by contrast, the specific activity showed dependence on the availability of oxygenated species free Pt sites. This finding indicates that the inhibition of Pt oxidation and less adsorption of non-reactive species may also play an important role in the enhanced ORR activity. Moreover, the degree of IL coverage on the Pt surface was estimated using bisulfate ions as an indicator. The surface coverage not only affected the ORR activity, but also the Pt dissolution process. This suggests that an optimal balance between activity and stability can be achieved on a partially covered Pt surface.

The oxygen reduction reaction (ORR) that occurs on the cathode poses a major hurdle for the efficient utilization of polymer electrolyte fuel cells (PEMFC). Extensive studies have focused on developing novel catalysts to improve the efficiency of this reaction.1,2 The ORR involves multiple steps, among which O2 + H+ + e− ↔ OHad and OHad + H+ + e− ↔ H2O act as the potential rate determining steps. Simultaneously optimizing the Gibbs free energies for both steps to completely eliminate the overpotential is very challenging, and a ∼350 mV overpotential is commonly observed, which is independent of the identity of the catalyst.3,4 The large overpotential has been generally attributed to the sluggish kinetics of the ORR and adsorption of oxygenated species (e.g. OHad) or other anions.5 The coverage of the adsorbed oxygenated species (θOad) is unfavorable for the reaction, and the availability of the free metal surface (as expressed by the (1-θH3O+) term) is one of the governing factors for the ORR activity.6 As a result, much effort has been dedicated to weakening the bonding of OH to the catalyst surface either by shifting the d-band center of Pt8 or by lateral repulsion from the supports (e.g. metal oxides).9,10 Anion adsorption on Pt also affects the ORR activity, and it is known that the occupation of active sites deactivates the sites and reduces the activity.11 In real-world membrane-electrode assembly (MEA), the Nafion membrane and ionomer, constituted by a Teflon-like backbone and an anionic cluster of sulfonic groups,13 are widely employed as indispensable components. The interface between the Nafion and the metal has received great attention due to the strong irreversible sulfonate anions adsorption on the Pt.12,14–16 The degree of sensitivity to the anions highly depends on the Pt facets.12 For example, the facet Pt(111) has been reported to be most sensitive to the anion adsorption.17,18 To accommodate operation of PEMFC under low humidity conditions, high ionomer to carbon ratios have been adopted to ensure sufficient proton transport,19 but the excessive sulfonic groups might reduce the catalyst performance.

In addition to the adsorption of non-reactive species, the substantial O2 diffusion resistance through the interface of ionomer and Pt was recently recognized and extensively investigated.20–22 Greszler et al.23 found that the O2 transport resistance in the thin ionomer film was much higher than in its bulk form. A DFT simulation also revealed a quick drop of O2 concentration when close to the Nafion/Pt interface.24 Although still a subject of active investigation, recent studies have pointed out that the reduced degree of freedom due to the adsorption of sulfonic acid and the low O2 solubility are the main contributors to the diffusion resistance.22

Ionic liquids (ILs) have been studied as a non-aqueous reaction media for electrochemical applications due to their low volatility, wide electrochemical windows, good ionic conductivity, and good chemical stability.25–28 Quite recently, high O2 solubility in some ILs has been utilized to address the issues of insufficient O2 concentration near the Pt surface. Snyder et al. pioneered the studies of using ILs as an ORR promoter.30,31 A protonic IL, [MTBD][bet], was encapsulated in porous PtNi nanoparticles, which showed improvements in both mass activity (mA gPt−1) and specific activity (mA cmPt−2) by ∼50% in the kinetically controlled regime. The higher O2 solubility in the IL than in aqueous electrolyte was suggested as one of the major causes for the performance enhancement. Zhang et al. also reported a simple IL impregnation method to modify a carbon supported Pt electrocatalyst.25 It was found that by filling catalyst pores with IL, the specific activity could be boosted. Higher O2 solubility was also considered as a contributor.

In one of the previous publications, the anion structure of the IL was reported to be associated with the O2 solubility.33 Therefore, in this work a number of ILs with various anion structures and O2 solubility were synthesized and studied in order to test the hypothesis that O2 solubility, as controlled by the choice of anion, determines the ORR activity. The chemical structures of ILs are displayed in Fig. 1. In order to understand how much the O2 solubility affects the ORR activity, a series of IL impregnated Pt/C catalysts were constructed and tested. In addition, adsorbed oxygenated species (θOad), IL coverage on the Pt/C, and catalyst durability were investigated.

**Experimental**

**Reagents.**—Pt/C catalyst (46.4 wt%, TEC10E50E) was purchased from Tanaka Kikinzoku Kogyo (TKK) and used as the ORR catalyst platform. HClO4 (70%), Isopropanol (99.5%), H2SO4 (99.99%), HNO3 (70%), HCOOH (99.99%), and Lithium bis(trifluoromethyl)sulfonyl)amide (99.95%), MTBD (98%), Potassium perfluorohexane sulfonate (98%) were purchased from Sigma Aldrich. Potassium nonafluorobutane sulfonate (98%) was purchased from Merck, lithium...
bis((perfluoroethyl)sulfonyl)amide (99%) was purchased from Iolitec, and potassium perfluoro(2-ethoxyethane)sulfonate was purchased from Matrix scientific. All the reagents were used as received without further purification.

**Synthesis of ILs.**—1-methyl-2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2-a]pyrimidin-9-ium bis((perfluoroethyl)sulfonyl)amide ([MTBD]beti]).—A solution of MTBD (2.51 g, 0.0164 mol) in water (100 mL) was cooled down to 0°C and Nitric Acid (1.47 g, 0.0164 mol) was added drop wise to the solution, followed by the addition of Lithium bis((perfluoroethyl)sulfonyl)amide (6.34 g, 0.0164 mol). The mixture was stirred for 1 h and the IL separated from the mixture as a viscous fluid phase beneath the aqueous phase. The resulting IL was washed 4 times with ultrapure water and dried under reduced pressure at 50°C for 18 h to obtain a colorless liquid.

