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

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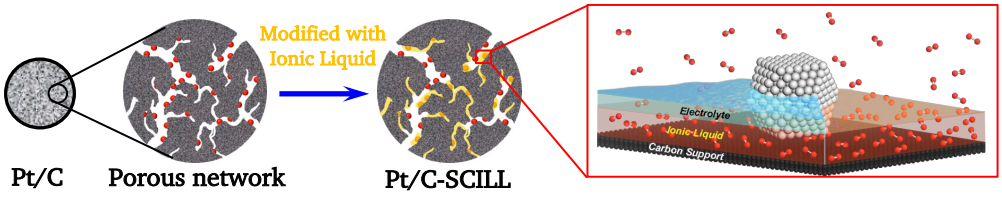
Introduction: High cost and poor stability of oxygen reduction reaction (ORR) electrocatalysts are the major barriers for broad-based application of polymer electrolyte membrane fuel cells (PEMFCs). We look beyond directly engineering the structures of active sites and disclose a facile and easy to scale up approach to improving Pt catalyst for ORR, by introducing tiny amounts of hydrophobic ionic liquid (IL) into commercial Pt/C catalyst. The ORR performance of these IL-modified catalysts can be readily manipulated by varying the degree of IL filling (α). Fine-Tuning α resulted in optimized catalyst at α = 50%, whose activity is 3.2 times higher than Pt/C and surpasses the activity target set for 2017-2020. Most recently, we disclose that introduction of a common and inexpensive IL ([Bmim][NTf_2]) to the Pt/C can also accelerate the ORR kinetics by preventing Pt sites from being oxidized and give birth to a Pt/C with record high mass activity (1.01 A mg^{-1}_{Pt}@0.9 V) for pure Pt catalysts. Besides, the IL-modified catalysts exhibit substantially enhanced stability relative to Pt/C. We believe that these findings open a new avenue for catalyst optimization for next-generation fuel cells.

Experimental Section

Synthesis: Modifying the active site microenvironment with ionic liquids

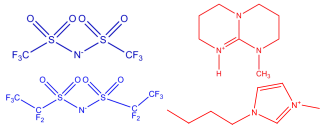


Materials

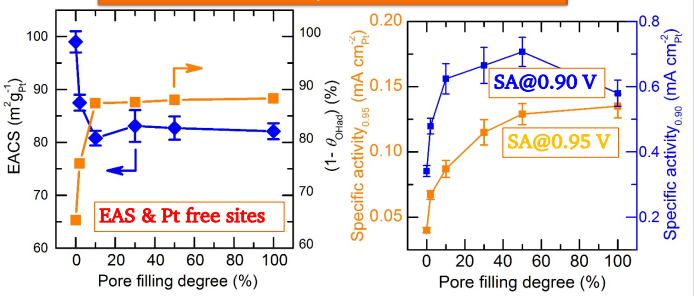
Catalyst: 20 wt.% Pt/C (JM HiSPEC)

Electrolyte: 0.1 M $HClO_4$

ILs: Anions Cations



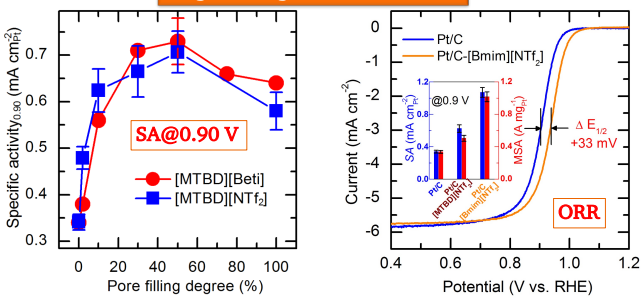
Electrochemical Analysis & ORR Performance



0.1 M $HClO_4$, room temperature, IL = [MTBD][NTf_2]; ORR: 10 mV s^{-1}, 1600 rpm

- Introducing IL into Pt/C leads to a reduction in EACS by up to 19%; Number of blocked Pt sites decreases significantly
- At high potential regions, SA increases strongly with pore filling degrees (α), and settles at α > 50

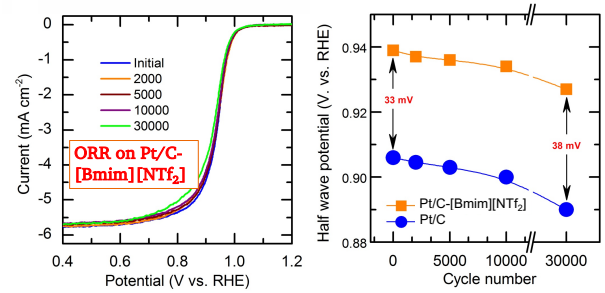
Engineering the IL Structure



0.1 M $HClO_4$, room temperature; ORR: 10 mV s^{-1}, 1600 rpm

- Pt activity towards ORR is not sensitive to the O_2 solubility in ILs
- Pt/C-[Bmim][NTf_2] exhibits the record high activity towards ORR, which is three times more active than the pristine Pt/C

Electrocatalytic Stability

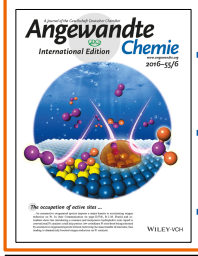


0.1 M $HClO_4$, 10 mV s^{-1}, room temperature, IL = [Bmim][NTf_2], α = 10

Stability testing conditions: 0.4 to 1.1 V in O_2-saturated 0.1 M $HClO_4$, 1 V s^{-1}

- Very good electrocatalytic stability was observed on the IL modified Pt/C catalyst.

Origin of the Boosting Effect



What we can learn...

- The IL phase would selectively locate at the defect /low coordinated Pt sites. (Evidenced by CO-stripping measurements)
- The hydrophobicity of IL would help suppress the surface oxidation of Pt. (Evidenced by CV, Tafel analysis, and CO-stripping)
- The defect sites with IL are still accessible for O_2 molecules.

Conclusions:

- **IL modification is a new methodology to engineer electrocatalysts.**
- **Pore diffusion limitation induced by the viscous IL can be reduced through partial filling of the particles.**
- **When structure-activity relation-ships are known, molecular variation of anion and cation can be employed for catalyst tuning.**

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