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Oxygenophilic ionic liquids promote the oxygen reduction reaction in Pt-free carbon electrocatalysts[†]

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We propose a novel idea to improve the surface properties of carbon-based Pt-free electrocatalysts in Polymer Electrolyte Membranes (PEMs) and Alkaline Fuel Cells (AFCs). Our concept is based on the addition of oxygenophilic and hydrophobic ionic liquids (ILs) to form a thin passivating layer at the triple point between the electrocatalyst-electrolyte-gas interface where the Oxygen Reduction Reaction (ORR) takes place.

The design of Pt-free electrocatalysts for the oxygen reduction reaction (ORR) in fuel cells or metal–air batteries represents a very important research direction due to the scarcity of Pt and the associated high costs.¹ One of the most common classes of Pt-free electrocatalysts is based on carbon materials due to their low cost and tuneable properties such as porosity, functionality and high electrical conductivity.² A large number of metal-free and precious-metal-free carbon materials have been reported in the literature, some of which could outperform commercial Pt, in particular in alkaline environments.³

Various techniques such as heteroatom doping⁴ or nanocasting⁵ have been applied to manipulate the intrinsic active sites including heteroatoms, edges, and defects⁶ as well as other critical properties such as conductivity,⁷ porosity and surface chemistry, all aiming towards the design of an ideal electrocatalyst.

In addition to engineering the carbon catalyst's physicochemical properties, manipulating the interface where the oxygen reaction takes place represents another, yet unexplored,

Conceptual insights

We report a new and general concept to improve the performance of Pt-free electrocatalysts in Polymer Electrolyte Membrane Fuel Cells (PEMFCs) and Alkaline Fuel Cells (AFCs) based on the addition of oxygenophilic and hydrophobic ionic liquids (ILs) to form a thin passivating layer at the triple point between the electrocatalyst-electrolyte-gas interface where the electrocatalytic reaction takes place. We demonstrate this concept for nitrogen-doped and Fe-nitrogen doped carbon electrocatalysts. The IL layer at the catalyst's surface provides a water-equilibrated secondary medium with a higher O2 solubility, while its hydrophobic nature prevents water from building-up locally. We validate that the use of protic ILs favours the oxygen reduction reaction (ORR) in both acidic and alkaline media. Our concept not only shows significant improvements in ORR in both alkaline and acidic electrolytes, but also represents a promising method to be implemented in other renewable energy technologies (i.e. metal-air batteries, supercapacitors) where nanocarbons with improved surface properties are required.

opportunity to boost its electrocatalytic activity, as this is where phenomena such as fast electron transport, high O_2 solubility and interaction with the electrolyte occur. Here, we present a new concept of interfacial control for such key processes governing the ORR at the triple point between the electrocatalyst, electrolyte and gas phase.

Ionic liquids (ILs) have gained remarkable attention as relatively low-cost green media for energy conversion reactions compared with currently commercialized Pt. Recently, hydrophobic ionic liquids (ILs) with a high O_2 solubility were employed to modify Pt nanoparticles, leading to improved kinetics, selectivity, and durability in the ORR performance.⁸ This concept has not been demonstrated yet for metal free electrocatalysts.

In this study we have selected a hydrophobic but aprotic IL, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide $([C_4C_1im][NTf_2])(IL1)$ to modify the interfacial microenvironment of a nitrogen doped graphene (GN) electrocatalyst prepared *via* a simple hydrothermal treatment of graphene and urea as described in detail in the ESI.† This composite was denoted as GN-IL1.

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Fig. 1 TEM images of (a) GN and (b) GN-IL1. The inset images show the static water contact angle measurements, respectively. (c) The XPS surveys and (d) N_2 sorption isotherms of GN and GN-IL1.

