

Emerging Applications of Solid Catalysts with Ionic Liquid Layer Concept in Electrocatalysis

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The concept of solid catalysts with ionic liquid layer (SCILL) originates from the field of heterogeneous catalysis, where it offers a unique way to regulate both the catalytic activity and selectivity. In recent years, applying this concept in electrocatalysis represented a new, exciting, and growing research field. Herein, emerging applications of the SCILL concept in the context of electrocatalysis for key energy storage/conversion processes such as oxygen reduction, oxygen evolution, and CO₂ reduction reactions are comprehensively reviewed. Alongside case studies highlighting the history, development and latest progress of the SCILL concept, mechanistic underpinnings on the roles of ILs in each application are critically discussed. At the same time, the key challenges and future opportunities in fully leveraging the SCILL concept for either regulating the performance of electrocatalysts or gaining mechanistic understandings for those electrocatalytic processes with complex reaction pathways are outlined.

1. Introduction

One of the ultimate goals in catalysis is to design catalysts with high activity, selectivity, and stability to enhance the overall chemical conversion process, make new conversion routes possible and/or reduce the required energy input.^[1,2] In this sense, great endeavors have been made to develop new catalytic systems toward more efficient chemical transformations and energy storage/conversions.^[3,4] Most of them focus on directly engineering the structure of active sites by constructing heterogeneous catalysts with varied particle sizes/shapes/surface compositions, and/or homogeneous catalysts with tailored molecular structures. Major guidelines are optimization of

both the steric structure and the energetic structure following the Sabatier principle.


Beyond the inherent nature of active sites, the microenvironments at the active sites created by additional species (e.g., atoms, functional groups/ligands, support, solvent) adjacent to the active sites can also contribute to the energy landscape of the catalytic reaction.^[1,5–7] The microenvironments can take effect by exerting electronic effect on the active site, controlling the local concentration or diffusion rate of reactants/intermediates at the catalyst surface, influencing the stability of specific transition state, or restricting the access of poisonous species to the active site, and therefore offers a new handle for improving the performance of catalysts.^[8–10] This new strategy is showcased by the ligand effect,^[11–14] and

pore confinement effect in heterogeneous catalysis,^[15,16] while a recently emerging approach is to directly modify this microenvironment by adding ionic liquids (ILs) to solid catalysts, which follows the so called “solid catalysts with ionic liquid layer” (SCILL) concept.^[17–21] Considering the variety and structural flexibility of ILs,^[22] the additional IL can enhance the degree of freedom in engineering the microenvironments adjacent to active sites, and thus provides a refreshing approach to steering catalytic reactions toward desired products.

The SCILL concept was first developed in heterogeneous catalysis,^[17] soon transferred to many reactions and is recently intensively applied to many electrocatalytic reactions, for example, oxygen reduction, oxygen evolution, carbon dioxide (CO₂) reduction, which play critical roles in future clean energy conversion technologies.^[23–25] In the present review, after a brief introduction to the history and development of SCILL concept, we present an overview about the exciting progress of the SCILL concept in electrocatalysis, by highlighting some exemplary applications and the latest mechanistic understandings of the roles of ILs, aiming at providing some guidelines on further exploring the potential of the SCILL concept as an innovative and generic tool to tune electrocatalysts for maximizing their efficiency.

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2. What is the SCILL Concept?

2.1. History

Room temperature ILs are usually defined as salts with melting point below 100 °C, featuring extremely low vapor pressure

(10^{-9} mbar), highly tunable solubility/miscibility, good thermal stability, high ionic conductivity, and non-flammability.^[26–28] These unique features have made ILs highly appealing to applications for catalysis.^[29,30] However, industrial applications of ILs (mainly as reaction media) are limited by the high cost and technical issues related to handling of ILs in large quantities.^[31,32] These drawbacks have stimulated the development of IL thin film technologies, which use ILs as thin film in order to take the advantage of the unique properties of ILs without bringing in concerns on either the cost or technical risk scaling with IL quantity.^[33] Among these efforts, two conceptually distinct approaches, that is, supported ionic liquid phase (SILP) and SCILL, can be seen as game changers.^[34,35]

The SILP concept was first introduced by Mehnert in 2002 for hydroformylation of 1-hexene,^[36,37] and was then applied to many other reactions such as hydrogenation,^[38–40] water gas shift reaction,^[41,42] alkene metathesis,^[43,44] hydroamination, and carbonylation of methanol.^[45] The SILP catalysts, which are prepared by immobilizing homogeneous catalysts in a supported thin IL film, can be seen as the case of supported homogeneous catalysts.^[21] The thin film of IL is held within the pores of the support by capillary force, electrostatic and/or hydrogen bond interactions.^[26] The SILP concept not only combines the advantages of homogeneous catalysis (high activity/selectivity under mild conditions) and heterogeneous catalysis (facile catalyst recycling/product separation, continuous operation), but also circumvents the drawbacks of conventional homogeneous catalysts involving biphasic IL/organic solvent media, because both the IL usage and mass transfer resistance are minimized due to the thin IL thickness and associated low diffusion resistance and high surface area for mass transfer between both fluid phases.^[17] As a strong analogy to the SILP, the SCILL concept was proposed for the first time by Jess et al. in 2007 for selective hydrogenation reaction.^[17] Both SILP and SCILL catalysts are prepared by coating solid support materials with a thin IL film, while in contrast to the SILP system composing of an inert support and a thin IL film containing homogeneously dissolved catalysts (e.g., metal complexes), the solid host material in a SCILL system itself is catalytically active (Figure 1). To be noted, solid materials in a SCILL system are not necessarily supported metal catalysts, and in some cases bulk or unsupported catalysts can also be directly employed as solid host materials for constructing SCILL systems.

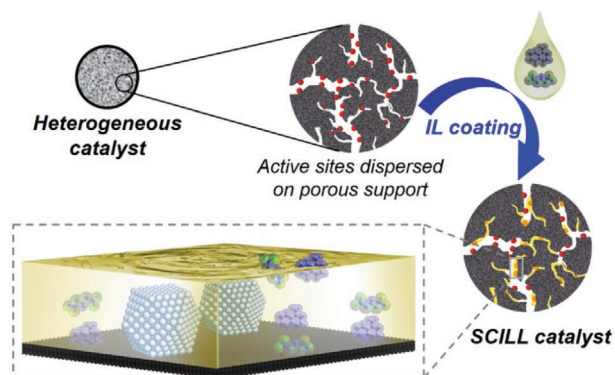


Figure 1. Schematic illustration of the SCILL concept.

The purpose of the SCILL concept is to explore the feasibility of improving the activity and/or selectivity of catalysts by introducing a new phase at the catalyst surface. As exemplified by Jess et al. in their conceptual work on consecutive hydrogenation of cyclooctadiene (COD) to cyclooctene (COE) and cyclooctane (COA), the presence of a small amount of IL 1-butyl-3-methylimidazolium octyl sulfate ($[C_4C_1im][C_8H_{17}SO_4]$) on Ni/SiO₂ catalysts increases the maximum yield of COE from 40 to 70% (Figure 2).^[17] Inspired by this pioneering work, numerous studies have been performed from both the applied and fundamental point of view, and the SCILL concept has been successfully applied to a wide range of heterogeneous catalytic processes such as hydrogenation,^[46,47] isomerization,^[48] and hydrodesulfurization reactions.^[49] These studies show great promise of the SCILL concept in tailoring the catalytic properties of heterogeneous catalysts. At the same time, many informative conclusions about the interfacial structures as well as mechanistic understandings of ILs on solid catalysts have been derived. In the following sections, we will briefly discuss these aspects, which will also constitute the basis of understanding the emerging applications of the SCILL concept in electrocatalysis.

2.2. Mechanistic Considerations

In the pioneering work of Jess et al., the enhanced selectivity to the intermediate COE on the SCILL catalysts was partially attributed to the low solubility of COE in the IL, which decreases the reaction rate of the consecutive hydrogenation.^[17] By examining some other hydrogenation reactions over SCILL systems, it is revealed that on a SCILL catalyst the reaction selectivity is sensitive to the solubility of both reactant and intermediate in the IL, while the reaction rate is mainly determined by the solubility of the reactant. In principle, a higher reaction rate can be achieved when the reactant has a higher solubility in the IL. These results point out the physical solvent effect of the IL, that is, the IL can take effect by modifying the effective local concentration of either reactants or intermediates at the active sites.^[26]

ILs can also take effect by modifying electronic structure of the solid catalysts (ligand effect). Claus et al. studied the selective hydrogenation of citral on IL coated Pd/SiO₂ catalysts, and found that the IL 1-butyl-3-methylimidazolium dicyanamide ($[C_4C_1im][N(CN)_2]$) increased the selectivity of partially hydrogenated product citronella up to 99% (40% on pristine catalyst).^[18,19] X-ray photoelectron spectroscopy (XPS) analysis revealed the IL promoted the surface oxidation of Pd, leading to weakened chemisorption of hydrogen on Pd.^[19] The exact ligand effect is, however, specific to both ILs and catalysts. Etzold et al. probed the IL modified copper foam catalysts using high resolution XPS and Auger spectroscopy, while no evidence of any ligand effect was identified.^[50] Lercher et al. found that, instead of promoting the surface oxidation of metal nanoparticles as proposed by Claus et al., the IL 1-butyl-2,3-dimethylimidazolium trifluoromethylsulfonate ($[C_4C_1C_1im][TfO]$) actually protected Pt against oxidation, and in return Pt enhanced the electron density of the IL at its N site.^[51] Libuda et al. studied IR spectroscopic features of adsorbed carbon monoxide (CO) on supported Pt nanoparticles using IR reflection absorption spectroscopy (IRAS), and observed that the IL 1-butyl-3-methylimidazolium

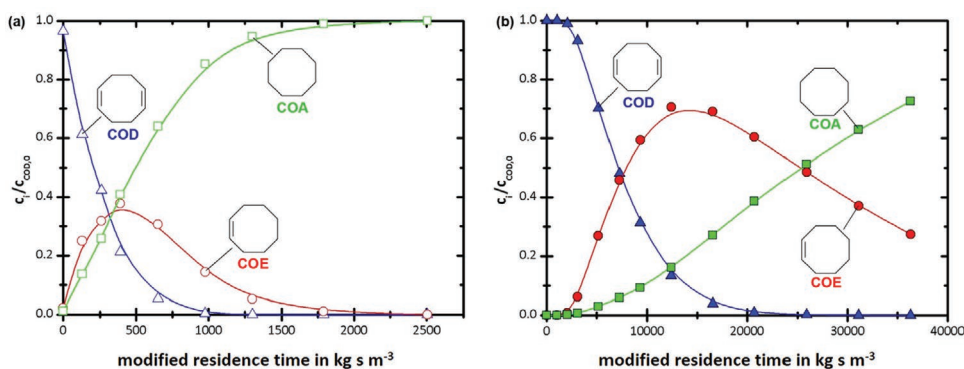


Figure 2. Residual content of COD and yields of COE and COA on a) pristine and b) IL modified Ni/SiO₂ catalyst. Reproduced with permission.^[17] Copyright 2007, John Wiley and Sons.

bis(trifluoromethylsulfonyl)imide ([C₄C₁im][NTf₂]) induced a red-shift of CO-band by over 30 cm⁻¹, implying that the IL acts as an electron donating ligand, which enhanced π backbonding from Pt to CO.^[52] Similarly, Uzun et al. also reported imidazolium-based ILs acted as electron donating ligands to supported iridium (Ir) cluster, and ligand effect (electron donation degree) showed dependency on the interionic interactions of IL molecules.^[53] These reports verified that ILs can act as surface ligands to modify the electronic structure of active sites, resulting in changes in the chemisorption of reactants/other surface species as well as altered catalytic properties of supported catalysts. Considering the Sabatier principle, which states that the adsorption of the reactive species should be neither too strong nor too weak, the SCILL concept raises the possibility to tune the surface electronic structure of metal active sites by rationally tailoring the molecular structure of ILs for optimum catalytic performance and thus tuning the binding strength of adsorbate.

Besides directly modifying the surface electronic structure of metal catalysts, IL may also limit the accessibility of reactants to specific active sites through competing adsorption. Claus et al. pointed out that the presence of the IL ([C₄C₁im][N(CN)₂]) restricted the accessibility of hydrogen toward the Pd sites due to the strong IL-Pd interactions,^[54] which contributed to the altered catalytic selectivity of Pd toward hydrogenation reaction. Libuda et al. demonstrate that the interaction between [C₄C₁im][NTf₂] and metal surfaces (Pt, Pd) was strong enough to partially replace the chemisorbed adsorbate such as CO molecules.^[55] All these results demonstrate that ILs are beyond a mere surface modifier but in many cases acting as an active participant during the catalytic processes.

Summing up, ILs in SCILL systems can function through a multifold manner: 1) ILs can modify the effective concentration and/or local mass transfer behavior of reactants and/or intermediates at the active sites, because of the different solubility and/or diffusion coefficient of these species in ILs compared to that in conventional reaction solvents;^[40,41] 2) ILs may act as surface ligands by directly interacting with the active sites, inducing varied surface electronic structure as well as adsorption/desorption properties; 3) ILs can be a selective weak poison for unwanted surface sites through competing adsorption, leading to altered product spectrum (reaction selectivity). Moreover, it is also reported that ILs in SCILL systems can provide a steric and electrostatic protection against agglomeration of

active metal nanoparticles, and therefore the SCILL concept in principle offers the opportunity to fully manipulate the catalytic properties (activity, selectivity, and stability) of a solid catalyst.

