Oxygen Reduction

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Accelerating Oxygen-Reduction Catalysts through Preventing Poisoning with Non-Reactive Species by Using Hydrophobic Ionic Liquids

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Abstract: *Developing cost-effective electrocatalysts for the oxygen reduction reaction (ORR) is a prerequisite for broad market penetration of low-temperature fuel cells. A major barrier stems from the poisoning of surface sites by nonreactive oxygenated species and the sluggish ORR kinetics on the Pt catalysts. Herein we report a facile approach to accelerating ORR kinetics by using a hydrophobic ionic liquid (IL), which protects Pt sites from surface oxidation, making the IL-modified Pt intrinsically more active than its unmodified counterpart. The mass activity of the catalyst is increased by three times to 1.01* $A\,mg^{-1}{}_{Pt}$*@0.9 V, representing a new record for pure Pt catalysts. The enhanced performance of the IL-modified catalyst can be stabilized after 30 000 cycles. We anticipate these results will form the basis for an unprecedented perspective in the development of high-performing electrocatalysts for fuel-cell applications.*

Low-temperature fuel cells (LTFCs) are expected to become a major clean energy for the future with particularly important applications in portable/transportation devices. However, the sluggish kinetics of oxygen reduction reaction (ORR) at the cathode has imposed a huge barrier for broad-based applications of LTFCs.[1] Platinum (Pt) is the best pure-metal ORR catalyst, but a large overpotential (300 mV) is still needed to overcome the slow ORR kinetics.[2] This substantial overpotential would bring down the overall LTFC thermal efficiency well below the thermodynamic limits.[3] The ORR kinetics in the low overpotential region are suppressed by the high coverage of nonreactive oxygenated species (e.g., OH_{ad}) on Pt,[4] a result of the overlap in potential between the onset of ORR and adsorption of oxygenated species.[2] In 2007, Stamenkovic et al. reported that the presence of Ni in an alloyed Pt_3Ni (111) catalyst could weaken the interaction between surface Pt and nonreactive oxygenated species by down-shifting the *d*-band center of Pt, resulting in higher number of active sites for O_2 adsorption and improved kinetics.[1a] Inspired by this work, intensive research efforts have been devoted towards enhancing ORR kinetics by combining Pt with one or more metal elements.[1d,5] However, the preferred leaching of the non-noble component(s) and associated phase separation would sometimes cause rapid catalyst degradation during potential cycling, especially in acidic medium.[6] The instability of surface structures during electrochemical redox process was also identified for bi-/multi-metallic catalysts.[7] Moreover, the complex procedures involved in the construction of bi-/multi-metallic systems and increasing effort in recycling of mixed-metal catalysts causes some economic concerns.[8] Developing alternative routes to cost-effectively accelerating ORR kinetics is still highly desirable.

Water molecules are considered as a major source of oxygenated species.[1a,2,4a,9] Jinnouchi et al. proposed, based on their combined DFT and Poisson–Boltzmann calculations, that the interface water itself may also lead to blockage of Pt sites.[4c] The difficulty to improve ORR kinetics thus lies in the dilemma that water is the reaction media as well as the reaction product but might also cause blockage of active sites.

Herein, we develop a facile approach to overcoming this dilemma, by modifying the catalyst surface to be hydrophobic by using a hydrophobic ionic liquid (IL), which leads to the formation of a solid catalyst with ionic liquid layer (SCILL).[10] The IL phase is supposed to partially replace water as the reaction media and more importantly, the created hydrophobic microenvironment at catalyst surfaces would help to preserve active sites by repelling water molecules from the product and aqueous electrolyte. Similarly IL-modified Pt catalysts has already been constructed by others and us, and exhibited enhanced activity for ORR which was rationalized by higher O_2 solubility in the IL ([MTBD][Beti], [MTBD][NTf_2]).[8,11] Herein, we demonstrate that the introduction of a common and inexpensive IL, such as 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_4C_1im][NTf_2]), to the Pt/C catalyst can efficiently reduce the overpotential and bring in a remarkable enhancement in activity; meanwhile, we discovered that the accelerated ORR kinetics on SCILL samples would originate from the higher accessibility of Pt sites protected by the hydrophobicity conveyed by IL. These unprecedented insights could be further exploited to design more efficient catalysts for saving precious metals in aqueous-phase electrocatalysis.