The TEM micrographs of the graphene flakes before and after IL modification are shown in Fig. 1. The micrographs are similar, indicating a uniform deposition of an ultra-thin IL layer onto the surface of the GN. The interaction between the IL and GN can take place *via* static-assisted CH– π hydrogen bond interaction as previously reported in the literature.⁹

Water contact angle measurements showed a clear increase from 89.4° to 126.5° after the introduction of hydrophobic ILs (insets in Fig. 1a and b). In addition, XPS measurements reveal a substantial amount of F (3.5 at%) and S (0.7 at%), as well as a higher O (3.6 at%) and N (1.2 at%) amount after the IL modification, arising from the anions of IL1 (Fig. 1c and Fig. S1, ESI†). The total nitrogen content of GN-IL1 (1.2 at%) is higher than that of GN (0.6 at%), while both can be assigned to three dominant configurations: pyridinic-*N* (*ca.* 398.55 eV), quaternary-*N* (*ca.* 400.43 eV) and oxidized-*N* (*ca.* 401.70 eV), respectively (Table S1, ESI†).¹⁰ The porosity and specific surface area (SSA) of GN before and after IL modification were evaluated

using nitrogen sorption (Fig. 1d and Table S2, ESI⁺). The SSA of GN-IL1 decreased by 67.8% compared to the pristine GN, while the pore volume in GN-IL1 decreased by 84.7% compared to GN. The decrease in surface area and pore volume from the pristine catalyst to the IL composite further confirms the presence of a thin IL coating on the surface of the porous graphene flakes (Fig. S2, ESI[†]). In addition, compared with GN, the pore width distribution of GN-IL1 showed a negative shift of 1-2 nm in the pore size range of 5-10 nm, which corresponds to the thickness of the ionic liquid layer coated at the electrocatalyst's surface. The TGA of GN-IL1 under air shows a pronounced mass reduction at a temperature of ca. 460 °C corresponding to the decomposition of the IL and another mass loss component at 502 °C corresponding to the decomposition of the pristine catalyst. (Fig. S3b, ESI⁺). The FT-IR spectrum of the composite material shows additional absorption bands between 1000 and 1300 cm⁻¹ ascribed to SO₂, and CF₃ vibration (Fig. S4, ESI^{\dagger}).

The results above confirm the successful and uniform coating of a thin IL layer onto the porous surface of the nanocarbon catalyst which can: (i) serve as a hydrophobic phase to facilitate the expulsion of water produced during the ORR; (ii) provide a higher O_2 solubility and diffusivity to improve the utilisation of active sites; and (iii) protect the catalyst from oxidation or degradation.

The ORR activity was firstly investigated in O_2 -saturated alkaline solution (0.10 M KOH) using a rotating-ring disk electrode (RRDE) with a rotation rate of 1600 rpm and a scan rate of 10.0 mV s⁻¹. A commercial Pt/C catalyst (20 wt%, Sigma) was also measured under the same conditions for comparison. The obtained linear sweep voltammetry (LSV) curves are plotted in Fig. 2a. The pristine GN catalyst exhibits a good reactivity with a diffusion-limiting current density of about 5.0 mA cm⁻²,



Fig. 2 ORR performances of the IL-modified GN catalyst. (a) LSV curves obtained in O₂-saturated 0.10 M KOH solution, (b) corresponding Tafel plots derived from the LSV results. (c) LSV curves obtained in O₂-saturated 0.10 M HClO₄ solution. The rotating rate was 1600 rpm, with a scan rate of 10.0 mV s⁻¹. (d) Current–time chronoamperometric responses of different samples in alkaline or acidic conditions. The catalyst loading for all tests was *ca.* 0.285 mg cm⁻² (IL was not included).

which is comparable to that of commercial Pt/C. This is due to the nitrogen-doping effect and to other topological defective sites on GN.⁶ Following modification with IL, the current density significantly increased from 4.6 mA cm⁻² to 5.1 mA cm⁻² at 0.4 V vs. RHE, exhibiting a more obvious diffusion-limiting region below 0.65 V. Further inspection of the LSV curve reveals that the half-wave potential ($E_{1/2}$) of the composite GN-IL1 after the IL modification was positively shifted by *ca.* 37 mV compared to the pristine GN catalyst, suggesting a significant decrease in overpotential. The Tafel plots for GN, GN-IL1, and Pt/C electrodes derived from the LSV results are presented in Fig. 2b. The Tafel slope has also clearly decreased from *ca.* 83.8 in the pristine catalyst to 77.1 mV dec⁻¹ after IL modification, which is much closer to that of Pt/C, indicating fast ORR kinetics.