2.3. Interfacial Structures of ILs

The interfacial structure of ILs at catalyst surfaces has been recognized to play a pivotal role in determining catalytic properties. Intensive research efforts have been made to gain a molecular level understanding of the structures of IL at solid surfaces, such as arrangement of anions and cations, orientation of end groups for bulky ILs, location of IL molecules at different specific sites, spatial distribution of ILs, and interfacial interactions of ILs with support or metal nanoparticles.^[56] There have already been some comprehensive works studying the distribution behavior of ILs within pores of porous materials or on surfaces of solid materials following the SCILL or SILP concept, while it turns out that the distribution behavior of ILs is highly dependent on the identities of both ILs and solid materials.^[20,57] On the way to achieving detailed understandings of the interfacial structures of ILs, great successes have been achieved using those well-developed surface science techniques, for example, XPS, X-ray absorption spectroscopy, low energy ion scattering, electron energy-loss spectroscopy (EELS), scanning tunneling microscope (STM).^[56] The extremely low IL vapor pressure (typically < 10⁻⁹ mbar) allows studying the IL structures of a SCILL catalyst under ultra-high vacuum conditions that are required for surface science techniques.^[58]

Steinrück et al. first used angle-resolved XPS (ARXPS) to study the arrangement, orientation, and ordering of IL thin films on single crystal Au and Ni surfaces,^[59,60] and found that the interfacial structure of ILs depend on the chemical identities of both the IL and substrate. On Au(111), they found that both 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₈C₁im][NTf₂]) and 1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [C₁C₁im][NTf₂] tend to stay in direct contact to the substrate for the first layer, with cation and anion adsorbed next to each other and forming a unique checkboard-like structures. The IL film tends to grow in a layer-by-layer mode, while the lengthy alkyl chains of [C₈C₁im] cation reorient and point away from surface with further increasing the IL coverages.^[61] Most recently, they drew the same conclusion on Ag(111) surface, showing that cation is adsorbed

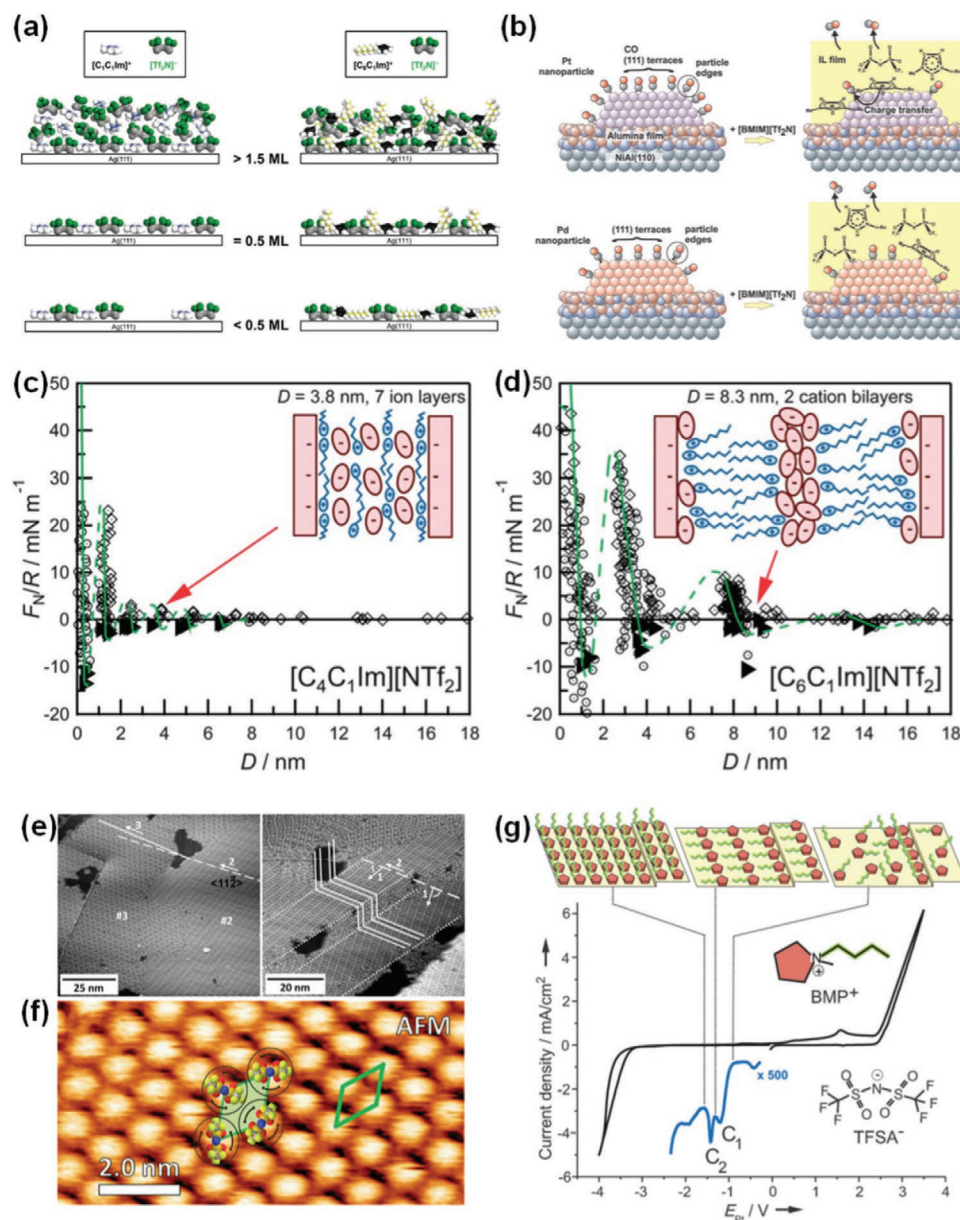


Figure 3. a) Scheme showing the IL arrangements at different coverages on Ag(111) surface based on ARXPS results. Reproduced under the terms of the Creative Commons Attribution License 4.0.^[62] Copyright 2020, The Author(s), Published by Informa UK Limited, trading as Taylor & Francis Group. b) Schemes for Pt and Pd nanoparticles supported on $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ surfaces in presence of IL $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ and adsorbed CO molecules. Reproduced with permission.^[55] Copyright 2011, Wiley-VCH Verlag GmbH & Co. KGaA. c,d) Surface force between two negatively charged mica surfaces in presence of ILs, as a function of separation distance. The insets show the proposed ion laying structure of ILs. Reproduced with permission.^[68] Copyright 2013, Royal Society of Chemistry. e) STM images showing 2D crystalline structure of $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$ on Au(111) surface at ≈ 110 K. Reproduced under the terms of the Creative Commons Attribution License 3.0.^[69] Copyright 2015, Royal Society of Chemistry. f) AFM images showing ordered structure of $[\text{C}_1\text{C}_1\text{im}][\text{NTf}_2]$ on Au(111) at 300 K. The inset shows the sketched model of $[\text{NTf}_2]$ anions with the experimentally determined real space unit cells. Reproduced under the terms of the Creative Commons Attribution License 4.0.^[70] Copyright 2020, American Chemical Society. g) CV of Au(111) in $[\text{C}_4\text{C}_1\text{Pyr}][\text{NTf}_2]$ at room temperature. The schemes show the proposed IL structures at different electrode potentials. Reproduced with permission.^[71] Copyright 2015, Wiley-VCH.

with cation lying flat on the metal surface at low IL coverages (<0.5 monolayer) regardless of the cationic chain length, while further increasing the IL coverage favors detachment of the long cationic chain from the Ag(111) surface, as shown in **Figure 3a**.^[62,63] Behm et al. characterized 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[\text{C}_4\text{C}_1\text{Pyr}][\text{NTf}_2]$ on Au(111) using STM and XPS and observed alternating cations

and anions on Au surfaces and orientation of the C_4 chains pointing toward the vacuum.^[64]

Vibrational spectroscopic techniques have also been intensively applied in understanding the interfacial structure of IL at solid surfaces, and many inspiring conclusions have been drawn. Baldelli et al. studied the molecular orientation of imidazolium-based ILs on a quartz surface using sum-frequency

generation technique, and disclosed that the molecular orientation of IL 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4C_1im][PF_6]$ depends sensitively to the surface contaminants (e.g., trace amount of water).^[65] Libuda et al. employed IRAS to study the specific interaction of IL $[C_4C_1im][NTf_2]$ with Pd/ Al_2O_3 /NiAl(110) model catalyst, and found that the IL molecules tend to adsorb strongly to those low coordinated Pd edge sites (Figure 3b).^[55] They also demonstrated that the IL/solid interactions as well as molecular orientation of IL on solid surfaces can be tailored by introducing suitable functional groups to IL molecules.^[66] Moreover, the interfacial structures of IL also show dependency on its specific molecular structure. For instance, an imidazolium-based IL with long alkyl side chains on its cation, namely 1,3-didodecylimidazolium $[C_{12}C_{12}im]$, exhibits a unique liquid-crystalline structure on a Pt(111) surface as revealed by their IRAS analyses.^[67] Ordered structure of imidazolium-based ILs with long side chains is also reported by Perkin et al., who studied the interfacial structures of $[C_4C_1im][NTf_2]$ and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_6C_1im][NTf_2]$ on an atomically smooth mica surface using a surface force balance.^[68] They revealed that elongation of side chain length from C4 to C6 led to structure rearrangement from alternating cation and anion monolayer structure of $[C_4C_1im][NTf_2]$ to lipid-like bilayer structure of $[C_6C_1im][NTf_2]$, as shown in Figure 3c,d. The long-range ordered structure of ILs (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_2C_1im][NTf_2]$, $[C_8C_1im][NTf_2]$) can also be identified on the Au(111) and Ag(111) surfaces using STM technique at 110 K, as shown in Figure 3e,f.^[69] Most recently, for the first time the images of the IL ($[C_1C_1im][NTf_2]$) on the Au(111) surface were directly captured using both STM and atomic force microscope (AFM) at room temperature (300 K), which clearly verified the long-range-ordered structure of the IL on single crystal surface.^[70] Based on these results, it can be seen that the specific molecular structures of IL at the IL/solid interface are determined by a complex interplay of a wide range of parameters including the nature of solid substrates, molecular structures (e.g., chain length, functional groups, identities of cation/anion) of ILs, and even surface contaminations. Nevertheless, transferring this knowledge to electrocatalytic systems following the SCILL concept should be made with caution, because a dynamic structure of ILs is to be expected on charged surfaces with varied electrode potentials (Figure 3g).^[71,72] Therefore, a new level of complexity is broached when assessing the interfacial structure of ILs in SCILL systems under electrocatalytic operating conditions.^[73]

3. SCILL Concept in Electrocatalysis

Intrigued by the great success of the SCILL concept in heterogeneous catalysis, growing research interests have been attracted to transfer the SCILL concept to electrocatalysis. These research endeavors are mainly motivated by the high demand of improved electrocatalysts that enable several key electrochemical conversion processes, especially those involving water, hydrogen, and oxygen (e.g., hydrogen evolution, oxygen reduction/evolution).^[74,75] These electrochemical processes coupling with renewable energy are expected to play a critical

role in mitigating the energy crisis and global warming due to the usage of fossil fuels.^[74] There have been intensive research efforts carried out to develop high-performing electrocatalytic systems for these key electrochemical reactions, and most of these efforts focus on direct structural engineering of active phases, that is, by tuning particle sizes/shapes, and/or surface compositions. However, it is a nontrivial task to synthesize catalytic materials with well-defined structures especially on a large scale, and at the same time recycling of some precious components, such as Pt in oxygen reduction reaction (ORR) catalysts and Ir/Ru in an OER catalyst, might involve complex procedures that can cause some economic concerns. Therefore, it is still highly desirable to develop alternative approaches to improving the efficiency of electrocatalysts. Over the past decade, substantial progress has been made in applying the SCILL concept in the field of electrocatalysis, which is first demonstrated for the ORR and soon successfully extended to oxygen evolution and electrochemical CO_2 reduction reactions (Figure 4).^[17,23,24,36,50,76–80] The electrocatalysts used for constructing SCILL systems include classic carbon supported Pt nanoparticles,^[24,73,76,81–83] bi-/multi-metallic Pt-based catalysts with innovative structures (e.g., alloys with well-defined shapes, nanoframes),^[23,77,80,84] and also emerging NPMCs, for example, iron-nitrogen-carbon (Fe–N–C), N-doped carbons, cobalt sulfide (CoS_2).^[78,79,85,86] A wide range of ILs have been employed for preparing SCILL-based electrocatalysts, as summarized in Figure 5. In the following section, a comprehensive overview of

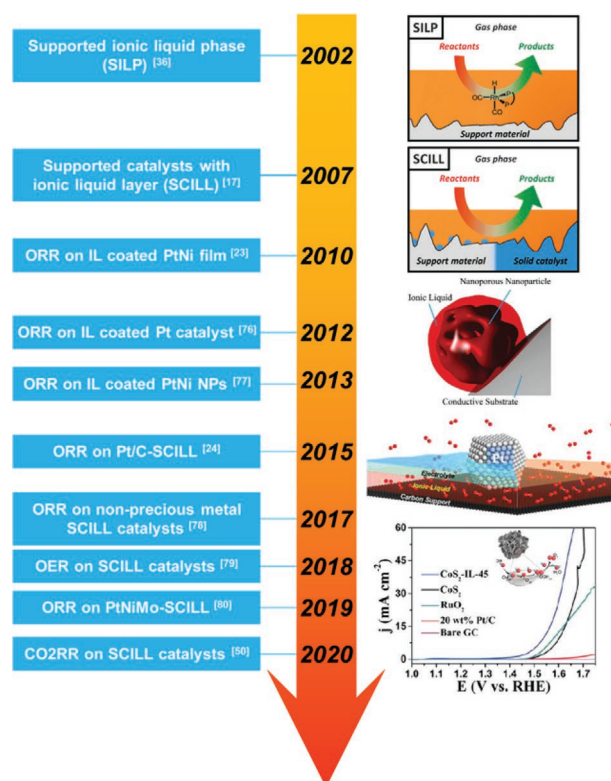


Figure 4. Historical development of SCILL concept in electrocatalysis. Reproduced with permission.^[58] Copyright 2010, Royal Society of Chemistry. Reproduced with permission.^[77] Copyright 2013, Wiley-VCH. Reproduced with permission.^[79] Copyright 2018, Royal Society of Chemistry.

