

Boosting Oxygen Reduction Catalysts through Preventing Active Sites Poisoning by Using Hydrophobic Ionic Liquids

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Developing low-cost, efficient and durable electrocatalysts for cathodic oxygen reduction reaction (ORR) is a prerequisite for the broad market penetration of low temperature fuel cells. A major barrier is stemming from the poisoning of surface active sites by non-reactive oxygenated species (e.g., OH_{ad}) and the slow ORR kinetics on Pt catalysts. Herein, we disclose a facile approach to accelerating ORR kinetics on Pt through a surface modification using hydrophobic ionic liquid (IL). It is demonstrated that introduction of a common and inexpensive IL as [C₄C₁im][NTf₂] to the carbon-supported Pt electrocatalyst (Pt/C) can efficiently reduce the overpotential of ORR and bring in a remarkable 3 times enhancement in activity. We discovered that the origin of accelerated ORR kinetics on IL-modified Pt catalysts lay in the higher accessibility of surface Pt sites preserved by the hydrophobic IL, as evidenced by voltammetry, Tafel plot and CO-stripping. (Figure 1).

We found that the ORR performance is highly sensitive to the nature of cations (Figure 1). The molecular variation reveals that the alkyl chain length of the imidazolium shows a pronounced influence on the intrinsic activity, and accessible electrochemically active surface area (EAS). The best performing IL [Bmim][NTf₂] results in a nearly 3 times higher activity than the pristine Pt/C in terms of both intrinsic and mass activity, which is substantially beyond the US Department of Energy activity target for 2017-2020. Furthermore, the enhanced performance can be stabilized after the repeated potential scanning up to 30000 cycles between 0.4 and 1.1 V in O₂-saturated 0.1 M HClO₄ solution.

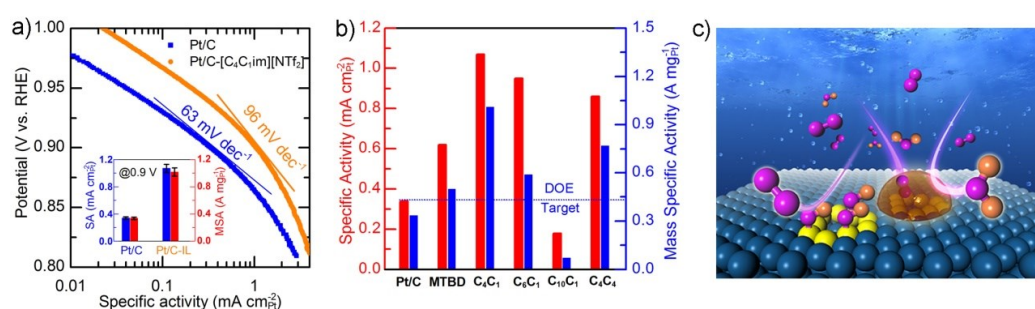


Figure 1. a) Tafel plots. The inset shows the activity comparison of the Pt/C before and after IL modification. b) Comparison of Pt activity for ORR. c) Scheme illustrating that the IL would help protect Pt sites from being oxidized by repelling water.

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REFERENCES

1. G.R. Zhang, M. Munoz, B.J.M. Etzold, ACS Appl. Mater. Interfaces 2015, 7, 3563.
2. G.R. Zhang, M. Munoz, B.J.M. Etzold, Angew. Chem. Int. Ed. 2016, 55, 2257.