We have also investigated the ORR performance under acidic conditions (0.10 M HClO₄). As shown in Fig. 2c, at high overpotentials, the current densities of GN-IL1 and GN both approach 6 mA cm $^{-2}$, which is comparable with Pt/C, showing also a good performance in acid. However, the overpotential is much higher than that of Pt/C (Fig. S5, ESI[†]), while the modification of ILs hardly brings about any improvements. This may be due to the inactivity of nitrogen/defected sites as active sites under acidic conditions.^{6a} IL1 is a typical aprotic IL with a limited H⁺ conductivity.^{8e} Its aprotic character can justify the contrasting ORR performance in alkaline and acidic media obtained otherwise under identical conditions. This hypothesis is supported by a further investigation in a protic IL as presented below. Nevertheless, we can clearly state that an improvement in stability in both base and acid can be achieved after the IL modification, as demonstrated via current-time chronoamperometric responses (Fig. 2d). The potential was set for the beginning of the diffusion-control region. After 14 000 s tests, the current retention of the GN-IL1 composite after the IL modification improved from 94.2% in the pristine GN to 96.2% in an alkaline medium, and from 70.7% to 93.2% in an acidic medium, respectively.

The perfluorinated side chains of $[NTf_2]^-$ anions induce hydrophobicity in our catalyst as confirmed by the contact angle measurements as shown in Fig. 1a and b. Besides, it also provides a high affinity to O2. The O2 solubility in $[C_4C_1 \text{ im}][NTf_2]$ was reported to be $\approx 2.3 \text{ mM}$,^{8e} which is much higher compared to the one in aqueous electrolytes (0.10 M KOH \approx 1.1 mM;¹¹ in 0.10 M HClO₄, \approx 1.2 mM).^{8a} Consequently, the IL layer on N-doped graphene's surface provides a hydrophobic and oxygenophilic secondary-phase between the solid catalyst and the liquid electrolyte as shown in Scheme 1. The higher oxygen solubility in the IL layer compared to the exterior electrolyte improves the oxygen diffusion towards the catalyst's active sites, increases the residence time, and improves the utilization of active sites, by facilitating a good interaction with its surface.^{8d} Furthermore, its hydrophobic nature can expel the formed water from the catalyst's surface, restricting the formation of oxygenated species, thereby freeing up active sites which become highly accessible. In addition, the IL phase partially replaces the electrolyte as a reaction medium and thus can protect the nanocarbon catalysts from external



Scheme 1 Schematic diagram of the synthesis process and the triple-phase interface between solid–liquid and gas.

oxidation or poisoning and prevent the catalyst particles from peeling off.^{8e} All these advantages can optimise the microenvironment between catalysts and an aqueous electrolyte, leading to substantially improved activity and stability for ORR catalysis.

To further elucidate the role of ILs in metal free ORR electrocatalysis we have replaced the $[C_4C_1im][NTf_2]$ with another similar IL, 1-ethylimidazolium bis(trifluoromethylsulfonyl) imide $([C_2im][NTf_2])$ (IL2) (Fig. S1b, ESI†). This IL is also hydrophobic with a high O_2 solubility, but this time a protic IL, meaning that it can facilitate protonic transport *via* hydronium (H₃O⁺) diffusion or proton hopping.^{8d} The nanocarbon catalyst modified by $[C_2im][NTf_2]$ (GN-IL2) shares a similar morphology, porosity, hydrophobicity, and composition with GN-IL1 (Fig. S6 and Tables S1, S2, ESI†). However, the LSV curves obtained in 0.10 M HClO₄ distinctly suggest an enhanced ORR performance of GN-IL2 compared with GN-IL1 with a positive shift in $E_{1/2}$ by *ca.* 31 mV (Fig. 3a). The improvement in protonic conductivity in the IL2 layer near the catalyst surface is in this case critical for such nanocarbon catalysts with a low intrinsic electrocatalytic activity in acid media.