Similar synthesis routes and purification processes were used to prepare the rest of the ILs:

1-methyl-2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2-a]pyrimidin-9-ium bis((trifluoromethyl)sulfonyl)amide ([MTBD][TFSI]).—The chemicals used to prepare [MTBD][TFSI] were: MTBD (2.25 g, 0.0146 mol), Nitric Acid (1.32 g, 0.0146 mol), and Lithium bis((trifluoromethyl)sulfonyl)amide (4.22 g, 0.0164 mol).

1-methyl-2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2-a]pyrimidin-9-ium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate ([MTBD][C6F13SO3]).—The chemicals used to prepare [MTBD][C6F13SO3] were: MTBD (3.00 g, 0.0196 mol), Nitric Acid (1.47 g, 0.0196 mol) and potassium nonafluorobutane sulfonate (8.58 g, 0.0196 mol).

1-methyl-2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2-a]pyrimidin-9-ium 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexane-1-sulfonate ([MTBD][C6F13SO3]).—The chemicals used to prepare [MTBD][C6F13SO3] were: MTBD (2.51 g, 0.0164 mol), Nitric Acid (1.47 g, 0.0164 mol) and Potassium perfluorohexane sulfonate (6.34 g, 0.0164 mol).

1-methyl-2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2-a]pyrimidin-9-ium 1,1,2,2-tetrafluoro-2-(perfluoropropoxy)ethanesulfonate ([MTBD][C2F5OC2F4SO3]).—The chemicals used to prepare [MTBD][C2F5OC2F4SO3] were: MTBD (2.00 g, 0.0131 mol), Nitric Acid (1.17 g, 0.0131 mol) and potassium perfluoro(2-ethoxyethane)sulfonate (4.62 g, 0.0131 mol).

**Impregnation of IL into Pt/C catalysts.**—A modified impregnation method was adopted. Typically, IL stock solutions with a concentration of 5 mg IL in 1 mL of isopropanol were prepared. 9.5 mg Pt/C catalyst was placed in a vial and first wet by 0.5 ml DI water, followed by adding the desired amount of IL stock solution to produce IL to carbon weight ratios (IL/C) of 0, 1.28, 2.56, and 3.84. The mixture was ultrasonicated for 20 min, and the solvent was slowly evaporated at 45°C into the ambient atmosphere. Finally, the obtained powder was further dried under high vacuum (−1 bar, room temperature) overnight.
$O_2$ solubility and diffusion coefficient measurements.—A gravimetric method was used to determine $O_2$ solubility in the ILs. The sample weight change during $O_2$ ab/desorption was monitored at a fixed temperature and pressure in a magnetic suspension balance (MSB) (Rubotherm GmbH). Initially, about 1 g of IL sample was added to the sample bucket and degassed to c.a. 10$^{-5}$ bar. After evaporating the water and other volatile impurities, the chamber was pressurized with $O_2$ to a certain pressure. The vapor-liquid equilibrium between $O_2$ and the IL sample was reached and confirmed by constantly weighing for at least 20 mins, and an absorption isotherm was recorded. The pressure in the sample chamber was then decreased in a stepwise manner to obtain a desorption isotherm. The absorption and desorption isotherms constituted a full isotherm. The values were corrected for buoyancy. The $O_2$ diffusion coefficient was obtained from a time-dependent absorption profile, and the $O_2$ absorption was mathematically modeled by a simplified mass diffusion process.34,35

Electrochemical measurements.—All electrochemical measurements were performed on an EC-LAB SP-300 (BioLogic) and the electrolytes were prepared with Millipore (Milli-Q Synthesis) water with a resistance greater than 18.2 MΩ · cm. A Pt wire (Pine) and a hydrogen reference electrode (Hydroflex,edaQ) were used as counter electrodes and reference electrode, respectively. All potentials in this work are reported against a reversible hydrogen electrode (RHE) unless specified otherwise. 8 mL DI water, 4.5 mL Isopropanol and 50 ul 5% Nafion dispersion (DS20, Ion Power) were added into the vial containing the prepared Pt/C-IL. The catalyst ink was subjected to 15 min ultrasonication in an ice bath. A 10 ul aliquot of this ink was pipetted onto the glassy carbon (GC) disk (5 mm diameter, Pine) and rotationally dried in air to form a uniform catalyst layer.52 For the control sample, a Pt/C catalyst layer were prepared in exactly the same manner as the Pt/C-IL catalyst, except without any IL. The calculated final Pt loading on the disk is 18 µg/cm$^2$ disk.

The catalyst coated GC was pre-conditioned in N$_2$-saturated 0.1 M HClO$_4$. Typically, the working disk was scanned from 0.05 V to 1.2 V with a scan rate of 100 mV s$^{-1}$ until the cyclic voltammetry (CV) curve didn’t change. After that, a stable CV was recorded from 0.05 V to 1.2 V at 50 mV s$^{-1}$. To study the anion adsorption effect of [MTBD][C$_4$F$_9$SO$_3$], ions was used as a direct indictor to qualitatively estimate the IL sorption peak on Pt(110) and Pt (100) in the presence of (bi)sulfate ions.