The IL-modified catalyst Pt/C-[C_4C_1im][NTf_2] was prepared by dispersing the Pt/C (20 wt %) in an isopropanol solution containing a certain amount of pure IL (Figure S1 in the Supporting Information), followed by multi-step solvent evaporation procedure.[8] The loading amount of IL in Pt/C-[C_4C_1im][NTf_2] was determined to be around 18 wt % by ICP-OES analysis. The possible influence of IL modification on the Pt particle size/distribution was probed by using transmission electron microscopy (TEM; Figure S2). It can be seen

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that Pt nanoparticles are evenly distributed all over the carbon support for both samples, and the statistical analyses verify that there's little change in average Pt particle sizes or distributions after the IL modification. The successful immobilization of IL on Pt/C was also confirmed by the infrared spectroscopy, as the IR features on Pt/C-[C_4C_1im][NTf_2] can be exclusively attributed to the pure IL (Figure S3). Moreover, it should be noted that the Pt/C-[C_4C_1im][NTf_2] alone became poorly dispersed in water, which was not the case for the Pt/C. Water contact angle measurements were therefore carried out on Pt/C and Pt/C-[C_4C_1im][NTf_2] catalyst films to verify the change of surface hydrophobicity after IL modification. As shown in Figure 1 a, the surface of the Pt/C can be completely wet by water. In contrast, the contact angle of water on the Pt/C-[C_4C_1im][NTf_2] was around 110° (Figure 1 b), demonstrating that a small amount of IL is sufficient to cause dramatic change in Pt/C surface from hydrophilic to hydrophobic state.

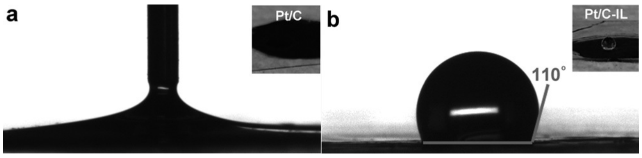


Figure 1. Static water contact angle measurements on a) Pt/C and b) Pt/C-[C_4C_1im][NTf_2]. Insets: photographs of both samples after placing a drop of water on the catalyst films.

The electrochemical behavior of the Pt/C and Pt/C-[C_4C_1im][NTf_2] were investigated by using the rotating disk electrode (RDE) technique. Figure 2 a shows the cyclic voltammetry (CV) curves of Pt/C and Pt/C-[C_4C_1im][NTf_2], respectively. Close inspection of the CV curves reveals that both samples have two distinctive potential regions corresponding to H adsorption/desorption on Pt in the potential region 0.05 to 0.4 V and the formation of surface oxygenated species (OH_{ad}) beyond 0.6 V. The H adsorption/desorption peaks on Pt/C-[C_4C_1im][NTf_2] are little different to those of as-received Pt/C, and the electrochemically active surface area (EAS) calculations further confirmed that Pt/C-[C_4C_1im][NTf_2] exhibited comparable EAS value to Pt/C (94.6 vs 99.0 $m\,g^{-1}{}_{Pt}$) as displayed in Figure 2 b, verifying that the site blocking effect from the IL is negligible.[11a] This result is counterintuitive, because [C_4C_1im][NTf_2] is a typical aprotic IL and supposed to have limited H^+ conductivity. It is likely that the trace amount of water in hydrophobic IL would facilitate the formation of interconnected water network within the IL,[12] which could aid H^+ transportation through direct hydronium diffusion, or proton hopping between hydronium and water molecules.[11c] Moreover, we found that the formation of oxygenated species was significantly suppressed on the Pt/C-[C_4C_1im][NTf_2] (Figure 2 a). Specifically, the coverage of oxygenated species (θ_{OH}) is reduced from 34.0 % on Pt/C to around 17.6 % on Pt/C-[C_4C_1im][NTf_2] (Figure 2 b). These results provide the first piece of evidence that the incorporation of IL into Pt/C can protect the surface Pt sites from the oxygenated species.