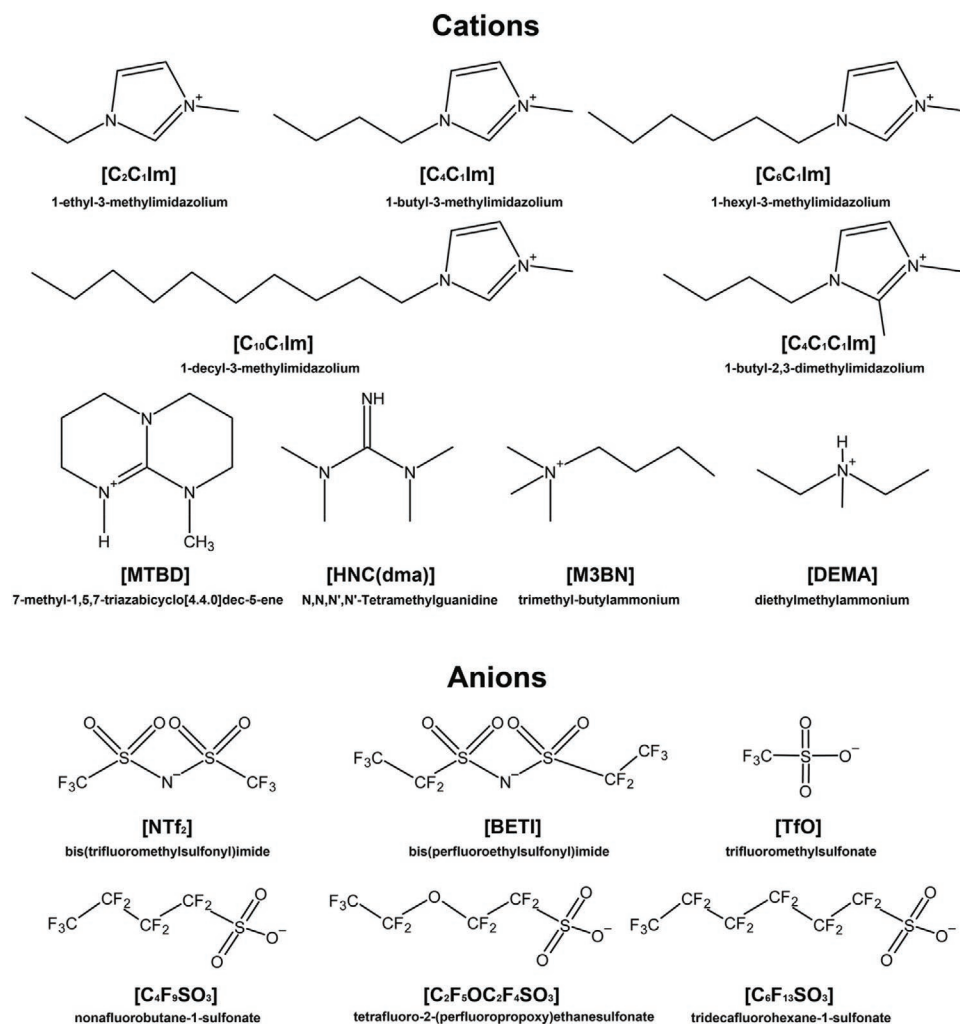


Figure 5. Molecular structures of cations and anions of ILs commonly employed for IL modification of electrocatalysts.

emerging applications of SCILL concept in developing electrocatalysts is presented.

3.1. The SCILL Concept in Developing Pt-Based ORR Catalysts

The high cost and limited stability of the ORR catalysts (e.g., Pt/C) represent a major barrier to the broad-based applications of low temperature fuel cell technology and metal-air batteries, which are expected to play important roles in the future clean energy scenario due to their high efficiency and low emission.^[87–89] Developing advanced ORR electrocatalysts has thus attracted enormous interest in electrochemistry over the past two decades.^[88–91] The first attempt to improve an ORR catalyst by introducing IL into a solid electrocatalyst, which in essence falls into the category of the SCILL concept, is pioneered by Erlebacher et al. in 2010 (Figure 6a).^[23] They discovered that the specific activity of nanoporous PtNi film toward the ORR was increased by a factor of 2–3 in acidic electrolyte after impregnating the catalyst with a hydrophobic IL 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene bis(perfluoroethylsulfonyl)imide ([MTBD]

[BETI]). It was found that hydrophobicity and capillary forces exerted by nanopores pulled the IL inside the catalysts and prevented it from being washed away by aqueous electrolyte. The IL boosting effect was also observed on PtNi nanoparticles and the superior performance of the IL impregnated catalyst can be transferred to a polymer electrolyte membrane fuel cell (PEMFC) (Figure 6b).^[77] The IL boosting effect was also successfully transferred to a highly active catalytic system, namely Pt₃Ni nanoframes, on which the specific activity of Pt toward the ORR at 0.95 V versus reversible hydrogen electrode (RHE) is increased from 1.5 to 2.0 mA cm⁻² after IL ([MTBD][BETI]) modification (Figure 6c).^[84] Similarly, Xie et al. reported that graphene supported Pt nanoparticles showed two times higher specific activity toward the ORR in 0.1 M HClO₄ after IL ([MTBD][NTf₂]) impregnation than its pristine counterpart (Figure 6d), and at the same time they found that the presence of IL improved the methanol tolerance of Pt catalyst.^[76] Nevertheless, despite the great similarity to the SCILL concept, the IL phase in these studies is usually introduced with little controllability. For instance, the IL impregnation was implemented by placing an IL droplet onto the catalyst coated rotating disk electrode (RDE)

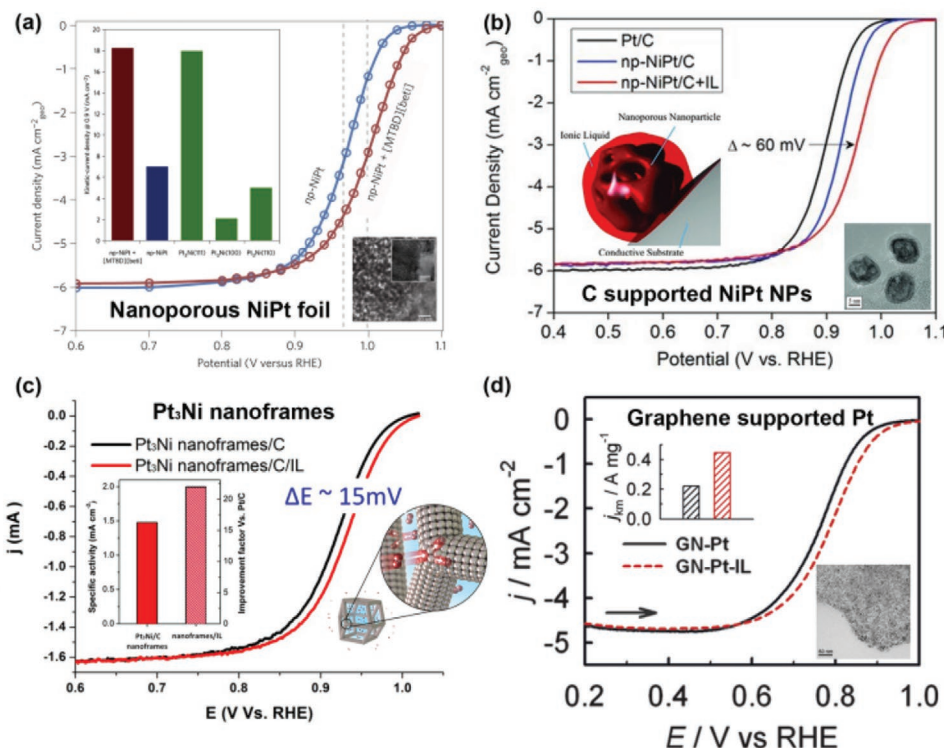


Figure 6. Pioneering works of the SCILL-based catalysts for the ORR. Polarization curves of pristine and IL modified ORR catalysts: a) Nanoporous NiPt foil ([MTBD][BETI]); b) Carbon supported NiPt nanoparticles ([MTBD][BETI]); c) Carbon supported Pt₃Ni nanoframes ([MTBD][BETI]); and d) Graphene supported Pt nanoparticles ([MTBD][NTf₂]). The insets in (a) show the specific activity (at 0.9 V) and TEM image of porous NiPt foil. The insets in (b) show the scheme and TEM image of IL encapsulated NiPt NPs. The insets in (c) show the scheme and the specific activity (at 0.95 V) and scheme of Pt₃Ni nanoframes. The insets in (d) show the specific activity (at 0.85 V) and TEM image of graphene supported Pt NPs. All these measurements were performed in 0.1 M HClO₄. Reproduced with permission.^[23] Copyright 2010, Springer Nature. Reproduced with permission.^[76] Copyright 2012, Royal Society of Chemistry. Reproduced with permission.^[77] Copyright 2013, Wiley-VCH. Reproduced with permission.^[84] Copyright 2014, AAAS.

while the excess IL was spun off from the RDE prior to a further cleaning procedure.^[23,76] Besides the ill-controlled loading amount of IL on solid catalysts, it is also difficult to achieve large scale production by employing the above procedure.

3.1.1. IL Loadings

Adapting the knowhow from the previous research on SCILL-based heterogeneous catalysts, Etzold et al. systematically explored the influence of IL loadings on Pt-based ORR catalysts, by impregnating varying amounts of IL ([MTBD][NTf₂]) into the pores of a carbon supported Pt catalyst (Pt/C),^[24] as shown in **Figure 7a**. The SCILL samples were prepared by dispersing Pt/C catalysts in an isopropyl alcohol solution containing a certain amount of pure [MTBD][NTf₂], followed by a multi-step solvent evaporation.^[24] It is disclosed that both the activity and stability of IL-modified Pt/C (Pt/C-SCILL) showed dependency on the pore filling degree of IL (α), which is defined as:

$$a = \frac{V_{IL}}{V_{pore,0} \cdot m_{cat}}, V_{IL} = \frac{m_{IL}}{\rho_{IL}} \quad (1)$$

where V_{IL} and $V_{pore,0}$ are the volume of the IL (mL) and specific pore volume of pristine Pt/C sample (mL g⁻¹), respectively;

ρ_{IL} is the density of the IL (≈ 1.5 g cm⁻³); m_{IL} and m_{cat} are the mass of the IL and catalyst (g), respectively. In this work, the pore filling degree has been well controlled in the range of 2% to 100%, as reflected by that α -values of SCILL samples determined experimentally using N₂-sorption agree well with their corresponding theoretical ones. Moreover, It is also found that the IL tends to first fill the micropores which is consistent with the observations in preparing heterogeneous SCILL catalysts with combined micro- and mesopores.^[17] These results provide a solid piece of evidence that the IL is immobilized within the pores instead of randomly adsorbed/aggregated on the outer surface of the catalyst, and the IL phase tends to be confined within the pores even at a low IL loading.^[24] As also the case for SCILL-based heterogeneous catalysts, the IL pore filling degree also imposes significant effect on the properties of an electrocatalyst. First, it is observed that the electrochemically active surface area (ECSA) of Pt, which defines the exposed Pt surfaces that can participate in an electrocatalytic process, has decreased by $\approx 12\%$ after introducing the IL at $\alpha = 2\%$ and by up to 19.2% at $\alpha \geq 10\%$ (Figure 7b,c). At the same time, the coverage of non-reactive oxygenated species (identified mainly as adsorbed hydroxyl groups) on Pt surfaces also decreases by over 20% on IL-modified samples compared to that on pristine counterpart (Figure 7b,c). This result provides a solid piece of evidence that the IL can help suppress the formation of