By using the Koutecky-Levich equation was used to determine the kinetic current ($i$) at each rotation rate ($n$) 52,33

\[
\frac{1}{i} = \frac{1}{i_l} + \frac{1}{i_H} \cdot \frac{1}{D} \cdot \frac{1}{c_i} \cdot \frac{1}{L^2} \cdot \frac{1}{n^2} \cdot \frac{1}{\eta^2}
\]

where $i_l$ is the limiting current, $c_i$ is the bulk concentration of $O_2$, and $D$ is the diffusion coefficient. The $O_2$ diffusion coefficients reported here are at 30 bar rather than 1 bar because significantly smaller uncertainty can be achieved at high pressure where the oxygen solubility is higher. This is a reasonable approach since pressure has little effect on the $O_2$ diffusion coefficient when $O_2$ is sparingly soluble, as is the case with iodine liquids. This is because there are no concerns that the viscosity of the $O_2$-IL mixture would decrease dramatically with increasing $O_2$ partial pressure.52,41

Because [MTBD][C$_2$F$_5$OC$_2$F$_4$SO$_3$], [MTBD][C$_6$F$_13$SO$_3$], and [MTBD][C$_4$F$_9$SO$_3$] are solids at room temperature, the direct measurement of solubility was very challenging. Fortunately, [MTBD][C$_2$F$_5$OC$_2$F$_4$SO$_3$], [MTBD][C$_6$F$_13$SO$_3$], and [MTBD][C$_4$F$_9$SO$_3$] are soluble in [MTBD][TFSI], so the overall $O_2$ uptake in mixtures of these three ILs with [MTBD][TFSI] could be measured at room temperature. The individual $O_2$ solubilities were calculated according to the Lever Rule (Equation 3), which assumes that the solution of the two very similar ILs was ideal.44,45 A summary of $O_2$ solubility and diffusivity in the ILs is presented in Table I.

$X_{O_2} = X_1 \cdot X_{O_2,1} + X_2 \cdot X_{O_2,2}$

Where $X_0$, $X_1$, and $X_2$ are mole fractions of individual ILs in the mixture, and $X_{O_2,1}$ and $X_{O_2,2}$ are the
Figure 2. $^1$H NMR of [MTBD]-based ILs: a) [MTBD][TFSI] in DMSO-d$_6$, b) [MTBD][beti] in DMSO-d$_6$, c) [MTBD][C$_4$F$_9$SO$_3$] in DMSO-d$_6$, d) [MTBD][C$_2$F$_5$OC$_2$F$_2$SO$_3$] in DMSO-d$_6$, e) [MTBD][C$_6$F$_3$SO$_3$] in MeOD-d$_4$. 

Downloaded on 2018-07-20 to IP 207.241.231.83 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
O₂ solubility in the pure individual ILs. For the diffusion coefficient of O₂ in the ILs that are solid at room temperature, elevated temperature was required to reach a liquid phase, so the values are reported at 60 °C.

Fig. 4 presented the electrochemical characterizations of Pt/C and Pt/C-ILs, (IL/C = 2.56) catalysts for all five of the ILs. Fig. 4a contains the cyclic voltammograms. It was found that the Pt/C-ILs suffered ECA loss compared to pristine Pt/C. The ECA loss for most ILs was moderate (10–13%), except for [MTBD][C₂F₅OC₂F₄SO₃], which showed a value of 28% (Fig. 4c). The differences in the ECA behavior might be due to the competition adsorption of ions in IL with hydrogen. Meanwhile, the onset potentials of Pt-oxides formation of Pt/C-ILs were positively shifted, in agreement with observation of suppression of Pt oxidation. Among Pt/C-ILs, Pt/C-[MTBD][C₂F₅OC₂F₄SO₃] showed the largest shift. In the diffusion regime, the limiting current of Pt/C-IL is slightly lower than the Pt/C, which is likely cause by the smaller (O₂)D_{2/3}IL than (O₂)D_{2/3}electrolyte.

Equation 4 shows the generally described kinetic ORR current expression form:

\[ i = n F K [O_2] (1 - \exp(-\beta F E / RT)) \exp(-\omega \theta / RT) \]  

Where n is number of electrons transferred, F is Faraday’s constant, \( K \) is a chemical rate constant, \( (1-\theta) \) is the available surface, \( \beta \) is a symmetry factor, \( E \) is the applied potential, and \( \omega \) is the energy parameter for the Temkin isotherm.

Equation 4 illustrated that the current density should be proportional to the oxygen concentration \([O_2]\), and a higher oxygen solubility in the ILs is expected to yield a proportional increase in the current density. The solubility study showed that the average oxygen concentration in ILs was improved by a factor of ~5–6 over aqueous 0.1 M HClO₄ solution. Unfortunately, neither the mass activity nor the specific activity show a six-fold improvement (Fig. 4d). For example, the highest mass activity of Pt/C-IL at 0.9 V is ~250 mA/mgPt, an increase of just ~27% compared to the Pt/C baseline. The rate of the heterogeneous reaction occurring at the Pt-electrolyte interface can be expressed as \( \frac{\partial [O_2]}{\partial t} = \frac{j}{2F} \), where \( \frac{\partial [O_2]}{\partial t} \) is the O₂ mole flux and \( j \) is the current density. Assuming the diffusion of O₂ within the IL layer follows Fick’s Law, then O₂ mole flux \( \frac{\partial [O_2]}{\partial t} \) is a product of the O₂ concentration gradient \( \frac{\partial [O_2]}{\partial x} \) and the O₂ diffusion coefficient \( D_{O2} \). As a result, the product of concentration (C) and diffusion coefficient (D) is usually considered an important parameter in evaluating the effectiveness of gas diffusion through a thin film. Therefore, \([O_2] \times D_{O2}\) at R.T. of the ILs investigated here was calculated and is included in column 4 of Table I. Although the \([O_2] \) in [MTBD][TFSI] and [MTBD][beti] is ~5 times higher than that in 0.1 M aqueous HClO₄, the product of \([O_2] \times D_{O2}\) for ILs doesn’t show any advantage over the aqueous electrolyte. This is consistent with the results shown in Fig. 4d, where the activity with [MTBD][TFSI] and [MTBD][beti] did not increase by a factor of 5. Thus, it appears that slow O₂ diffusion through the ILs and long mean free path within the ILs counteract the high O₂ concentration benefit at the electrolyte/IL interface and limit the O₂ concentration at the Pt interface. Unlike the nanoporous PtNi nanoparticle that can encapsulate the IL inside the particles, the selected Pt/C platform in this work has no inner space to accommodate IL. As a consequence, the IL would only form a thin layer covering the catalyst surface. (Fig. 5) The difference of collision frequency of oxygen with inner wall of nanoporous Pt and with flat Pt might be one of the main reasons that we did not observe the proportional increase of current density. Even though the effect of high O₂ solubility in the ILs on the ORR activity was not significant in the