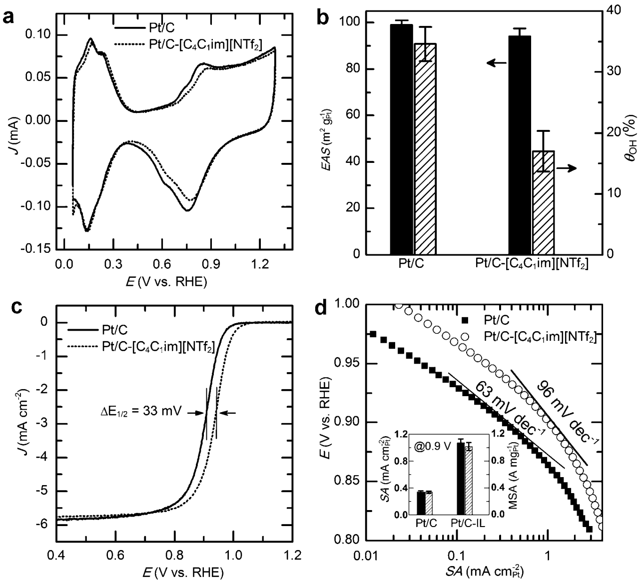


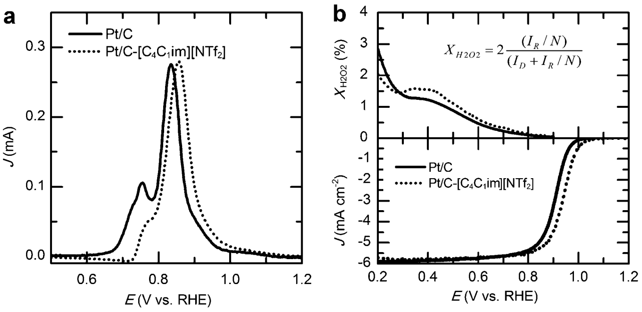
Figure 2. a) Cyclic voltammetry curves on Pt/C and Pt/C-[Bmim][NTf_2] catalysts in N_2-saturated 0.1 M $HClO_4$ solution at a scanning rate of 20 $mV\,s^{-1}$. b) Histograms showing the EAS and hydroxy surface coverage (θ_{OH}) at 0.9 V. c) Polarization curves recorded in O_2-saturated 0.1 M $HClO_4$ solution. d) ORR Tafel plots extracted from the polarization curves shown in (c). Inset: the activity of the Pt/C catalysts before and after IL modification.

The ORR performance was measured at room temperature in O_2-saturated 0.1 M $HClO_4$ solution with a scan rate of 10 $mV\,s^{-1}$ and a RDE rotation rate of 1600 rpm. A characteristic set of polarization curves recorded on the Pt/C and Pt/C-[C_4C_1im][NTf_2] catalysts are displayed in Figure 2 c. Two distinguishable potential regions can be observed: diffusion-limiting-current region below 0.7 V and mixed kinetic–diffusion-control region between 0.8 and 1.0 V. Further inspection indicates that after IL modification, the half-wave potential ($E_{1/2}$) has positively shifted by 33 mV, reflecting a significantly decreased overpotential and accelerated ORR kinetics on the Pt/C-[C_4C_1im][NTf_2]. The kinetic current was calculated from the polarization curves by using the Koutecky-Levich equation and normalized to the EAS of Pt to quantitatively compare their specific activity, and plotted in Figure 2 d as a function of electrode potential. The specific activity (SA) at 0.9 V is chosen as a standard metric for assessing the activity of different ORR catalysts.