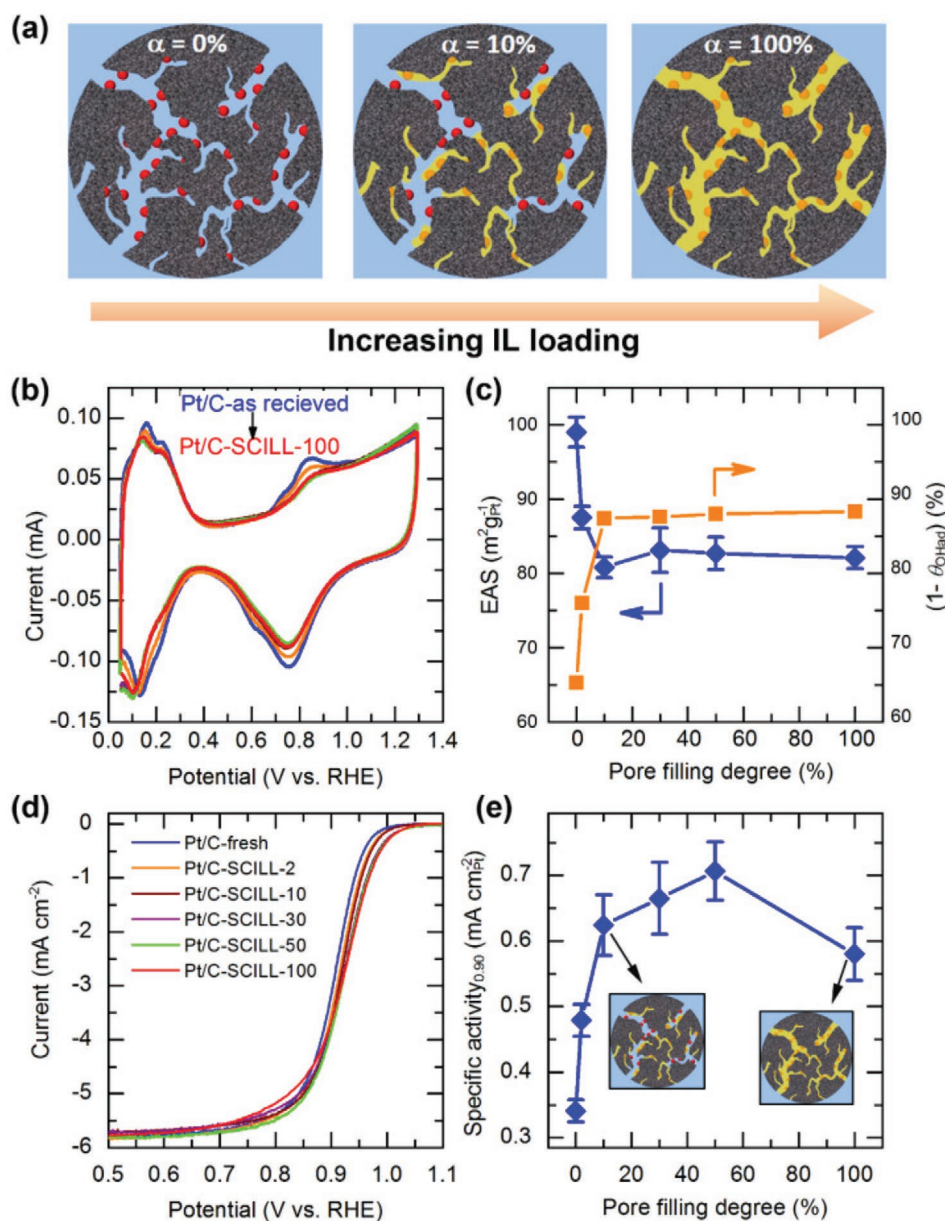


Figure 7. a) Schematically illustration of the SCILL systems with different pore filling degrees. The Pt NPs, carbon support and IL are shown in red, black, and yellow, respectively. b) CV curves of Pt/C-SCILL systems in N_2 -saturated 0.1 M HClO_4 . c) ECSA of Pt and free Pt sites plotting against the pore filling degrees for Pt/C-SCILL. d) ORR polarization curves and e) specific activity of pristine Pt/C and Pt/C-SCILL at different pore filling degrees. Reproduced with permission.^[24] Copyright 2015, American Chemical Society.

non-reactive oxygenated species on Pt surfaces, which is highly desirable for an active ORR catalyst considering that these non-reactive oxygenated species acts as the major cause for the slow ORR kinetics.

The electrocatalytic measurements show that all Pt/C-SCILL samples exhibit superior ORR activity to pristine Pt/C catalyst in terms of both specific and mass activity in 0.1 M HClO_4 . The specific activity of Pt at 0.95 V increases monotonously with the pore filling degree of IL. The maximum value (0.13 mA cm^{-2}) is observed on the SCILL sample at $\alpha = 100\%$, on which the pore of the catalyst is in principle fully flooded by the IL, and is 3.4 times that of pristine Pt/C (0.04 mA cm^{-2}). Intriguingly, when the specific activity is compared at a lower potential, that

is, 0.9 V , where diffusion-limitation plays a more significant role in controlling the reaction rate, the maximum specific activity is obtained at $\alpha = 50\%$, and a dramatic activity drop is observed when further increasing α to 100% (Figure 7d,e). This volcano dependence of specific activity on α -value can be seen as a consequence of the combined action of IL-induced positive and negative effects. Specifically, the presence of IL can on one hand help suppress the formation of non-reactive species on Pt and facilitate the ORR kinetics; on the other hand, the viscous nature of IL gives birth to almost two orders of magnitudes lower diffusion coefficient of O_2 molecules in IL than that in aqueous solutions, which may restrict the mass transfer process especially at high overpotential conditions and consequently

a low apparent kinetics. The study showed the importance to engineer the IL and active site interface at the nanoscale and thus the influence of the immobilization procedure.

3.1.2. Origin of the IL Boosting Effect

Despite the great promise of the SCILL concept in boosting the ORR activity of Pt-based electrocatalysts, a consensus understanding about how Pt activity gets improved using IL has not been reached yet. In their pioneering work, Erlebacher et al. assumed that the accelerated reaction kinetics of the ORR on IL-impregnated PtNi foil or nanoparticles originated from the higher solubility of O₂ in [MTBD][BETI] (2.9 mM) than that in aqueous electrolyte (1.2 mM). By employing another hydrophobic IL tetra-*n*-butylphosphonium 4,4'-trimethylene-dipyridine ([TBP][TMDP]) with lower O₂ solubility (0.9 mM), no boosting effect can be observed as reflected by an increase in the ORR overpotential.^[23,77] To study the effect of O₂ solubility in ILs, Etzold et al. compared the ORR performance of Pt/C catalysts modified with two ILs ([C₄C₁im][NTf₂] and [C₄C₁im][BETI]) possessing different O₂ solubility (2.28 vs 2.90 mM) in 0.1 M HClO₄. First they found that the ORR activity of the both IL-modified catalysts was two to three times more active than the pristine Pt/C, but the ORR activity of both IL-modified catalysts were indistinguishable, indicating that the IL boosting effect is less likely (solely) stemming from the high O₂ solubility in ILs.^[81] Second, by inspecting the cyclic voltammetry (CV) curves of pristine and IL modified Pt/C (Pt/C-[C₄C₁im][NTf₂]) catalysts, they revealed that the oxidation peak corresponding to formation of oxygenated species was significantly suppressed in presence of the IL. Moreover, Tafel slope analyses show that, compared to the Tafel slope on pristine Pt/C (63 mV dec⁻¹), IL modified Pt/C exhibits a Tafel slope of 96 mV dec⁻¹ (@0.9 V), being more close to the intrinsic Tafel slope of ORR on Pt surface that is free from any oxygenated species (120 mV dec⁻¹). These results suggest that the presence of IL could make Pt be less prone to forming surface oxygenated species. Considering that the high coverage of the nonreactive oxygenated species is one of the major causes for the slow reaction kinetics at low overpotential region.^[81] They proposed that the IL boosting effect on the ORR activity would mainly originate from protection of Pt sites from the oxygenated species (Figure 8).^[81] In view of that O₂ solubility in ILs is highly sensitive to the

nature of the anion, Huang et al. comprehensively studied the influence of O₂ solubility in ILs on the ORR activity of Pt/C catalysts by surveying a number of hydrophobic ILs with different anions in acidic electrolyte.^[82] They found no direct correlation between the ORR activity and the O₂ solubility in ILs, and also demonstrated that the ORR activity exhibited linear dependence on the availability of Pt sites free from oxygenated species.^[82] These results point out that the beneficial role of ILs in boosting the ORR activity can originate from the suppression of nonreactive oxygenated species on Pt. As suggested by Huang et al, the high solubility of O₂ in ILs may not necessarily lead to enriched O₂ at the Pt surfaces, largely due to the much lower diffusion coefficient of O₂ in viscous ILs than that in conventional aqueous electrolytes. The long mean free path of O₂ within ILs has compromised the beneficial role of high O₂ solubility, and the product of O₂ solubility and diffusion coefficient for ILs is not advantageous to that for aqueous electrolytes.^[82] Nevertheless, conclusive results on the role of high O₂ solubility in ILs remain elusive. Recommendation for future research in this direction is to vary the O₂ solubility without substantially changing other structural properties of ILs.

3.1.3. Molecular Variations of ILs

IL modification shows great promise to be an effective approach to improving the Pt catalysts toward the ORR. Inspired by the great variety and structural flexibility of ILs, attempts were made to further boost the ORR activity of Pt by tailoring the molecular structures of ILs. The physicochemical properties of ILs such as ionic conductivity, thermal/electrochemical stability, volatility, density, and viscosity are determined by the complex interactions between ions (e.g., intermolecular force, Columbic force, hydrogen bond) in addition to the identity of both anions and cations.^[92–94] Task specific designs of ILs thus offer the possibility to rationally tune catalytic properties of a SCILL systems at a molecular level.^[57,95] In the following section, some recent advances in exploring the IL boosting effect on the Pt-catalyzed ORR through molecular variation of ILs are introduced.

Cation engineering: IL cations are usually composed of organic heterocycles (e.g., imidazolium, thiazolium, triazolium, pyrrolidinium, pyroazolium), or quaternary ammonium/phosphonium.^[96] Compared to anion engineering, modifications on cations are more common in literature because they

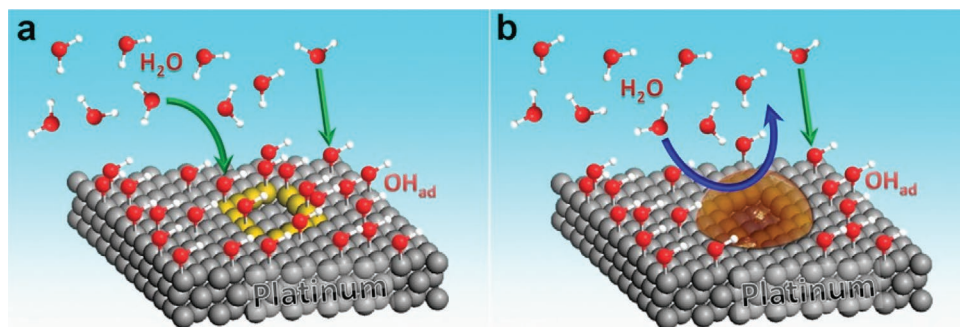


Figure 8. A schematic illustration showing that the IL help protect low-coordinated Pt sites from being poisoned by nonreactive oxygenated species. a) Pt/C and b) Pt/C-SCILL. Reproduced with permission.^[81] Copyright 2016, Wiley-VCH.

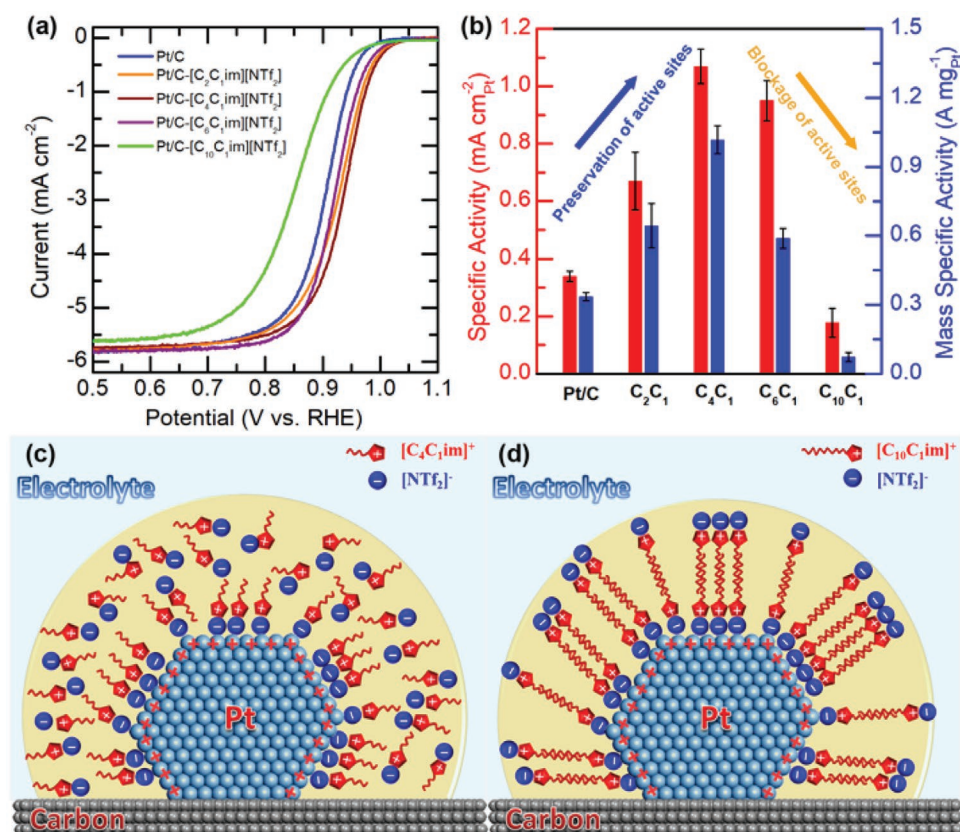


Figure 9. a) ORR polarization curves of pristine and IL modified Pt/C catalysts and b) comparison of mass and specific activity of Pt for the ORR at 0.9 V versus RHE. c,d) Schemes showing the proposed structures of IL-modified Pt/C samples with short and long alkyl chains in imidazolium cations on positively charged electrodes. Reproduced with permission.^[73] Copyright 2018, American Chemical Society.

can be targeted at specific properties of cations (e.g., molecular size, orientation, charge distribution).^[97] Erlebacher et al. investigated a number of hydrophobic ILs with different anions ([MTBD], [C₄C₁IM], HNC[DMA], [M₃BN]) in NiPt-IL composite catalysts using a unique planar flow cell with 0.25 M HClO₄ as the electrolyte, and correlated the ORR performance with the physical properties (e.g., water contents, viscosity, O₂ solubility) of ILs.^[98] They found that all NiPt-IL composite catalysts exhibited a more positive half-wave potential than the pristine counterpart, and suggested that more significant IL boosting effect on the ORR could be obtained using the ILs with higher O₂ solubility and lower water contents. To be noted, excess amounts of ILs were used to prepare the PtNi-IL composite catalysts, and the resultant thickness of IL layer (≈250 μm) is significantly thicker than those systems using the thin film RDE technique, and therefore the role of ILs might deviate from that deduced from conventional RDE setups.