**Table I. The solubility and diffusion coefficient of oxygen in ILs used in this study.**

| Sample          | Form   | \([O_2]\) at R.T. and 1 bar (mM) | \(D_{O2}\) \(10^{-6}\) cm²/s at 30 bar | \([O_2]\) \(\times D_{O2}\) at R.T. \((10^{-6}\) mol·cm⁻¹·s⁻¹) |
|-----------------|--------|---------------------------------|-------------------------------------|-------------------------------------|
| [MTBD][beti]    | Liquid | 5.9                             | 1.76 @ R.T.                         | 10.21                               |
| [MTBD][TFSI]    | Liquid | 5.5                             | 3.04 @ R.T.                         | 16.72                               |
| [MTBD][C₂F₅OC₂F₄SO₃] | Solid  | 8.1                             | 22 @ 60 °C                         | -                                   |
| [MTBD][C₂F₅SO₃] | Solid  | 10.9                            | 16 @ 60 °C                         | -                                   |
| [MTBD][C₂F₆SO₃] | Solid  | 8.4                             | -                                  | -                                   |
| 0.1 M HClO₄⁴⁹   | Liquid | 1.18                            | 19 @ R.T.                           | 22.42                               |

*The melting point of [MTBD][C₂F₅OC₂F₄SO₃] is ~59 °C. A temperature higher than 60 °C was required to completely melt it.
Figure 4. Electrochemical characterization of Pt/C and Pt/C-IL systems (a) Cyclic voltammetry curves in N$_2$-saturated 0.1 M HClO$_4$. (b) Polarization curves in O$_2$-saturated 0.1 M HClO$_4$ at a rotation speed of 1600 rpm. (c) ECA of Pt/C-ILs. (d) Mass activity (MA, mA/mgPt) and Specific activity (SA, uA/cm$^2$Pt) measured at 0.9 V. The IL/C ratio was 2.56 for all Pt/C-ILs. (e) Plot of SA against (1-$\theta$$_{OH}$).

Selected Pt/C platform, its potential benefit should not be neglected in the specific catalyst structure. Besides, ILs with wider oxygen solubility window may be more helpful to better assess the effect of O$_2$ solubility.

Interestingly, the specific activity (SA, mA cm$^{-2}$) correlated to the activity per available Pt site. Motivated by the fact that comparable mass activities were achieved with less accessible Pt surface and less Pt-oxides formation. The specific activity was plotted against the fraction of oxides free Pt sites (1-$\theta$$_{OH}$), which is shown in Fig. 4e. The specific activity clearly depends on (1-$\theta$$_{OH}$) and a linear relationship can be seen. The $\theta$$_{OH}$ of most Pt/C-ILs are between 0.4~0.5, except for Pt/C-[MTBD][C$_6$F$_5$SO$_3$], which has significantly lower coverage by oxides. As mentioned above, previous studies mainly attributed the promotion of ORR activity to the higher O$_2$ concentration in ILs...
and the increased attempt frequencies,30–32 but Zhang et al. recently suggested a different mechanism. They integrated Pt/C with two ILs with different O2 solubility and found that the one with higher O2 solubility actually did not outperform the other one, and the performance differences were very small.38 Their study suggested that the ORR is not sensitive to the O2 solubility, but that suppression of nonreactive species (e.g. Pt-oxides) is what contributes to the activity enhancement in the presence of ILs. We hypothesize that the IL providing a lateral repulsion of oxygenated species and weakening of the -OH adsorption is the mechanism for the IL coating improving specific activity. CO displacement and CO stripping results also shows a reduced anion adsorption on Pt and a delay of Pt-OH formation (Fig. S2).

Since the Pt/C modified with [MTBD][C4F9SO3] showed the highest specific activity, further investigations were conducted with this IL. The morphology of [MTBD][C4F9SO3] on the Pt/C was studied by TEM and the image is shown in Fig. 5. A thin layer can be detected on the Pt/C. Owing to its amorphous contrast, this is evidence of the presence of IL. The IL formed a continuous layer (1~2 nm) covering the catalyst surface. Fig. 6 displays the electrochemical characterization of Pt/C-[MTBD][C4F9SO3] with various IL/C ratios. One can easily see that the ECA decreases quickly with increasing IL/C ratio and a 40% loss is observed at IL/C = 3.86. Meanwhile, Fig. 6b shows that the onset potential of Pt-oxides formation was positively shifted and the resulting amount of oxides (QOH) under potential range (0.6 V – 1.2 V) was suppressed accordingly. The loss of ECA and reduction of Pt-oxides formation will be comprehensively discussed below.