As shown in the inset of Figure 2 d, the corresponding SA of the Pt/C-[C_4C_1im][NTf_2] catalyst is 1.1 $mA\,cm^{-2}{}_{Pt}$, which is 3.1 times that of the Pt/C catalyst (0.34 $mA\,cm^{-2}{}_{Pt}$). Moreover, since high mass-specific activity (MSA) is more essential in view of practical applications, we also normalized the kinetic current against the loading amount of Pt on each catalyst. Notably, Pt/C-[C_4C_1im][NTf_2] catalyst possesses a MSA of 1.01 $A\,mg^{-1}{}_{Pt}$, which is 3 times greater than that of the Pt/C catalyst (0.33 $A\,mg^{-1}{}_{Pt}$) and substantially surpassing the MSA target (0.44 $A\,mg^{-1}{}_{Pt}$ @0.9 V) set by US Department of Energy for 2017–2020. As far as we know, the Pt/C-[C_4C_1im][NTf_2] catalyst presents the highest MSA for ORR on pure Pt catalysts, demonstrating the great advantage of the SCILL concept for Pt saving catalysts.

Tafel analysis was conducted to understand how Pt activity is improved after the IL modification. At low electrode potentials, the Tafel slope is approximately -120 mV/dec on both catalysts, but rapidly increases to -60 mV/dec at high potentials, which is consistent with prior work.[2,4a,11a] The intrinsic Tafel slope on clean Pt is -120 mV/dec which can be observed at low potentials, and the deviation from this value at high potentials is ascribed to the blockage of Pt by oxygenated species.[13] The changes in Tafel slope can thus be employed as an indicator of the changes in the coverage of oxygenated species on Pt. As shown in Figure 2 d, the pristine Pt/C catalyst has a Tafel slope of 63 mV/dec at 0.9 V, while in contrast Pt/C-[C_4C_1im][NTf_2] catalyst has a slope of 96 mV/dec, which is more close to the intrinsic Tafel slope of ORR on clean Pt surface. These results provide another piece of evidence that the IL on the SCILL sample protects Pt sites from the oxygenated species.

To unambiguously probe how the IL can alter the adsorption behavior on Pt surfaces, we conducted CO-stripping tests on Pt/C and Pt/C-[C_4C_1im][NTf_2] catalysts. Figure 3 a shows the background-subtracted CO-stripping curves on these two samples, and two intriguing phenomena can be observed: 1) the clearly resolved pre-peak centered at 0.75 V on Pt/C, owing to the oxidation of CO adsorbed on defect or low-coordinated sites,[14] is attenuated on Pt/C-[C_4C_1im][NTf_2]; 2) the main peak position on Pt/C is positively shifted by 24 mV after IL modification. The attenuated pre-peak on Pt/C-[C_4C_1im][NTf_2] may arise from blockage of defect sites by IL or restricted accessibility of CO to defect sites, however, these reasons are contradicted with the well-maintained EAS value after IL modification and appreciable CO solubility in [C_4C_1im][NTf_2].[15] It is generally accepted that the oxidation of CO in both the pre- and main peaks required adsorption of oxygenated species (Langmuir–Hinshelwood mechanism) which can be formed at lower potential on defect sites.[16] It is thus expected that the restricted formation of oxygenated species on Pt in the presence of IL would influence the CO oxidation. Interestingly, only the pre-peak was selectively suppressed, implying that the IL preferentially locates at the defect sites. The hydrophobicity conveyed by the IL phase would restrict the formation of oxygenated species at defect sites and result in an attenuation of the pre-peak on the SCILL sample. Regarding the positive shift of the main peak, this is an indicator of a stronger bonding between CO molecules and Pt surfaces in the presence of IL.[17] It can be concluded that the presence of IL could actually efficiently decouple the adsorption of reactant molecules (O_2 and CO) and of nonreactive oxygenated species on Pt. As far as we know, this is the first attempt to simultaneously make the Pt surface more reactive to reactants and more tolerant to nonreactive species, which has long been desired as a breakthrough in ORR catalysis.[2]



$$X_{H2O2} = 2\frac{(I_R/N)}{(I_D + I_R/N)}$$

Figure 3. a) Background-subtracted CO-stripping curves on the pristine and IL-modified Pt/C. b) RRDE measurements on Pt/C and Pt/C-[Bmim][NTf_2]. Lower panel: ORR polarization curves in 0.1 M $HClO_4$; upper panel: fraction of formed H_2O_2. Inset: calculation of H_2O_2 fractions, where I_R represents the ring current, N is the collection efficiency, and I_D is the disk current.

