

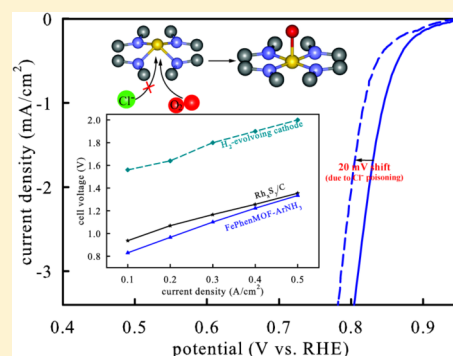
Highly Active and Stable Fe–N–C Catalyst for Oxygen Depolarized Cathode Applications

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Supporting Information

ABSTRACT: Anion immunity toward the oxygen reduction reaction (ORR) has tremendous implications in electrocatalysis with applications for fuel cells, metal–air batteries, and oxygen depolarized cathodes (ODCs) in the anodic evolution of chlorine. The necessity of exploring ORR catalysts with immunity to anion adsorption is particularly significant considering that platinum group metal (PGM) catalysts are costly and highly vulnerable to impurities such as halides. Herein, we report a metal organic framework (MOF)-derived Fe–N–C catalyst that exhibits a dramatically improved half-wave potential of 240 mV compared to the state-of-the-art Rh_xS_y/C catalyst in a rotating disk electrode in the presence of Cl[−]. The Fe–N₄ active sites in Fe–N–C are intrinsically immune to Cl[−] poisoning, in contrast to Pt/C, which is severely susceptible to Cl[−] poisoning. As a result, the activity of Fe–N–C decreases only marginally in the presence of Cl[−], far exceeding that of Pt/C. The viability of this catalyst as ODCs is further demonstrated in real-life hydrochloric acid electrolyzers using highly concentrated HCl solution saturated with Cl₂ gas as the electrolyte. The introduction of Fe–N–C materials as ODC catalysts here overcomes the limitations of (i) the low intrinsic ORR activity of Rh_xS_y/C as the state-of-the-art ODC catalyst; (ii) the vulnerability to Cl[−] poisoning of Pt/C as the state-of-the-art ORR catalyst; and (iii) the high cost of precious metals in these two materials, resulting in a cost-effective ODC catalyst with the overall performance exceeding that of all previously reported materials.



INTRODUCTION

The recycling of high-value chlorine gas from abundant aqueous hydrochloric acid is widely used in industry by utilizing chlorine gas as a reactant.^{1,2} The recycling of chlorine gas that evolved in the anodic compartment as feedstock in chemical plants reduces the risks emanating from large storage tanks of chlorine gas in industrial plants.³ However, such benefit comes at the price of intensive energy consumption. Typically, a metric ton of chlorine gas consumes ~1500 kWh of power based on hydrochloric electrolyzers employing conventional hydrogen-evolving cathodes under standard conditions,⁴ and the overall chlorine generation in all of its forms (i.e., chlor alkali and HCl recycling) accounts for 2% of the total energy consumption in the United States (or any industrially developed country).^{5,6} Moreover, safety concerns as a consequence of crossover arising from hydrogen-evolving cathodes is an ever-present danger, especially during uncontrolled shutdown conditions.^{6,7} Theoretically, these issues can be addressed by the invocation of oxygen depolarized cathode (ODC) technology as a replacement for the hydrogen evolution cathodic reaction.^{2,4,6,8,9} A comparison of the cell configurations with standard hydrogen-evolving cathodes and ODCs is displayed in Scheme 1. In comparison with a lowering of the thermodynamic cell potential from 1.36 to 0.13 V via the application of the ODC process, a practical cell voltage reduction of ~1 V at 0.3 A cm^{−2} is expected, entailing energy

savings of up to 30% (Scheme 1c).^{2,10,11} Translating and sustaining such enormous energy savings via the ODC process, however, has been challenging owing to both the lack of active ODC electrocatalysts and their long-term durability under the highly corrosive and poisonous environments of the Cl₂-saturated concentrated HCl electrolyte. Hence, new catalysts with high ORR activity, stability, and immunity to Cl[−] poisoning possess tremendous potential for impact in terms of energy conservation.

The harsh operating conditions of the ODC process severely limit the choice of electrocatalysts.^{12–15} The use of Pt and Pt alloys, the current state-of-the-art ORR catalysts for low and medium temperatures in acids,^{16–19} is ruled out for hydrochloric acid electrolyzers because of the lack of anion immunity and, more importantly, stability. ORR-active noble metals such as platinum are seriously poisoned even at a low concentration of anions, such as PO₄^{3−} and Cl[−], with concomitantly higher overpotentials and poorer kinetics of ORR.^{20–22} In terms of durability, a substantial dissolution of Pt occurs in the highly corrosive Cl₂-saturated HCl electrolyte especially during

Special Issue: Fundamental Interfacial Science for Energy Applications

Received: February 24, 2017

Revised: April 23, 2017

Published: April 26, 2017