Subbaraman et al. coated planar Pt with a thin Nafion film and observed the formation of Pt oxides was hindered compared to the Nafion free Pt.12 It was claimed that the adsorption of sulfonate anions was competing with adsorption of oxygen species on the Pt surface, resulting in a positive shift of the onset potential of Pt oxidation. Since the [MTBD][C4F9SO3] contains a similar SO3− group, it’s speculated that the anion of the IL might impose a similar effect. To elucidate this possibility, the anion precursor, K[C4F9SO3], was considered to simulate the [C4F9SO3]− adsorption on Pt/C. The [C4F9SO3]− concentrations varied from 0 mM to 1 mM in 0.1 M HClO4. One has to mention that the total mole content of available [C4F9SO3]− in the aqueous electrolyte solution is far higher than that in the catalyst layer when [MTBD][C4F9SO3] is used (e.g. the mole content of [C4F9SO3]− in a 1 mM aqueous solution is ~3000 times higher than in the catalyst layer at IL/C = 3.86 when using [MTBD][C4F9SO3]), ensuring an adequate anion supply for the adsorption process. Fig. 7 presents the voltammograms and polarization curves of Pt/C in the presence of various [C4F9SO3]− concentrations. It was found that the changes of CV between 0 M and 1 mM [C4F9SO3]− were insignificant, especially in the hydrogen under potential deposition (Hupd) and Pt redox regions. A slight negative shift of linear sweep voltammetry (LSV) was observed at 1 mM compared to 0 M. K[C4F9SO3] generated a lot of foam in the electrolyte due to its the hydrophobic fluoroalkyl chain, and purging with N2 or O2 accelerated the bubble formation and bursting. The situation became even worse in rotational operation. The disruption of local gas transport near the rotating disk might be the cause of the small change of ECA and of LSV. Unlike polymers, it is anticipated that the anion and cation of the IL would populate the surface but be mobile to a certain degree. It is also possible that the ion orientations are changed by applying an electrical potential.51 Therefore, during an anodic potential scan, the negatively charged anion might head toward the Pt and occupy the sites. However, the small changes of CV and ORR imply that the binding strength of [C4F9SO3]− on the Pt surface is weak and would not affect the Pt electrochemical behavior very much. In summary, the anion adsorption study suggests that the loss of ECA and decrease of Pt-oxides formation found in Pt/C-[MTBD][C4F9SO3] is not due to anion occupation.
Electrochemical Impedance Spectroscopy (EIS) is commonly adopted to measure the effective proton conductivity within the catalyst layer in MEA. While in the rotating disk electrode (RDE) setup, due to the thinness of the catalyst layer and the abundance of electrolyte, the associated protonic resistance has been largely neglected. Nonetheless, it is essential to study the proton diffusion in Pt/C-IL. Three electrodes with different catalyst layers on GC were fabricated according to the RDE preparation described in the Experimental section. The nafion and IL amounts are exactly the same as detailed in the Experimental section. One has to mention that the experiment was not designed to measure the proton conductivity of either nafion ionomer or individual ionic liquid, but the overall proton diffusion resistance within the catalyst layer. The three electrodes are as follows: (1) Nafion only; the catalyst layer consisted of Pt/C and Nafion only (Pt/C-Nafion); (2) IL only; the catalyst layer consisted of Pt/C and IL ([MTBD][C4F9SO3]) only; and (3) Nafion-IL; the catalyst layer consisted of Pt/C, IL and Nafion (see Experimental section on Pt/C-IL ink preparation for details). Fig. 8a presents the Nyquist plots, and the intercept of the linear portion on the x-axis was extracted to calculate the effective catalyst layer protonic resistance, $R_{H^+}$ (the inset shows an example how to obtain $R_{H^+/3}$; details can be found in Ref. 36). All the protonic resistance was normalized to the area of catalyst layer. The values extracted from the data for Pt/C-Nafion is $1.65 \ \Omega \cdot \text{cm}^2$, which agrees well with the reported value. Unlike the Nafion only catalyst layer, the EIS response of the IL only catalyst layer shows a sluggish increase at low frequency, implying an increase in the proton diffusion resistance. The resulting $R_{H^+}$ was $5.14 \ \Omega \cdot \text{cm}^2$, which is much higher than the Pt/C-Nafion value. Interestingly, the Nafion-IL prepared catalyst layer showed a much smaller resistance c.a. $0.17 \ \Omega \cdot \text{cm}^2$. In the IL modified membrane system, it has been reported that the proton generated from the polymer –SO3H group associates with the IL, and hopping and diffusion mechanisms carry the proton to the SO3⁻ site of the IL. In this study, the proton may follow a similar transport mechanism. While the exact mechanism of reduced $R_{H^+}$ is still under investigation, we hypothesize that a more uniform catalyst layer in the co-presence of IL and Nafion may contribute to a decrease in proton diffusion resistance. EIS was also performed at various IL/C ratios and the results are summarized in Fig. 8b. It was found that in the IL/C range studied, the additional IL does not restrict sufficient proton supply within the catalyst layer.

In real MEA, the Nafion ionomer distribution and its coverage on the Pt surface largely determines the fuel cell performance, because the transport of O₂ and protons is controlled by the thickness of the ionomer. Also, the carbon structures greatly affect the ionomer dispersion on the catalyst surface. In an attempt to estimate IL coverage on the catalyst surface, we note that hydrogen adsorption behavior on low index Pt(hlk) facets differs dramatically in HClO₄ and H₂SO₄ solutions, such as the Pt(100) and Pt(110). With the aid of sensitivity of hydrogen adsorption region, we designed a method to study the IL coverage on the Pt. Fig. 9a showed the CV behaviors of Pt/C in 0.1 M HClO₄ and 0.5 M H₂SO₄ aqueous solutions, respectively. Pt/C in H₂SO₄ showed two sharper peaks in the
Figure 9. Electrochemical characterizations. (a) Cyclic voltammetry plots of Pt/C in N$_2$-saturated 0.1 M HClO4 and 0.5 M H$_2$SO$_4$, respectively (b) Cyclic voltammetry plots of Pt/C with an IL/C ratio of 2.56 in N$_2$-saturated 0.1 M HClO4 and 0.5 M H$_2$SO$_4$, respectively. (c) Cyclic voltammetry plots of Pt/C with various IL/C ratios in N$_2$-saturated 0.5 M H$_2$SO$_4$. (d) ECA of Pt/C-IL systems measured in N$_2$-saturated 0.1 M HClO4 and 0.5 M H$_2$SO$_4$. (e) CV curves of Pt/C with K[C$_4$F$_9$SO$_3$] concentrations from 0 mM to 1 mM in N$_2$-saturated 0.5 M H$_2$SO$_4$.