The protic IL modified GN (GN-IL2) also delivers a significantly improved activity and accelerated kinetics in an alkaline medium. Its activity is superior to the aprotic IL modified GN, GN-IL1 (Fig. 3b). In this case, the $E_{1/2}$ of GN-IL2 has further increased by *ca.* 17 mV compared with GN-IL1, and was



Fig. 3 Further insights into the IL modification strategy for enhanced ORR catalysis: (a) ORR LSV curves obtained in O_2 -saturated 0.10 M HClO₄ solution for GN-IL1 and GN-IL2. (b) ORR LSV curves obtained in O_2 -saturated 0.10 M KOH solution, and the corresponding Tafel plots (inset). The catalyst loading for all tests was *ca.* 0.285 mg cm⁻² (IL was not included).

positively shifted by ca. 55 mV compared with the pristine GN. The Tafel slope further decreased to 69.2 mV dec^{-1} , which is even lower than that of the commercial Pt/C catalyst (77.1 mV dec⁻¹). Despite the hydrophobic character of the ILs ascribed to the [NTf₂]⁻ anions, they can also dissolve a significant amount of water.^{8d,e,12} The water molecules form an interconnected water network in the IL phase, promoting H_3O^+/OH^- transport^{8d,e} in an acidic medium, while providing sufficient H₂O reactants for the ORR in an alkaline medium. The "N-H" acidic site of the imidazolium cation in $[C_2 im]^+$ in IL2 compared with $[C_4 C_1 im]^+$ in IL1 almost triples the mole fraction solubility of water (with large dipole moment) from ca. 0.2 to 0.6, due to hydrogen bonding.¹² The anion determines the solubility of nonpolar O2 in ILs, while the cation can make little difference.¹³ Therefore, in this case, we believe that the OH⁻ transportation is the rate-limiting step. The protic IL2 with a much higher water solubility is more beneficial than the aprotic IL1 with limited water solubility. A rotating ring disk electrode (RRDE) test demonstrated an in-depth study of the reaction pathway (Fig. S7a and c, ESI^{\dagger}), in which electron transfer number (*n*) and H₂O₂ yield were calculated and compared (Fig. S7b and d, ESI⁺). GN, GN-IL1, GN-IL2 show similar n values of ca. 3.8 in a basic medium, and HO_2^- formation lower than 20% for all the samples. In an acidic medium, the H_2O_2 yield is even lower than 10%, while the *n* values remain close to 3.8.

Electrochemical impedance spectroscopy (EIS) was recorded in the mixed diffusion-controlled region near the half-wave potential to further investigate the electrode–electrolyte interface. Fig. S8 (ESI†) shows the Nyquist plots of GN, GN-IL1 and GN-IL2. In both electrolytes, GN-IL1 and GN-IL2 show similar charge transfer resistance at high frequency. However, at lower frequency controlled by a mix of the charge-transfer and masstransfer process, the resistance of the IL-coated catalysts appears to be similar or slightly higher compared with our pristine catalyst. This is because our ionic liquid layer has a lower electronic conductivity compared with the pristine catalyst, but this is compensated by an improved mass diffusion of oxygen and protons.

In order to prove that our strategy can be employed as a general and universal method for improving the electrocatalytic activity of any Pt-free elecrocatalysts, iron/nitrogen-doped graphene (GNFe) was employed instead of GN (see details in the ESI,† Fig. S9). As shown in Fig. S10 (ESI†), the diffusion-limiting current density is increased above 6 mA cm⁻² and the $E_{1/2}$ is positively shifted by *ca.* 33 mV after IL2 modification (GNFe-IL2), indicating the similar performance improvement in both metal-free and precious-metal-free nanocarbon catalysts.

We have demonstrated for the first time in the literature a general and effective strategy to improve the ORR activity of nanocarbon-based electrocatalysts *via* a facile modification with suitable ILs at room temperature. The IL layers at the nanocarbon's surface provide a water-equilibrated secondary medium with a much higher O₂ solubility and a hydrophobic nature which prevents water from building-up locally. It also confers a good $H^+/H_3O^+/OH^-$ conductivity. We have also demonstrated that the water solubility in the selected ILs can significantly determine the ORR activity. The cost of the ionic

liquid is more than ten times lower compared with a commercial catalyst (Pt group metals) for the ORR. This modification strategy exhibits a remarkable ORR improvement in both alkaline and acidic electrolytes. This work opens new research directions in efficient Pt-free catalyst development *via* tailoring the interfaces at the triple point.

Further research will involve other ILs with higher hydrophobicity, oxygenophilicity and proton conductivity along with more fundamental understanding of the IL-electrocatalyst–O₂ interface.

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