In addition to catalytic activity, selectivity, and stability are another two critical criteria for evaluating the performance of a catalyst. Rotating ring disk electrode (RRDE) measurements were performed on Pt/C and Pt/C-[C_4C_1im][NTf_2] catalysts to investigate the possible influence of the IL phase on the ORR pathway or on H_2O_2 formation (Figure 3 b). The mole fraction of H_2O_2 generated during ORR on both catalysts is less than 3 %, demonstrating that the reaction is predominantly taking place via the desirable 4-electron pathway, and the additional IL phase imposes little effect on the selectivity as evidenced by the comparable plots for the H_2O_2 fraction (Figure 3 b).

The stability of the Pt/C-[C_4C_1im][NTf_2] was evaluated by potential cycling between 0.4 to 1.1 V for up to 30 000 cycles in an O_2-saturated 0.1 M $HClO_4$ solution. After the first 2000 cycles, no recordable loss in either EAS or SA was observed (Figure 4 a). After 30 000 cycles, Pt/C-[C_4C_1im][NTf_2] catalyst exhibits an EAS of 85 $m g^{-1}{}_{Pt}$, a SA of 1.05 $mA\,cm^{-2}{}_{Pt}$, and a MSA of 0.90 $A\,mg^{-1}{}_{Pt}$. Although there's a slight drop in MSA owing to the EAS loss, the degraded Pt/C-[C_4C_1im][NTf_2] is still 2.6 times more active than the fresh Pt/C. Figure 4 b shows the evolution of the $E_{1/2}$ with increasing the cycle numbers, which also demonstrates the superiority of the SCILL sample for ORR. These results confirm that the activity-boosting effect from the IL modification can be well maintained, which would be of highly importance for application of SCILL materials in LTFCs.

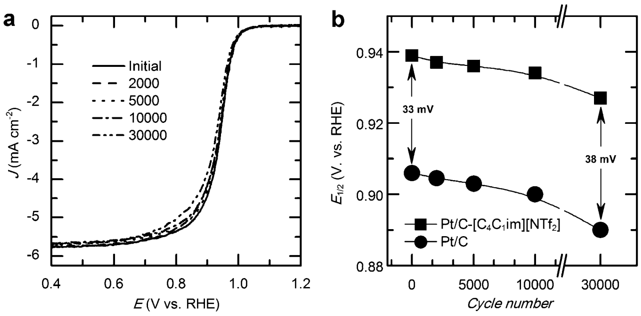


Figure 4. a) Polarization curves for ORR on Pt/C-[C_4C_1im][NTf_2] after different potential cycles in O_2-saturated 0.1 M $HClO_4$ solution. b) $E_{1/2}$ of ORR on Pt/C and Pt/C-[C_4C_1im][NTf_2] after varied potential cycles.

The superior electrochemical stability of the Pt/C-[C_4C_1im][NTf_2] also evidenced that possible IL leaching is indeed negligible, which is a benefit of the hydrophobic nature of the IL. Further demonstration of the importance of hydrophobicity for this SCILL system is shown in Figure S4, which shows CV and ORR polarization curves recorded on the pristine Pt/C and the modified Pt/C prepared by using a hydrophilic IL [C$_3$(NH$_2$)C$_1$im]Br. It is observed that 1) CV curves on these two samples are perfectly overlapped; 2) the half-wave potential of the Pt/C-[C$_3$(NH$_2$)C$_1$im]Br is slightly negatively shifted by 4 mV. These results indicate that the hydrophilic IL might not survive in aqueous electrolyte and consequently has little promotional effect on the catalytic activity of Pt/C towards ORR. The influence of the hydrophobicity on Pt activity towards ORR was further studied by intentionally decreasing the hydrophobicity, which was achieved by lowering the IL loading amounts from 18 wt% to 7 wt%. Not surprisingly we found that the polarization curve has negatively shifted by 12 mV, and the specific activity is decreased by 36% relative to those of the original Pt/C-[C$_4$C$_1$im][NTf$_2$] (Figure S5), which was indeed consistent with our previous observation.[8] Therefore, the hydrophobicity should be a key property which is required from an IL to improve the performance of Pt catalysts towards ORR.