Hupd region, which we assign to the signature hydrogen adsorption on Pt(100) and Pt(110), respectively. In contrast, the Pt(110) adsorption peak was less sharp and Pt(100) became more broader in HClO$_4$. The different hydrogen adsorption on low index Pt facets behavior was mainly due to the attraction of (bi)sulfate anion into the diffusion layer below 0.4 V and its coupling effect with hydrogen for adsorption.\textsuperscript{59} Meanwhile, the onset potential of Pt oxidation shifted positively in H$_2$SO$_4$ relative to in HClO$_4$ (Figs. 9a and 9b), indicating a competition mechanism between the adsorption of oxygenated species and (bi)sulfate ions.\textsuperscript{60,61} For the Pt/C-[MTBD][C$_4$F$_9$SO$_3$] (IL/C = 2.56) catalyst (Fig. 9b), the Hupd regions were virtually identical in the two acids. The sharp adsorption peak on Pt(110) was absent, while peak for adsorption on Pt (100) remained broad. The peak for Pt(110) was shifted slightly to a higher potential, which is due to a pH effect.\textsuperscript{62} This finding implies that the IL might be preventing Pt from having direct contact with the (bi)sulfate ions. Taking advantage of the sensitivity of Pt(100) and Pt(110) to the (bi)sulfate ions, we performed CVs of Pt/C-[MTBD][C$_4$F$_9$SO$_3$] with various IL contents in 0.5 M H$_2$SO$_4$. The CV plots are overlaid and shown in Fig. 9c. At an IL/C ratio of 1.28, although the ECA suffered a loss, the pronounced hydrogen adsorption peaks on Pt(110) and Pt(100) can still be seen clearly, indicating that Pt is still accessible to the (bi)sulfate ions. Increasing IL/C to 2.56 and 3.84, the characteristic hydrogen adsorption peaks disappear and show behavior similar to that seen in HClO$_4$. More importantly, the CV plots of IL/C = 2.56 and 3.84 almost overlap for the entire potential range, showing similar ECA values and the amount of Pt-oxides formed. The comparison of ECA of Pt/C-[MTBD][C$_4$F$_9$SO$_3$] measured in 0.1 M HClO$_4$ and 0.5 M H$_2$SO$_4$ are presented in Fig. 9d. No significant ECA changes were observed at IL/C = 0 in either electrolyte, suggesting that (bi)sulfate ions do not affect the available Pt sites in the H upd region.\textsuperscript{12,14} However, between IL/C = 1.28 and 2.56 the ECAs obtained in 0.1 M HClO$_4$ were greater than in 0.5 M H$_2$SO$_4$. 
To explore the additional loss of ECA of Pt/C-[MTBD][C4F9SO3] in H2SO4, same anion adsorption studies using K[C4F9SO3] were conducted and these are shown in Fig. 9e. Throughout the K[C4F9SO3] concentration range studied, the changes in the CV curves in 0.5 M H2SO4 were clearly different from those observed in 0.1 M HClO4. The ECA loss was much larger (21% in H2SO4 vs. 8% in HClO4 at 1 mM), and the decrease of Pt oxidation/Pt-oxides reduction region was more noticeable. All these findings provide evidence that the co-presence of [C4F9SO3]− and (bi)sulfate affect the processes of hydrogen adsorption on Pt and Pt-oxides formation. This suggests that between IL/C = 1.28 and 2.56, Pt was partially covered by IL but it was still accessible to the (b) sulfate. Increasing the IL/C ratio to 3.84, the ECAs and Pt-oxide formation were identical in both electrolytes, implying that contact between the Pt and the (b)sulfate ions was limited. In summary, with the aid of the different CV behaviors in HClO4 and H2SO4 we are able to roughly estimate the IL coverage on Pt. At low IL/C ratios, Pt is partially covered by IL. Further increasing the IL/C ratio to 3.84 or beyond yields full coverage on the Pt surface.

We have shown that the IL loading effect on CV (Fig. 6) is closely associated with surface coverage. Therefore, the influence of IL loading on the ORR activity was further studied. The polarization curves are displayed in Fig. 10a. It was found that the half-wave potential of Pt/C-[MTBD][C4F9SO3] shifted positively by ~11 mV at IL/C = 1.28 and ~20 mV at IL/C = 2.56 compared to the pristine Pt/C, indicating an enhanced ORR performance. However, excessive IL content caused a negative shift of half-wave potentials. Correspondingly, a volcano dependence of ORR activity on IL/C was revealed (Fig. 10c), that is, MA and SA initially increased with increasing IL content followed by a decrease. As discussed in Fig. 4, the (1-θOH) heavily influenced the specific activity; therefore, the SA was plotted against the (1-θOH) and this is illustrated in Fig. 10d. A similar volcano-dependence of SA on (1-θOH) was observed. Between IL/C = 0 and IL/C = 2.56, SA increased with a decrease in (1-θOH). The IL coverage study revealed that the Pt is partially covered for those IL/C ratios, and a triple solid/liquid/gas (Pt/electrolyte/O2) reaction phase was maintained. Even though the Pt/C-[MTBD][C4F9SO3] suffered a loss of active surface area (Fig. 9d), the protection of the surface from nonreactive species by the IL leads to an increase in SA. The mass activity is a product of ECA and SA, and the beneficial increase in SA is offset somewhat by the decrease in ECA. Consequently, the gain of mass activity was limited to ~50 mA mgPt−1. Tafel plots (Fig. 10b) also indicate that in the kinetic region of 0.9 V or above, the differences in intrinsic activity (j0) between IL/C up to 2.56 were small. When the Pt surface was fully coated by IL (IL/C = 3.56 or above), the slow O2 diffusion more than offsets the suppression of nonreactive species and this becomes the dominant factor. As detailed above, the lower O2 diffusion coefficient in the IL and a longer diffusion pathway appears to restrict the efficient O2 flux, leading to a dramatic decrease in the ORR activity.