Imidazolium-based ILs are amongst the most studied and common modern ILs, which can be easily synthesized through alkylation of a N-alkylimidazole and subsequent metathesis reaction to incorporate certain anion.^[99] The variations to the alkyl chain length on the imidazolium ring can be realized through modifying the alkyl substituents, which offers imidazolium-based ILs great structural flexibility.^[96] Accordingly, Etzold et al. systematically investigated the effect of cationic chain length of imidazolium-based hydrophobic ILs on the electrochemical properties of IL modified Pt/C catalysts, by varying

alkyl chain length from C2 to C10 (Figure 9).^[73] It is revealed that both ECSA and the ORR activity of Pt shows dependency on the cationic chain length of ILs (Figure 9) in 0.1 M HClO₄. The optimized ORR performance was obtained at medium chain length (C4), as a trade-off between the suppressed formation of oxygenated species on Pt and the surface blockage induced by ILs with elongated cationic chain (Figure 9b). Specifically, the short chain ILs (i.e., [C₂C₁im][NTf₂]) cannot effectively suppress the formation of those oxygenated species on Pt due to their limited hydrophobicity and therefore the Pt activity is not fully boosted after IL modification; however, using ILs with too long cationic chains (e.g., [C₆C₁im][NTf₂], [C₁₀C₁im][NTf₂]) can lead to another extreme, which may end in formation of lipid-like structures of cations on Pt (Figure 9c), along with dramatically reduced ECSA and Pt activity toward the ORR. This study demonstrates the feasibility of optimizing the catalytic performance of a SCILL catalyst through rationally engineering the molecular structure of ILs.

Anion engineering: The nature of anion usually plays a more fundamental role in determining the physicochemical properties of ILs than that of cations.^[100] Etzold et al. studied the effect of anion on the ORR properties of Pt/C catalysts by replacing the [NTf₂]⁻ anion with [BETI]⁻, while it turns out that modification of the anion actually brings about little influence on the catalytic performance of resultant Pt/C catalysts in acidic electrolyte.^[81] Huang et al. conducted a systematic study on the anion effect of ILs on the ORR properties of Pt/C catalysts

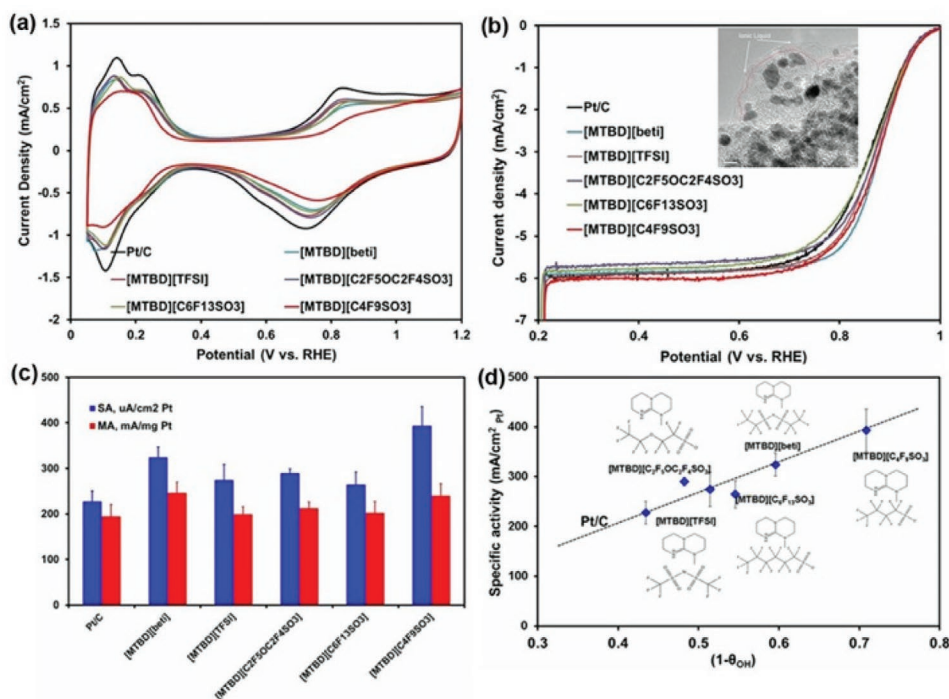


Figure 10. a) CV curves of Pt/C and Pt/C-IL systems in N_2 -saturated 0.1 M $HClO_4$ solution. b) ORR polarization curves in O_2 -saturated 0.1 M $HClO_4$ solution. c) Summary of the mass and specific activity toward the ORR at 0.9 V. d) Plot of specific activity against available Pt sites. Reproduced under the terms of the Creative Commons Attribution License 4.0.^[82] Copyright 2017, The Author(s), Published by ECS.

using a variety of hydrophobic ILs with different anions, which include $[NTf_2]^-$, $[BETI]^-$, $[C_4F_9SO_3]^-$, $[C_2F_5OC_2F_4SO_3]^-$, and $[C_6F_{13}SO_3]^-$.^[82] Combination of these anions with a common cation, that is, $[MTBD]^+$, leads to the formation of various ILs possessing different O_2 solubility and diffusion coefficient. The Pt/C catalyst modified with $[MTBD][C_4F_9SO_3]$ exhibited the highest specific activity (at 0.9 V) toward the ORR in 0.1 M $HClO_4$, while at the same time, it also suffered a loss ($\approx 25\%$) of ECSA due to the presence of the IL (Figure 10). They also found that the O_2 solubility of ILs actually plays a minor role in boosting the ORR performance of Pt catalyst, since the beneficial effect of high O_2 solubility of ILs is largely compromised by the slow diffusion coefficient of O_2 molecules within IL phase. Instead, the specific activity of Pt showed a linear dependence on available Pt sites ($1 - \theta_{OH}$) after IL modification (Figure 10d), and they also proposed that the IL boosting effect would originate from the suppression of non-reactive species on Pt in presence of ILs.^[82]

Capacitive deposition approach: Besides directly engineering the anion or cation structures of ILs, there are also some other approaches leading to molecular variation of ILs. Most recently, Snyder et al. reported a unique sequential capacitive deposition method to introduce IL molecules onto Pt/C catalyst, which was implemented through sequential exposure of the catalyst coated RDE electrode to electrolytes containing either the anion or cation under positive or negative potentials.^[101] Thereby, the double layer capacitive charging acts to pull the ions, resulting in formation of a thin conformal layer of the desired IL within the catalyst. The as-prepared IL modified catalysts can also exhibit enhanced ORR activity and stability in 0.1 M $HClO_4$. This novel method also

raises the possibility to facilely vary the chemical identity of either anions or cations of ILs for catalyst modification.

Polymerization approach: Another approach involves the usage of polymerized IL for improving Pt-based ORR catalysts, which might deviate from the strict definition of a SCILL system. For instance, Ghilane et al. synthesized polymerized IL (poly vinyl-imidazolium-methyl) directly onto glassy carbon electrode using a surface initiated atom transfer radical polymerization process.^[83] The poly (IL) exhibits a unique brush like morphology and can be employed as a host platform for Pt catalysts, on which enhanced ORR activity in acidic electrolyte can be obtained due to either an enlarged interface between Pt and conductive substrate, or an improved dispersion of Pt catalysts.^[83] Similarly, Fang et al. reported that a polymerized IL (poly(DMVBA3-TfO-co-St₇)) can improve the ORR activity of Pt/C catalyst, which was partially benefiting from the aromatic rings induced rigid structure of the poly (IL), facilitating O_2 transportation to Pt sites.^[102]

3.1.4. Electrochemical Stability

Poor electrochemical stability of state-of-the-art Pt-based ORR catalysts is another major barrier to the market penetration of the PEMFC technology.^[103,104] Besides reporting the IL boosting effect on the ORR activity, more and more recent works start addressing the IL modification effect on catalyst stability. In 2015, Etzold et al. reported for the first time that the presence of IL ($[MTBD][NTf_2]$) could improve the stability of a Pt/C catalyst, as demonstrated by a much less loss in ECSA of Pt in SCILL

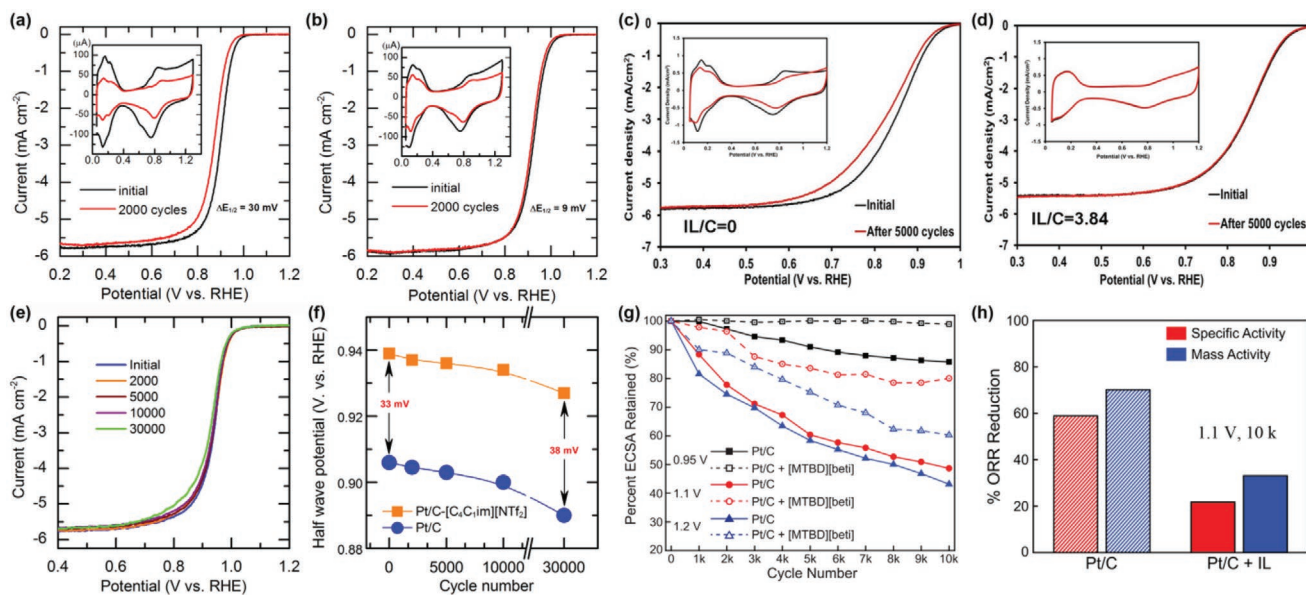


Figure 11. ORR polarization curves of a) pristine and b) IL ([MTBD][NTf₂]) modified Pt/C before and after 2000 potential cycles between 0.4 and 1.4 V in O₂-saturated 0.1 M HClO₄. Reproduced with permission.^[24] Copyright 2015, American Chemical Society. CV and ORR polarization curves of c) Pt/C and d) Pt/C-[MTBD][C₄F₉SO₃] before and after 5000 potential cycles between 0.6 and 1.0 V in N₂-saturated 0.1 M HClO₄. Reproduced under the terms of the Creative Commons Attribution License 4.0.^[82] Copyright 2017, The Author(s), Published by ECS. e) ORR polarization curves on IL ([C₄C₁im][NTf₂]) modified Pt/C after different potential cycles between 0.4 to 1.1 V (O₂-saturated 0.1 M HClO₄). f) ORR half-wave potentials of pristine and IL modified Pt/C after different potential cycles. Reproduced with permission.^[81] Copyright 2016, Wiley-VCH. g) Percentage of retained ECSA and h) percentage of ORR activity reduction of pristine and IL ([MTBD][BETI]) modified Pt/C during the accelerated stability test with a lower potential limit of 0.6 V in Ar-saturated 0.1 M HClO₄. Reproduced with permission.^[101] Copyright 2019, American Chemical Society.