In addition to providing an innovative approach to boosting the performance of Pt catalysts for ORR, the construction of SCILL samples would enable a better understanding about how Pt activity is improved by using an IL. The promotional effect of ILs was previously assumed to originate from the high O$_2$ solubility in ILs.[18] To make this solubility effect clear, another SCILL sample was prepared by modifying Pt/C using an IL ([C$_4$C$_1$im][Beti]) with higher O$_2$ solubility (2.90 vs. 2.28 mM in [C$_4$C$_1$im][NTf$_2$]). Surprisingly, the performance of Pt/C-[C$_4$C$_1$im][Beti] was little different to that of Pt/C-[C$_4$C$_1$im][NTf$_2$] (Figure S6). The EAS and SA for Pt/C-[C$_4$C$_1$im][Beti] were 89.1 m^2 g$^{-1}_{\mathrm{Pt}}$ and 0.97 mA cm$^{-2}_{\mathrm{Pt}}$, respectively, even slightly lower than those of Pt/C-[C$_4$C$_1$im]-[NTf$_2$]. These results show that the promotional effect of IL could be not that sensitive to the O$_2$ solubility.

Based on the implications of the results presented above we propose a possible mechanism for the observed activity-boosting effect. For Pt/C catalysts, Pt atoms at the defect sites tend to be easily oxidized (Figure 5a), owing to their higher reactivity.[1a,14e] By introducing the hydrophobic IL, these sites could be selectively protected from oxidation (Figure 5b), while still accessible to the reactants. It was assumed that the high O$_2$ solubility in IL is the reason for the superiority of IL-modified Pt catalysts, while our results indicate that the ORR activity is not sensitive to O$_2$ solubility. We also reveal that the presence of IL could decouple the adsorption of nonreactive species and reactants, thus increasing the available sites for adsorption of reactants, while strengthening the adsorption of reactants on Pt. Both of these virtues are highly desirable for an excellent ORR catalyst, and thus it is not surprising to observe the superior performance of the IL-modified Pt/C with a record high activity for ORR.

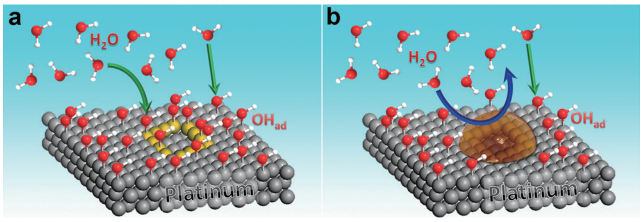


Figure 5. Scheme for the interfacial microenvironments at a) Pt/C, and b) Pt/C-SCILL, showing that the IL would selectively locate at the defect sites and protect the Pt sites from hydroxy species.

In conclusion, we have disclosed that in addition to combining Pt with other metal elements, introduction of hydrophobic ILs could be employed as a facile approach to producing high-performing catalysts for ORR with an impressive activity enhancement factor (over three times). We found that the activity enhancement on the SCILL sample would arise from the protection of Pt sites from the oxygenated species. Moreover, the presence of the IL phase could simultaneously make Pt surfaces more tolerant to poisonous species and more reactive to reactants. These findings open a new avenue for constructing high-performance ORR catalysts for LTFCs. Considering the great variety of ILs, there is undoubtedly much room left for further boosting the catalytic activity of precious-metal-saving catalysts, by rationally manipulating the cationic and/or anionic structures of ILs.

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Keywords: hydrophobicity · ionic liquids · nonreactive oxygenated species · oxygen reduction · supported catalysts

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