Finally, the durability of Pt/C-[MTBD][C4F9SO3] was examined using a protocol suggested by US DOE. Fig. 11 shows the polarization curves and cyclic voltammetry before and after 5000 cycles in the applied potential. The ECA loss and ORR activity loss at 0.9 V are summarized in Table II. Pronounced CV and ORR behavior changes were found for Pt/C, compared by 17.4% ECA loss, 30.3% specific

Figure 10. Oxygen reduction reaction on Pt/C-IL systems. (a) ORR polarization curves of Pt/C with various IL/C ratios in O2-saturated 0.1 M HClO4 at a rotation speed of 1600 rpm. (b) ORR Tafel plots of Pt/C-IL systems. (c) Mass activity (MA, mA/mgPt) and Specific activity (SA, uA/cm2Pt) calculated at 0.9 V. (d) Correlation between the specific activity and free Pt sites (1-θOH).
activity loss, and 42.4% mass activity loss. In contrast, the losses were alleviated and less noticeable degradations were found at high IL content, demonstrating the protective effect of the IL. We adopted X-ray photoelectron spectroscopy analysis with N1s as an indicator to study the IL leaching in each step of electrochemical measurement. The results showed that the majority IL leaching occurred at the initial pre-conditioning, but was drastically reduced afterwards and the loss became less significant (not shown here). One can also observe that the change of CV of Pt/C-IL before and after cycling was small (inset in Figs. 11b–11d), suggesting the remaining IL in the catalyst layer helped to mitigate the Pt dissolution. Extensive research efforts have been undertaken to probe the Pt dissolution mechanism, and it is generally accepted that Pt dissolution occurs during anodic scan and cathodic scan, respectively.\(^{63,64}\) Basically, Pt-oxides are formed during the anodic scan through Pt\( + H_2O \rightarrow PtO + 2H^+ + 2e^- \) and Pt\( + 2H_2O \rightarrow PtO_2 + 4H^+ + 4e^- \), where an anodic dissolution takes place. The reductive dissolution follows a reaction pathway PtO\(_2\) + 4H\(^+\) + 2e\(^-\) \rightarrow Pt\(^{2+}\) + 2H\(_2O\). One can easily find the presence of water is one of the key factors to generate the Pt-oxides and initiate the subsequent dissolution. Unlike Nafion, which has a hydrophilic domain, the [MTBD][C\(_4\)F\(_9\)SO\(_3\)] IL is relatively hydrophobic, with low water solubility that can provide a lateral repulsion force to reject water. Thus, reduced adsorption of water molecules on Pt is expected when the IL is present. The IL coverage can also affect the Pt dissolution process. In a partially covered Pt surface, a three-phase system remains and water can still attach to the Pt. Under full IL coverage, the water in contact with Pt will be reduced, except for the small amount of water dissolved in the IL. Overall, the alleviation of Pt dissolution is mainly attributed to protection by the IL. One has to mention, the smallest performance loss at an IL/C of 3.84 was achieved at a sacrifice of ORR activity thus, a compromise of performance and stability should be taken into consideration.

**Table II. Summary of ECA, Specific activity and Mass activity loss after 5000 potential cycling.**

| IL/C  | ECA loss, % | Specific activity loss, % | Mass activity loss, % |
|-------|-------------|---------------------------|-----------------------|
| 0     | 17.4        | 30.3                      | 42.4                  |
| 1.28  | 6.7         | 23.3                      | 28.5                  |
| 2.56  | 7.7         | 8.2                       | 15.3                  |
| 3.84  | 2.8         | 3.2                       | 5.9                   |

**Conclusions**

We have examined a series of [MTBD]-based ILs with various anion structures to study the effect of oxygen solubility on ORR activity. ILs with higher oxygen solubility do not improve the ORR activity in the kinetic controlled region (either mass activity or specific activity). On the other hand, the specific activity correlates well with availability of Pt sites (1-4). A study of surface coverage revealed that ILs actually form a protective layer that reduces the adsorption...
of non-reactive species, which boosted the specific activity in return. Investigation of the influence of IL loading suggests that excess IL should be avoided in order to maintain three-phase contact between the solid catalyst, liquid and gaseous reagent, and a reasonable IL coverage on Pt should be chosen to balance the ORR activity and stability.