catalysts than that in pristine Pt/C (38% vs 66%) after subjecting the catalysts to repeated potential cycling.^[24] It is observed that the double layer charging region in the CV curves of SCILL samples is well maintained after the stability tests, indicating that carbon corrosion, which represents a major cause for cathode catalyst degradation, is suppressed over SCILL samples (Figure 11a,b). In a follow-up work, they demonstrated that an IL([C₄C₁im][NTf₂]) modified Pt/C catalyst exhibited almost no performance loss during the accelerated durability test in 0.1 M HClO₄ (ADT, 2000 potential cycles between 0.4 to 1.1 V vs RHE), while further increasing the cycle number up to 30000 has induced only a slight drop in ECSA (< 9%). The stability performance of this SCILL sample is also superior to that of pristine sample which exhibits a much more significant drop in the half-wave potential after the stability test (Figure 11e,f). IL-induced stabilization effect on ORR catalysts has also been documented in some other recent studies. Huang et al. reported that the ADT-induced losses in both ECSA and mass activity of Pt/C were significantly alleviated after being impregnated with hydrophobic IL ([MTBD][C₄F₉SO₃]), as shown in Figure 11c,d.^[82] Specifically, the loss in ECSA was reduced from 17.4% to 2.8%, while the loss in mass activity (@0.9 V) was reduced from 42.4 to 5.9% in acidic electrolyte. Moreover, they also found that a higher loading amount of IL was more efficient to stabilize the catalyst. Choi et al. investigated the electrochemical stability of Pt/C and PtNiRu/C with/without hydrophobic IL coating in 0.1 M HClO₄, and observed that IL coated catalysts always exhibited lower activity loss than their pristine counterparts during chronoamperometry measurements (@0.7 V for 9000 s).^[105] More recently, Snyder et al. studied the stability performance of Pt/C catalysts with and without an thin film coating of IL

([MTBD][BETI]), and also observed that the IL-coated Pt/C suffered from much less significant loss in both ECSA and ORR activity in 0.1 M HClO₄ after potential cycling for up to 10000 cycles with different upper potential limits (Figure 11g, 12h).^[101]

It is generally accepted that the improved electrochemical stability of Pt-based catalysts after IL modification can arise from reduced Pt dissolution, lower degree of Pt particle agglomeration or suppressed carbon corrosion.^[103] To unambiguously explore the working mechanisms of ILs in stabilizing Pt-based ORR catalysts, Etzold et al. studied the electrochemical stability of a series of Pt/C catalysts modified with imidazolium-based ILs using combined identical location transmission electron microscopy (TEM) and in situ scanning flow cell coupling to an inductively coupled plasma mass spectrometer (SFC-ICP-MS) analyses (Figure 12). First, it is revealed that all the IL modified samples exhibit improved stability compared to the pristine Pt/C, as evidenced by less significant loss of the ORR half-wave potentials of SCILL samples; second, the stabilizing effect of ILs appears to be insensitive to the nature of cations. Identical location TEM results indicate that pristine Pt/C suffers from severe Pt dissolution, as many particles become much smaller after the ADT as shown in Figure 12a,b. In contrast, Pt nanoparticles on the IL modified Pt/C are well maintained (Figure 12c,d), which implies that an IL can improve the stability of Pt/C by suppressing the dissolution of Pt nanoparticles. To quantify the Pt dissolution during ADTs, they employed an in situ SFC-ICP-MS setup (Figure 12e), which can be used to accurately determine the concentration of dissolved Pt in the electrolyte. They confirmed that SCILL samples exhibit much lower Pt dissolution rate during the degradation tests (Figure 12f), providing another piece of solid evidence that the

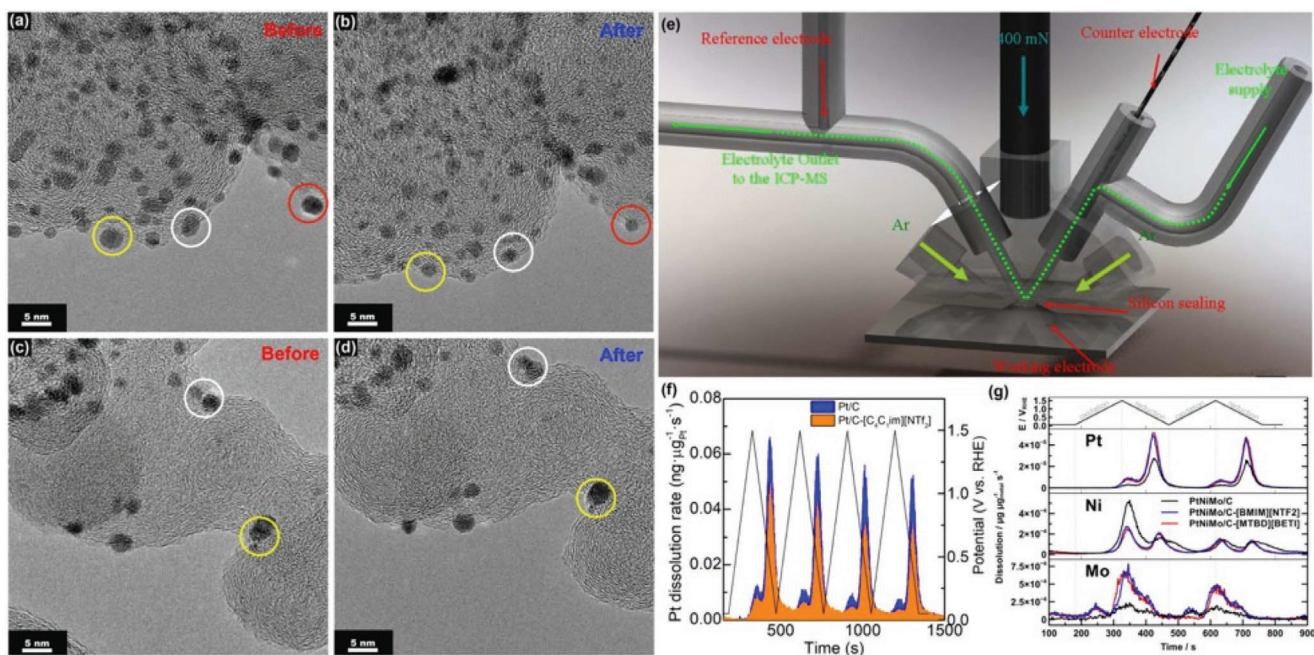


Figure 12. Identical location TEM images of a,b) pristine Pt/C and c,d) IL $[(C_4C_{1im})[NTf_2]]$ modified Pt/C before and after stability tests (2000 potential cycles between 0.4 and 1.4 V in O_2 -saturated 0.1 M $HClO_4$ electrolyte). Reproduced with permission.^[73] Copyright 2018, American Chemical Society. e) A scheme showing the in situ electrochemical scanning flow cell setup before connecting to an ICP-MS for online elemental analysis of the electrolyte. Reproduced with permission.^[104] Copyright 2012, Wiley-VCH. f) Dissolution profiles of pristine and IL $[(C_4C_{1im})[NTf_2]]$ modified Pt/C during four consecutive CV tests between 0.05 and 1.5 V at a scan rate of 10 mV s^{-1} . g) Potential resolved dissolution profiles recorded by in situ ICP-MS for Pt, Ni, and Mo of PtNiMo/C with/without ILs during two consecutive CV tests between 0.05 and 1.5 V at a scan rate of 10 mV s^{-1} . Reproduced with permission.^[80] Copyright 2019, American Chemical Society.

improved electrochemical stability of SCILL samples mainly originate from the suppressed Pt dissolution in presence of ILs.

To be noted, the presence of ILs does not necessarily lead to an improved electrochemical stability. One recent study on the effect of IL modification on the degradation behavior of trimetallic PtNiMo/C catalysts indicates that the presence of IL $[(C_4C_{1im})[NTf_2]]$ has resulted in an enhanced degradation of catalysts (Figure 12g).^[80] Based on in situ SFC-ICP-MS analyses, the IL has selectively accelerated the dissolution of base metal components (i.e., Ni, Mo) in trimetallic PtNiMo/C catalysts, due to hindered formation of passivating oxide layer in presence of the ILs.^[80] Therefore, despite that the SCILL concept shows great promise to improve the performance of ORR catalysts, unexpected degradation mechanism may emerge especially on those advanced catalysts with complex structures. Further extensive research is still needed to identify ILs that won't aggravate dissolution of base metals before leveraging the full potential of the SCILL concept in boosting ORR catalysts

3.1.5. ORR Pathways

The ORR can proceed through two reaction pathways, that is, two- electron pathway to produce H_2O_2 and four-electron pathway to produce water.^[75] To clarify the possible influence of IL modification on the ORR pathways, Etzold et al. performed rotating ring disk electrode (RRDE) measurements on a series of IL-modified Pt/C samples in 0.1 M $HClO_4$.^[24,73,81] The RRDE consisting of a RDE glassy carbon disk and Pt ring is widely employed to quantify the formed H_2O_2 during the ORR.^[106]

It turns out that the mole fraction of H_2O_2 formed during the ORR is lower than 4% for all of the samples regardless of the presence of ILs, identity of ILs being studied or loading amounts of IL on solid catalysts, implying that the ORR on IL modified Pt/C catalysts is proceeding predominantly through the preferred four-electron pathway to produce water, and the presence of IL imposes little impact on the ORR reaction pathway. Nevertheless, it appears that the effect of ILs on the ORR pathway is sensitive to the identity of ORR catalysts. For instance, Ghilane et al. demonstrated that the presence of a polyimidazolium based IL shifts the ORR pathway on carbon dots from two-electron pathway to nearly four-electron pathway over a broad potential range in 0.1 M $HClO_4$.^[86] Opallo et al. prepared carbon paste electrodes (CPEs) using IL $[(C_4C_{1im})[NTf_2]]$ that contains decamethylferrocene as an electron donor, which falls into the category of SILP catalyst.^[107] They found that the IL-impregnated CPE can selectively reduce O_2 into H_2O_2 at the interfaces of IL-aqueous electrolyte (0.1 M $HClO_4$), during which decamethylferrocene that dissolved in the IL phase acted as a reaction mediator to reduce O_2 molecules and thereafter was regenerated at the CPE. These results imply that the introducing IL phase into solid catalysts holds great promise to tune the ORR performance of NPMCs, which will be detailed in the following section.

3.2. The SCILL Concept in Developing NPMCs for the ORR

NPMCs emerge as another important class of the ORR catalysts, which are expected to be inexpensive alternatives to precious

Pt-based catalysts.^[108] Representative NPMs mainly include metal oxides and carbon based materials such as pyrolyzed iron-nitrogen-carbons (Fe–N–C), surface-functionalized carbons, heteroatom doped carbons and metal organic framework derived carbons.^[109] Inspired by the great success of the SCILL concept in improving the ORR performance of Pt-based catalysts, there's growing research interest in applying the SCILL concept for boosting the ORR performance of NPMs.

In 2011, Kim et al. reported that covalent attachment of the IL 1-(3-aminopropyl)-3-methylimidazolium bromide on the graphene nanosheet resulted in a much higher limiting current toward the ORR in 0.1 M KOH, along with a positively shifted onset potential relative to that of the pristine counterpart, which was attributed to combined actions of high ion conductivity and high O₂ solubility of the IL.^[110] Titirci et al. disclosed for the first time that modifying nitrogen-doped carbon (GN) using IL ([C₂C₁im][NTf₂]) can improve its ORR activity in both alkaline and acidic electrolyte, as evidenced by positive shifts in half-wave potential by 31 and 55 mV, respectively (Figure 13a–c).^[78,111] In their follow-up work, Titirci et al. also demonstrated that the ORR activity of IL-modified Fe–N–codoped carbon particles outperformed that of the commercial Pt/C catalyst in alkaline electrolyte, which was attributed to the promoted oxygen adsorption and facilitated proton transfer in presence of the IL ([C₂C₁im][NTf₂]).^[112] Kramm et al. reported almost in parallel the boosting effect of IL on the ORR performance of Fe–N–C electrocatalysts which are generally considered as the most promising NPMC category toward the ORR.^[85] The Fe–N–C electrocatalysts were synthesized through a pyrolysis approach, and the IL modification was implemented by coating the as-prepared Fe–N–C catalysts with hydrophobic IL ([C₄C₁C₁im][NTf₂]) with the IL pore filling degree ranging from 10 to 50%. It is found that introducing IL can be an effective way to improve both the catalytic activity and stability of NPMs for the ORR in alkaline electrolyte, which is consistent with the observation on Pt-based ORR catalysts. The most pronounced performance enhancement was observed on the SCILL sample with medium pore filling degree of IL (≈20%). The IL seems to take effect in boosting the ORR activity by increasing the electrochemically assessable surface area of Fe–N–C catalysts, as reflected by a good correlation between the ORR activity and the double layer charging current.^[85] Du et al. reported that the IL ([C₄C₁im][NTf₂]) can also boost the ORR performance of ZIF-derived carbon (ZnCoNC) in acidic electrolyte (Figure 13d–f). Specifically, the diffusion limiting current is enhanced by a factor of 1.6 and electron transfer number is increased from 2.6 to 3.9.^[113] Most recently, the SCILL concept has been successfully applied to perovskite oxide-based ORR catalysts.^[114] The presence of a hydrophilic IL 1-butylimidazolium-3-N-propanesulfonate N, N-bis(trifluoromethylsulphonyl)amine has boosted the intrinsic activity of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3–δ} (BSCF) perovskite oxide toward the ORR in 0.1 M KOH by 2.7 times, along with a positively shifted half-wave potential of 40 mV. It is also uncovered that the IL can take effect by promoting the exposure of catalytically active sites, and a charge transfer from BSCF to the IL was also identified, which might lead to an optimized surface electronic structure of BSCF toward the ORR. All these works emphasize the great importance