References

1. M. Shao, Q. Chang, J.-P. Dodelet, and R. Chenitz, Chemical Reviews, 116, 3594 (2016).
2. Y.-J. Wang, N. Zhao, B. Fang, H. Li, X. T. Bi, and H. Wang, Chemical Reviews, 115, 3233 (2015).
3. M. T. M. Koper, Journal of Electroanalytical Chemistry, 660, 254 (2011).
4. M. T. M. Koper, Chemical Science, 4, 2710 (2013).
5. J. X. Wang, N. M. Markovic, and R. R. Adzic, The Journal of Physical Chemistry B, 117, 12440 (2005).
6. N. Markovic, H. Gasteiger, and P. N. Ross, Journal of The Electrochemical Society, 144, 1591 (1997).
7. N. M. Markovic, H. A. Gasteiger, and P. N. Ross, The Journal of Physical Chemistry, 99, 3411 (1995).
8. V. R. Stamenkovic, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas, and N. M. Markovic, Science, 315, 493 (2007).
9. J. Zhang, M. B. Vukmirovic, K. Sasaki, A. U. Nilekar, M. Mavrikakis, and R. R. Adzic, Journal of The American Chemical Society, 127, 12480 (2005).
10. K. Huang, K. Sasaki, R. R. Adzic, and Y. Xing, Journal of Materials Chemistry, 22, 16824 (2012).
11. K. Sasaki, L. Zhang, and R. R. Adzic, Physical Chemistry Chemical Physics, 10, 159 (2008).
12. R. Subbaraman, D. Stremcik, A. P. Paulikas, V. R. Stamenkovic, and N. M. Markovic, ChemPhysChem, 11, 2825 (2010).
13. K. A. Maurice and R. B. Moore, Chemical Reviews, 104, 4535 (2004).
14. Y. Ayato, K. Kunitsumi, M. Osawa, and T. Okada, Journal of The Electrochemical Society, 153, A203 (2006).
15. J. Chistumoff and B. Pivovar, Journal of The Electrochemical Society, 162, F890 (2015).
16. Y. Furuya, T. Mashio, A. Ohama, and K. Shinozuka, Meeting Abstracts, MA2012-02, 260 (2012).
17. P. N. Ross, Journal of The Electrochemical Society, 126, 67 (1979).
18. P. N. Ross, Journal of The Electrochemical Society, 126, 78 (1979).
19. A. Ohma, T. Mashio, K. Sato, H. Iden, Y. Ono, K. Sakai, K. Akizuki, S. Takaichi, and K. Shinozuka, Electrochimica Acta, 56, 10832 (2011).
20. Y. Kurihara, T. Mabuchi, and T. Tokumasa, ECS Transactions, 69, 691 (2015).
21. H. Liu, W. K. Epting, and S. Litster, Langmuir, 31, 9853 (2015).
22. A. Kongkanand and M. F. Mathias, The Journal of Physical Chemistry Letters, 7, 1127 (2016).
23. T. A. Greszler, D. Caufl, and P. Sinha, Journal of The Electrochemical Society, 159, F831 (2012).
24. R. Jimmouchi, K. Kudo, N. Kitano, and Y. Morimoto, Electrochimica Acta, 188, 767 (2016).
25. A. Ikezawa, K. Miyazaki, T. Fukutsuka, and T. Abe, Journal of The Electrochemical Society, 162, A1645 (2015).
26. L. Johnson, A. Ejigu, P. Licence, and D. A. Walsh, The Journal of Physical Chemistry C, 116, 18048 (2012).
27. H. Munakata, T. Tashita, M. Haibara, and K. Kanamura, ECS Transactions, 33, 463 (2010).
28. J. B. Rollins and J. C. Conboy, Journal of The Electrochemical Society, 156, B943 (2009).
29. X.-Z. Yuan, V. Alizate, Z. Xie, D. G. Ivey, and W. Qu, Journal of The Electrochemical Society, 161, A451 (2014).
30. J. Snyder, T. Fujita, M. W. Chen, and J. Erlebacher, Nat Mater, 9, 904 (2010).
31. J. Snyder, K. Liviu, and J. Erlebacher, Advanced Functional Materials, 23, 5494 (2013).
32. G.-R. Zhang, M. Munoz, and B. J. M. Etzold, ACS Applied Materials & Interfaces, 7, 3562 (2015).
33. M. Haibara, S. Hashizume, H. Munakata, and K. Kanamura, Electrochimica Acta, 132, 208 (2014).
34. A. Yokozeki, International Journal of Refrigeration, 25, 695 (2002).
35. M. B. Shiflett and A. Yokozeki, Industrial & Engineering Chemistry Research, 44, 4453 (2005).
36. K. Shinohara, J. W. Zuck, R. M. Richards, B. S. Pivovar, and S. S. Kocha, Journal of The Electrochemical Society, 164, F55 (2017).
37. J. Chlistunoff and B. Pivovar, Journal of The Electrochemical Society, 164, F660 (2017).
38. T. R. Garrick, T. E. Mylan, M. K. Carpenter, and A. Kongkanand, Journal of The Electrochemical Society, 164, F660 (2017).
39. M. Gonzalez-Miquel, J. Bedia, C. Abrusi, J. Palomar, and F. Rodriguez, The Journal of Physical Chemistry B, 117, 3398 (2013).
40. C. Moya, J. Palomar, M. Gonzalez-Miquel, J. Bedia, and F. Rodriguez, Industrial & Engineering Chemistry Research, 53, 13782 (2014).
41. Z. Lei, J. Han, B. Zhang, Q. Li, J. Zhu, and B. Chen, Journal of Chemical & Engineering Data, 57, 2153 (2012).
42. M. B. Shiflett and A. Yokozeki, Journal of Chemical & Engineering Data, 54, 108 (2009).
43. G. A. Somorjai, P. Yang, and V. R. Stamenkovic, John Wiley & Sons, Inc (2001).
44. J. Erlebacher, K. Huang, Y. Li, L. Yan, and Y. Xing, RSC Advances, 4, 9701 (2014).
45. Z. Chen, Y. Kang, Z. Zhu, W. Huang, H. L. Xin, J. D. Snyder, D. Li, J. A. Herron, M. Mavrikakis, M. Chi, K. L. More, Y. Li, N. M. Markovic, G. A. Somorjai, P. Yang, and V. R. Stamenkovic, Science, 343, 1339 (2013).
46. R. Hayes, N. Bortsenko, M. K. Tan, P. C. Howlett, F. Endres, and R. Atkin, The Journal of Physical Chemistry C, 115, 6855 (2011).
47. Y. Ono, A. Ohma, K. Shinozuka, and K. Fushinoba, Journal of The Electrochemical Society, 160, F779 (2013).
48. S. Y. Kim, S. Kim, and J. M. Park, Nat Commun, 1, 88 (2010).
49. S. Y. Kim, J. Lee, and M. J. Park, Macromolecules, 47, 1099 (2014).
50. F. Lu, X. Gao, S. Xie, N. Sun, and L. Zheng, Soft Matter, 10, 7819 (2014).
51. K. Ikeda, N. Nonoyama, and Y. Ikogi, ECS Transactions, 33, 11890 (2010).
52. T. Mashio, A. Ohma, and T. Tokumasa, Electrochimica Acta, 202, 14 (2016).
53. Y.-C. Park, H. Tokiwa, K. Kakimura, M. Watanabe, and M. Uchida, Journal of Power Sources, 315, 179 (2016).
54. P. W. Faguy, N. Markovic, and P. N. Ross, Journal of The Electrochemical Society, 156, 1638 (1959).
55. J. I. Matsuzawa, W. B. Schneider, J. C. Meier, U. Biedermann, P. U. Biedermann, A. Cuesta, A. A. Auer, and K. J. J. Mayrhofer, Physical Chemistry Chemical Physics, 15, 8058 (2013).
56. G. Inzelt, B. Berkes, and Å. Kriston, Pure and Applied Chemistry, 83, 269 (2011).
57. W. Sheng, Z. Zhuang, M. Gao, J. Zheng, J. G. Chen, and Y. Yan, Nat Commun, 6 (2015).
58. K. Sasaki, M. Shao, and R. Adzic, in Polymer Electrolyte Fuel Cell Durability, F. N. Büchli, M. Inaba, and T. J. Schmidt Editors, p. 7, Springer New York, New York (2009).
59. Y. Sugawara, T. Okayasu, A. P. Yudav, A. Nishikata, and T. Tsuru, Journal of The Electrochemical Society, 159, F779 (2012).