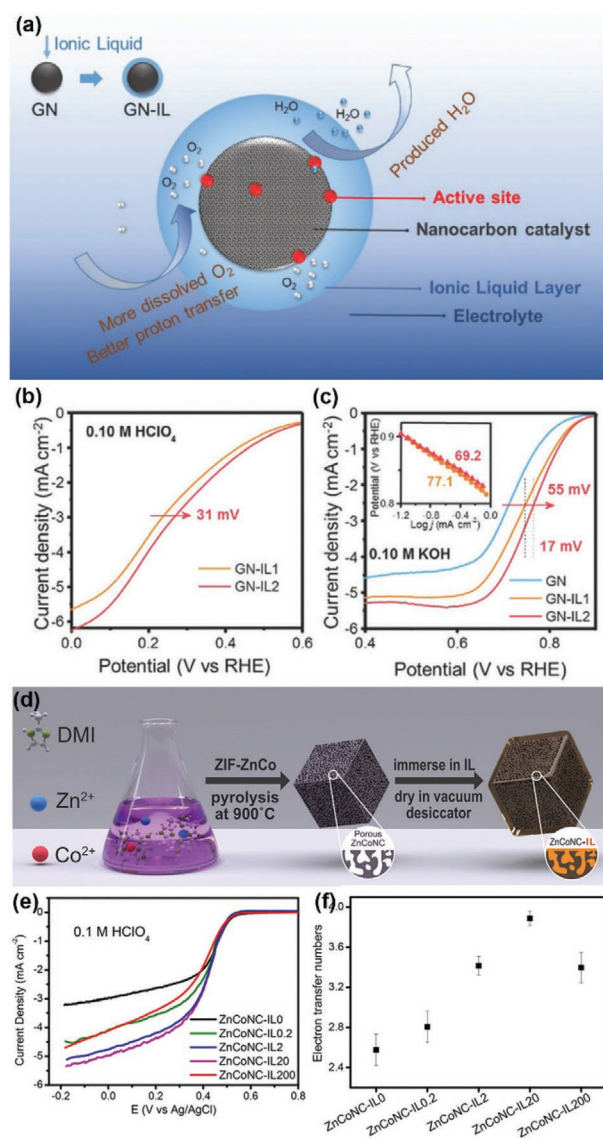


Figure 13. a) A scheme showing the synthesis and triple phase interface between solid-liquid and gas. ORR polarization curves of N doped graphene (GN) modified with [C₄C₁im][NTf₂] (IL1) and [C₂C₁im][NTf₂] (IL2) in b) acidic and c) alkaline electrolyte. Reproduced with permission.^[78] Copyright 2017, Royal Society of Chemistry. d) A scheme showing the synthesis of IL ([C₄C₁im][NTf₂]) modified ZnCoNC catalysts. e) ORR polarization curves of the pristine and IL modified catalysts in acidic electrolyte and f) corresponding average electron transfer numbers during the ORR. Reproduced with permission.^[113] Copyright 2019, American Chemical Society.

of the SCILL concept in optimizing the NPMs toward the ORR, again demonstrating that the SCILL concept holds great potential to be a generic method in improving the ORR catalysts besides directly engineering structures of active sites. Many factors (e.g., accessible surface area, hydrophobicity, oxophilicity, H⁺/water/OH⁻ conductivity) have been invoked for the IL boosting effect on NPMs, while a consensus conclusion remains elusive. Further extensive efforts especially those based on spectroscopic/microscopic techniques and theoretical calculation/simulations approaches are still greatly desired.

3.3. Practical Applications of SCILL-Based ORR Catalysts in PEMFCs and Metal-Air Batteries

Although a huge number of high-performing ORR catalysts have been developed to date, their impressively high activity in most cases is reported based on the thin-film RDE technique due to its facile accessibility and well-established testing protocols.^[89] However, typical testing conditions of the RDE technique are far away from those of practical fuel cell membrane electrode assemblies (MEAs). For instance, due to the limited solubility and poor mass transfer of O₂ in aqueous electrolyte, the achieved current in RDE setups is usually 2 to 3 orders of magnitude lower than that in MEAs. Moreover, the technical issues in a real fuel cell such as MEA related factor/components, different ionomer content and deposition methods in preparing catalyst layers cannot be reflected in RDE tests. Therefore, despite that the RDE technique offers a convenient way to quickly evaluate the performance of a catalyst toward the ORR, there is in many cases a performance gap between RDE and MEA for the same catalyst.^[89] Transferring the superior performance of catalysts from RDE to MEA is a task being of paramount importance in this field. The first piece of work on IL modified ORR catalysts following this line of thought was reported by Erlebacher et al. in 2013, in which they attempted to transfer the IL-induced increase in activity of PtNi/C catalyst from the half-cell RDE measurement to a PEMFC.^[77] They found that the activity boosting effect of the IL ([MTBD][BETI]) in PEMFCs was not as pronounced as that in RDE measurements in the low overpotential region (> 0.85 V). Further increasing the loading amount of IL can lead to a comparable IL boosting factor as in the RDE (> 0.85 V); however, the performance of the PEMFC in the high overpotential region is largely compromised, which is even inferior to that over the pristine PtNi/C catalyst.^[77] Cai et al. demonstrated that incorporation of IL ([C₆C₁im][TfO]) into Pt/C catalysts can increase the peak power density of a high temperature PEMFC (operated at 120 °C) from 415 to 512 mW cm⁻².^[115] The improved

performance was ascribed to the facilitated proton transportation due to the presence of the IL.^[115] It is also inspiring to observe that the IL boosting effect can not only be transferred to an MEA but also be maintained at an elevated temperature, which is of highly importance for practical applications. Du et al. studied the IL ([MTBD][NTf₂]) modification effects on the performance of a commercial Pt/C catalyst in PEMFCs, and found that the IL increased the peak power density of the PEMFC by a factor of 1.8, which was attributed to combined actions of improved O₂ transportation and facilitated water expelling capability in the presence of the IL.^[116] The best MEA performance is obtained at an optimal IL loading of 2 wt%, which is much lower than that observed in half-cell RDE measurements, again demonstrating the different behavior of ORR catalysts in MEA and RDE tests (Figure 14a). Most recently, an attempt on implementation of ILs in MEAs was made by Neyerlin et al., who studied the MEA performance of Pt/C catalyst in presence of a sulfonated poly IL block copolymer (SPILBCP).^[117] First, they found that the SPILBCP can replace the conventional Nafion as an ionomer, and the fabricated MEA (Nafion-free) exhibited a two times higher specific activity (@0.9 V) relative to that using pristine Pt/C catalyst, which was comparable to that obtained using RDE. The IL boosting effect was assumed to benefit from the suppressed formation of Pt oxide in the presence of the IL. Nevertheless, the IL incorporated electrode also suffered from severe loss (up to 70%) in ECSA at low relative humidity (i.e., 30%), which resulted in inferior MEA performance at high current densities (> 200 mA cm⁻²) due to the lacking of a connected ionomer networks for proton transportation. Combined usage of SPILBCP with Nafion ionomer can alleviate the performance loss. Improved MEA performance in both kinetic and mass-transport limited region can be obtained.^[117] Based on these reports, it appears that transferring the improved ORR performance from RDE to MEA remains a challenging task. Rationally engineering the microenvironments created at the local interfaces of catalysts, ionomers and the IL phases is key to fully leverage the SCILL

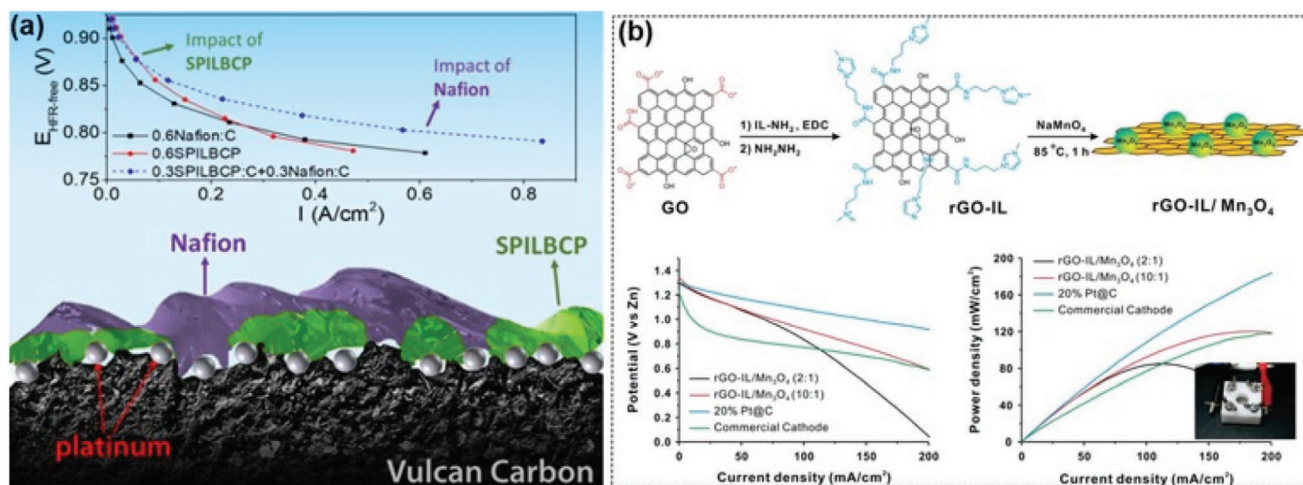


Figure 14. a) MEA performance of Pt/C mixed with Nafion and/or polymerized IL (80 °C, 100% RH, 150 kPa_{abs} total pressure) along with a scheme showing the interfacial structures of electrocatalysts. Reproduced with permission.^[113] Copyright 2020, American Chemical Society. b) A Scheme showing the synthesis of IL modified reduced graphene oxide anchoring manganese oxide, along with its electrochemical performance (polarization curve & power density plot) in a zinc-air battery. Reproduced with permission.^[10] Copyright 2011, Royal Society of Chemistry.

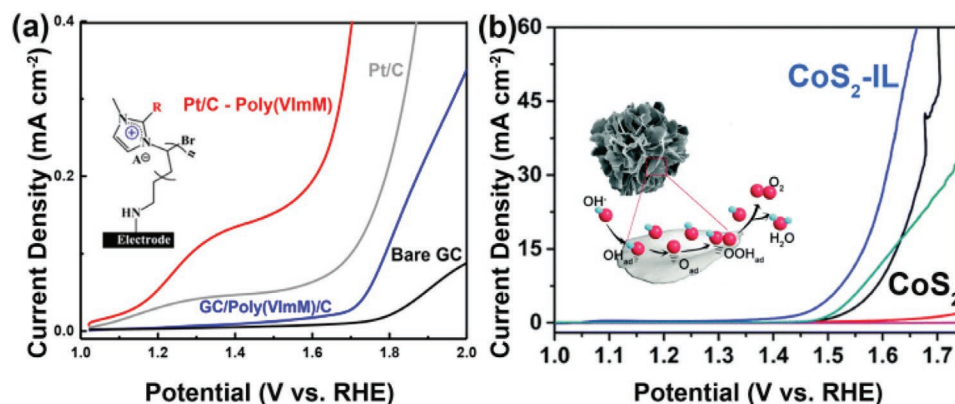


Figure 15. a) OER polarization curves of Pt/C with/without polymerized IL (inset) in 0.1 M KOH electrolyte. Reproduced with permission.^[83] Copyright 2018, American Chemical Society. b) OER polarization curves of pristine and IL ([MTBD][NTf₂]) modified CoS₂ microsphere (inset) along with other reference catalysts in 0.1 M KOH electrolyte. Reproduced with permission.^[79] Copyright 2018, Royal Society of Chemistry.

concept in boosting the ORR catalysts in PEMFCs. As a starting point, finding out an optimized recipe for a homogeneous catalyst dispersion and deposition in presence of ILs and ionomers would be a task with priority.

The practical application of IL modified ORR catalysts (reduced graphene oxide anchoring manganese oxide) has also been demonstrated in a zinc-air battery, and a maximum peak power density of 120 mW cm⁻² was achieved, which even surpassed the air electrode employing commercial MnO_x or 20 wt% Pt/C catalysts (Figure 14b).^[110] Nevertheless, as an innovative concept, the practical applications of the SCILL in constructing advanced electrocatalysts for metal-air batteries is still not common. Anyway, taking the successful applications of the SCILL concept in PEMFCs into account, we ascertain that a wide scope of opportunities in the field of metal-air batteries is waiting.

3.4. Applications of the SCILL Concept in Other Electrocatalytic Processes

Oxygen evolution reaction: Inspired by the success of the SCILL concept in modifying the properties of ORR catalysts, growing efforts have been devoted to applying the SCILL in the electrocatalytic OER. As the reverse reaction of the ORR, OER (or water oxidation) is key to many energy conversion/storage technologies (e.g., electrolysis of water or CO₂, unitized regenerative fuel cells, rechargeable metal-air batteries), which represent promising options to store renewable energies.^[118] The slow OER kinetics leads to a high overpotential for the reaction to proceed and also low energy efficiency. Tremendous efforts have been made to lower the overpotential by developing innovative catalytic systems, which mainly include noble metal oxides (IrO₂, RuO₂), 3d transition metal oxide/hydroxide and their derived sulfide and phosphide.^[75] The influence of IL modification on the OER properties was first demonstrated on Pt/C, which is usually considered as a poor catalyst for the OER, and it is found that the presence of a hydrophobic IL ([dema][TfO]) reduced the overpotential of the OER by up to 300 mV in acidic electrolyte.^[25] Similar IL boosting effect on the OER was also observed in alkaline electrolyte on both precious metal and NPMs. For instance, Pt/C catalyst modified by an

imidazolium-based polymerized IL can exhibit a 200 mV lower overpotential (at 2 mA cm⁻²) toward the OER than the pristine catalyst in 0.1 M KOH (Figure 15a).^[83] Xu et al. studied the OER on pristine and IL ([MTBD][NTf₂]) modified CoS₂ microspheres in 0.1 M KOH, and demonstrated that the overpotential (at 10 mA cm⁻²) can be reduced by 430 mV in presence of the IL (Figure 15b).^[79] Despite of these successful attempts, it remains controversial about the mechanism of ILs in boosting the performance of OER catalysts.^[79] Luo et al. proposed that the enhanced OER performance of IL modified Pt/C catalyst in acidic electrolyte would benefit from the high O₂ solubility and diffusivity.^[25] However, Xu et al. pointed out that the thin IL film on an IL modified catalyst could be quickly saturated with O₂, especially at high current densities of the OER.^[79] Moreover, due to the viscous nature of ILs, the O₂ diffusion coefficient of ILs is usually much lower than that of aqueous solutions. Therefore, the boosted OER performance of IL modified catalysts was less likely related to either the solubility or the diffusivity of O₂ in ILs, but instead might originate from the hydrophobicity of the IL which can help expel the produced water away from catalytically active sites, or from the facilitated adsorption of OH⁻ due to the IL modified charge density of the catalytically active sites.^[79]

Electrochemical CO₂ reduction reaction: The electrochemical CO₂ reduction reaction (CO₂RR) provides not only a promising solution to offset the increased atmospheric CO₂ concentration, but also an attractive approach to obtaining value-added chemicals from CO₂, and at the same time represents an excellent future option to store the intermittent renewable electricity (e.g., solar, wind energy).^[119–121] The key to realizing the economic viability of the CO₂RR is developing high performing electrocatalysts, to selectively accelerate the production of value-added products (e.g., hydrocarbons, alcohols). Numerous intrinsic properties of ILs including high CO₂ solubility, high ionic conductivity, wide electrochemistry windows and great structural flexibility make ILs appealing media for the CO₂RR.^[27,122–124] The ILs were employed either as electrolyte or electrolyte additive, which took effect by lowering the energy barrier for the formation of CO₂^{-•} anion via complexation.^[123,125] However, most of the ILs suffer from expensiveness which would restrict the large-scale application of ILs in CO₂RR process, and limited diffusion rate of CO₂ within ILs

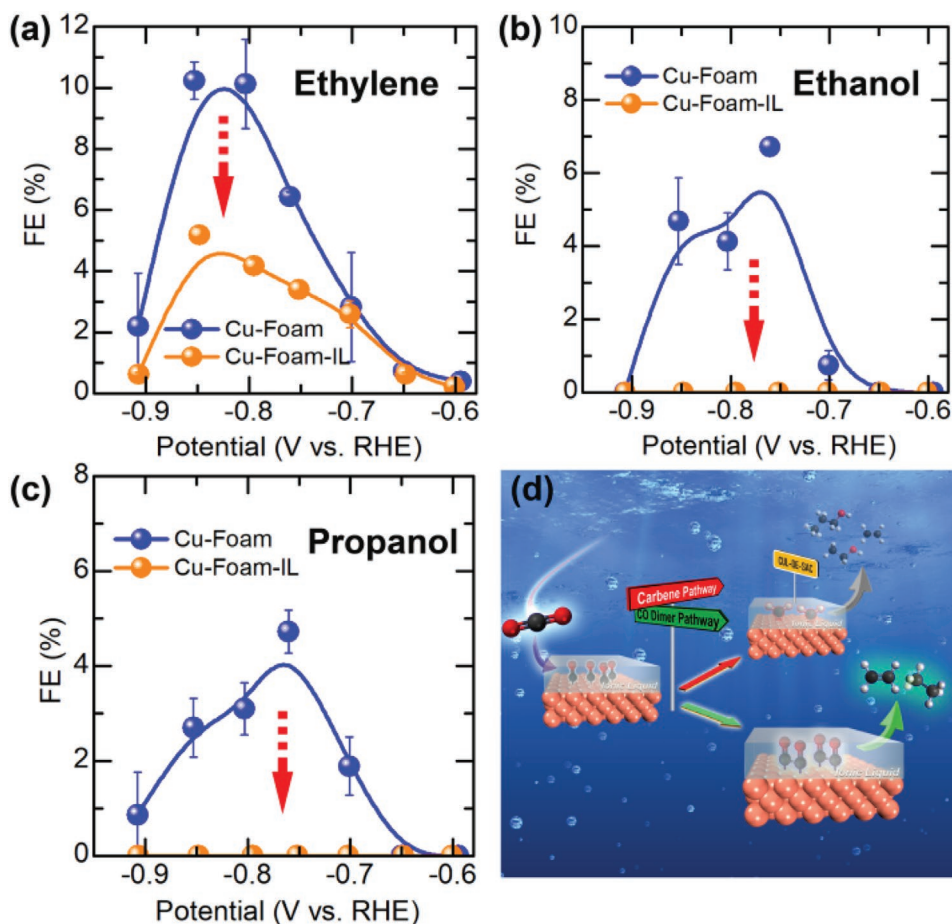


Figure 16. a–c) Faradaic efficiencies of ethylene, ethanol, and propanol on Cu foams with/without IL (electrolyte: 0.1 M KHCO_3). d) A scheme illustrating that the IL has selectively suppressed the reaction pathways toward ethylene, ethanol, and propanol. Reproduced under the terms of the Creative Commons Attribution License 4.0.^[50] Copyright 2020, The Authors, Published by Wiley-VCH GmbH.

due to their viscous nature would lead to rather low overall CO_2 reduction current.^[123] Diluting ILs with aqueous solution can to some extent alleviate the above issues, while only hydrophilic ILs which might be prone to hydrolysis can be used,^[126,127] and would also cause some economic concern in separating the liquid CO_2RR products from IL-containing electrolytes. In view of this, the SCILL concept appears to be a promising approach to overcome the above dilemma of using ILs for the CO_2RR , due to the small amount of ILs to be used.

Following this line of reasoning, Etzold et al. performed a proof-of-concept study by constructing a SCILL-concept based Cu foam catalyst which was modified with a small amount of $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$.^[50] Cu foams were chosen as a combined consideration of the unique catalytic property of Cu to produce value-added products with pronounced faradaic efficiency and abundance of pores in the foam structure which is desirable to immobilize/confine IL phase. It is found that the IL molecules significantly altered the product spectrum by selective suppressing the formation of ethylene, ethanol, and n-propanol, without disturbing FE or partial current densities of others. In other words, the IL molecules can act as a chemical trapping agent, which selectively interacts with one or more intermediates (identified as carbene or other species can convert to carbene) leading to the formation of those suppressed products.

Chemical trapping is originated in the field of organic chemistry and is demonstrated to be an effective way to study reaction mechanisms, which is deduced using a chemical trapping agent that can form stable compound with certain reaction intermediate(s). Here, although the presence of the IL has not boosted the performance of Cu foam toward the CO_2RR , the response in product distribution to the IL modification provides a unique way to disentangle the complex reaction networks of various products, as summarized in **Figure 16**. Importantly, this unprecedented yet simple approach can be applied to existing electrochemical cells and in every electrochemical laboratory without the need for costly spectroscopic set-up or access to beam lines. This work demonstrates the possibility to probe the reaction pathways of the electrocatalytic CO_2RR process using the IL as a chemical trapping agent, while before the SCILL concept can be employed as a new generic approach to modulating the performance of a CO_2RR catalyst, mechanistic understandings about the interactions of the IL with the catalyst and key reaction intermediate need to be obtained, on the basis of extensive spectroscopic and/or microscopic techniques.

Hydrogen evolution reaction: Hydrogen evolution reaction (HER) represents a clean way to produce hydrogen with high purity. The major bottleneck of the HER lies in lacking of active and robust electrocatalysts. Most recently, Zhang et al. studied

the HER performance of Pt/C catalyst before and after coating with two hydrophobic ILs, that is, 1,8-Diazabicyclo[5.4.0]-7-Undecene bis(trifluoromethylsulfonyl)imide ([DBU][NTf₂]) and [C₄C₁im][NTf₂].^[128] Both IL coated Pt/C catalysts exhibited impressively high activity toward the HER. Specifically, their current densities at an overpotential of 40 mV are 2.8 and 4.2 times higher than that of the pristine Pt/C, along with a much superior electrochemical stability. The beneficial role of ILs is assumed to arise from improved H⁺ conductivity and also suppressed dissolution of Pt under electrochemical operation conditions.

4. Concluding Remarks and Outlook

This review addressed the emergence and development of the SCILL concept, and summarized the latest progress of the SCILL concept in the field of electrocatalysis by highlighting its exemplary applications. The presence of ILs can take effect by modifying the microenvironments created at interfaces of solid electrode and liquid electrolyte through either the solvent effect, ligand effect, chemical trapping effect, and/or hydrophobic nature of ILs. The emerging SCILL concept opens a new avenue to improve the performance of an electrocatalyst by modulating the local concentration of reactants/products, accessibility of catalyst surfaces, and/or binding strength of intermediates, which complements to direct structural engineering of catalysts and enriches the toolbox to steering an electrocatalytic reaction toward the desired direction.

Despite of the success and great promise of the SCILL concept in either boosting electrocatalysts or gaining mechanistic insights into electrocatalytic processes, many scientific and technical issues need to be addressed before the SCILL concept can be employed as a generic approach to improving electrocatalysts especially those involved in key energy conversion/storage processes. To this end, the research activity is recommended to be strengthened in the following fields:

(1) How to probe the molecular structures of ILs at the electrochemical interfaces?

Knowledge about the exact role of ILs in electrocatalysis and interactions between ILs and solid catalysts remains elusive. To cope with this, the interfacial structures of ILs, that is, spatial distribution, molecular orientation, structural dynamics and chemical state of IL molecules at electrode interfaces under electrochemical operation conditions need to be properly addressed based on both experimental and theoretical approaches.

Experiments: The breakthrough from experiment perspective relies on cutting edge spectroscopic (e.g., Raman/IR, spatially resolved EDS/EELS, ARXPS, X-ray/neutron scattering) and microscopic (e.g., STM, AFM, TEM) techniques, especially those under in situ/operando electrochemical conditions.

Theoretical calculations/simulations: Theoretical calculation and simulation at electrified surfaces are also desired for gaining in-depth understandings of the interfacial structures of IL molecules. For instance, ab initio calculations can be employed to probe the energy minimized molecular structures on electrode surface as well as possible interactions between IL

molecules and electrocatalysts/reaction intermediates; molecular dynamics simulations can be used to analyze the dynamic structure of ILs at varied electrode potentials and molecular orientation arrangements at electrode surfaces.

(2) How to effectively immobilize ILs?

Immobilization methods: Previous methods of IL immobilization (e.g., drop casting, impregnation, physical vapor deposition, and capacitive deposition) suffer from either poor/limited controllability of IL distributions within catalysts, or difficulty for scaling up. Novel methods for controlled deposition of ILs still need to be developed, in order to not only introduce a conformal IL layer on a catalyst, but also be feasible for scale-up synthesis.

Immobilization stability: Immobilization stability of ILs during electrochemical operations needs to be addressed. Despite the hydrophobicity of ILs in principle can help prevent ILs from leaching into aqueous electrolyte, the leaching dynamics of ILs in contact with aqueous electrolyte and its dependence on electrode potential, identity, and porosity of solid catalysts, molecular structure/functional groups of ILs remain unaddressed. As a starting point, stabilizing the immobilized IL through local anchoring of ILs to the catalyst support surface via covalent/non-covalent bonding may hold great promise and deserve comprehensive studies.

(3) How to engineer the structure of ILs and electrocatalysts in a SCILL system?

ILs: ILs feature great variety and structural flexibility, which provide the basis of rational design and synthesis of ILs with desired molecular configuration, hydrophobicity, solubility. Recent progress in gaining mechanistic insights into the role of ILs in electrocatalysis and interactions between ILs and electrodes have made it possible to design task-specific ILs, in which various functionalities can be rationally introduced for different electrocatalytic processes. The success of this endeavor can enable us to take the full leverage of the SCILL concept in developing superior electrocatalysts.

Active phase: Knowledge about the interactions between ILs and electrocatalysts have so far mainly been obtained on Pt-based catalysts. It is highly desirable to understand how ILs interact with metals or heteroatoms (in NPMCs) with different local coordination environments, which can be implemented by preparing single metal nanoparticles with different particle sizes or well-defined shapes, bi-/multi-metallic nanoparticles with different surface compositions, or NPMCs incorporated with various heteroatoms.

Support materials: Carbon materials are widely used as supports for electrocatalysts. In principle, due to their hydrophobic nature, most carbon materials can be easily wetted by hydrophobic ILs. However, a detailed understanding about how the porosity, graphitization degree, and surface chemistry can influence the distribution and/or immobilization stability of ILs is still not reached, which requires systematic studies by carefully engineering the structure of carbon supports, that is, introducing surface functional groups, tuning the pore

size/distribution/hierarchical structure, and creating surface defects.

(4) How to expand the SCILL concept to other electrocatalytic processes?

Inspired by the great success of the SCILL concept in improving catalytic performance or deciphering the complex reaction pathways of electrocatalytic processes, it now becomes highly desirable to study whether the SCILL concept can be expanded to some other electrocatalytic reactions especially those involve water, hydrogen, protons, and oxygen/oxygenated species. The presence of ILs can play an influential role on local concentration, mass transfer, and adsorption/activation of these species at electrode surfaces, and thus altered catalytic activity, stability, and selectivity are to be expected. Of particular interest are electrocatalytic synthesis processes, in which modifying the microenvironments at electrode surfaces using ILs might be highly promising to help steer the reaction toward desired product(s). We ascertain that applying the SCILL concept to other electrocatalytic processes is going to be an exciting research field and a wide scope of discoveries is waiting.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

CO₂ reduction, electrocatalysis, ionic liquid, liquid-solid interfaces, oxygen evolution, oxygen reduction

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