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Engendering anion immunity in oxygen consuming cathodes based on Fe-N_x electrocatalysts: Spectroscopic and electrochemical advanced characterizations

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ABSTRACT

Oxygen reduction reaction (ORR) is the key reaction utilized for several potentially promising technologies such as in energy conversion (fuel-cells) or as oxygen depolarized cathodes (ODC) in anodic evolution of bulk chemicals such as chlorine. In the latter case elimination of one volt out of a theoretical maximum of 1.34 V (in case of hydrogen evolution electrode) provides very significant energy savings. Here we report iron based Fe-N_x catalyst with promising activity compared to state of the art noble metal catalysts (Rh_xS_y) for hydrochloric acid recovery systems. A combined electrochemical and synchrotron-based spectroscopic approach is used to probe the structural and elec tronic properties of the active centers. The surface sensitive delta-mu (Δm) analysis of the near edge X-ray absorption fine structure (NEXAFS), supported by first-principles calculations, reveals the immunity of the Fe-N_x-C_y active centers to chloride poisoning. Initial stability studies show that even after a harsh corrosive treatment, the catalyst ORR activity remains comparable to the current state of the art precious based material. Our study opens up promising avenues for developing affordable and robust oxygen consuming electrodes.

1. Introduction

Catalyst poisoning is a widely recognized problem in elec trocatalysis that inhibits catalytic activity resulting from both specific adsorption (i.e. chemisorption) of anionic species [1–4] (especially in aqueous acidic pH) and non-specific interactions [5] such as passivation via degradation of the electrolyte or other species at the interface. Such poisoning issues, especially specific adsorption, are particularly germane in the case of supported noble metal catalysts (e.g. Pt, Rh, Ru) resulting in increase of overpotential [4–7], and its side effects such as corrosion and eventual metal dissolution. This specific adsorption of specifically halide ions such as chloride and bromide [8] is mainly initiated at positive potentials with respect to the potential of zero charge, which is a factor relevant to the onset and preservation of the ORR.

A cure for this poisoning involves the use of ODC electrodes for bulk production of chemicals such as chlorine, a vital chemical for waste water treatment and other chemical and pharmaceutical applications [9]. Two major processes for chlorine production are electrolytic conversion of brine solution (chlor-alkali cells) [10] and recycling of hydrochloric acid [11,12] where major progress has been made through the use of ODC electrodes in membrane cells in lieu of hydrogen evolving cathodes [13]. This results in saving 1 V (room temperature theoretical potential of ORR being 1.23 V and that of chlorine evolution, 1.36 V vs. RHE), which constitutes major energy savings amounting to an average of ~700 kWh per ton of Cl_2 (g) [14]. This figure is particularly impressive if we consider that currently 2% of total energy consumption in USA is used for chlorine production [9]. Despite the use of noble metals (typically Ag for chlor-alkali and the more expensive Rh_xS_y for HCl recovery), there is a severe inhibition of ORR activity as a result of halide poisoning. Unlike the alkaline pH of the chlor-alkali process, HCl recovery process is especially challenging due to the presence of a harsh chlorine saturated acidic environment in which transition beyond the potential of zero charge results in immediate poisoning by anions [15], even at very low concentrations [8]. Moreover, as chloride ions are carried from the anode through the ion conducting membrane during normal cell operation or during cathode flooding in an uncontrolled power shutdown, the Cl^- concentration on the cathode can rise to 1–5 molar. At these concentrations platinum is known to dissolve [15]. The only catalyst known to withstand the corrosive and poisonous presence of chloride anions is rhodium sul-

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fide (Rh_xS_y) [11,16]. Rh_xS_y, although stable (extremely expensive but successfully commercialized [15,17]) in a chlorine saturated chloride environment, is still susceptible to poisoning with a high overvoltage for ORR albeit lower than supported Pt electrocatalysts [16]. This is particularly relevant because, in contrast to supported Pt and Pt alloy nano-particles, Rh_xS_y is a composite of three crystalline phases [18], and hence it does not present a contiguous metal surface as is the case with a supported nano-particle (Pt/C for e.g.,). Promoting ORR in a halide ion containing acidic pH requires the use of very selective sites, which would be immune to anion adsorption. Multi-phasic Rh_xS_y is one such case where the Rh_3S_4 phase provides the active sites for ORR [18]. A logical extension of this argument points toward Heme type moieties, which are one of the most selective sites in this context. Recently, significant advances in ORR electrocatalyst activity have been reported with such bio-inspired active sites [19–22] hereto referred to as metal N-C systems. In contrast to decades of prior efforts [23–25] wherein organic macrocycles containing metallo-Heme type centers (e.g. phthalocyanines or porphyrins) were pyrolyzed on electronically conducting supports such as carbon black, a significant improvement in activity has been achieved more recently with formation of metal-N coordinated sites using non Heme containing simple precursor materials. One early rendition, which we have referred to as the 'reactive polymer approach', involved the use of poly(vinyl amine guanidine) [26].

In this work, we explore the behavior of an ODC cathode electrode containing Fe-N type active sites in operation in the harsh chlorine saturated HCl environment typical of the HCl recovery process. We delineate the efficiency of such Fe-N_x based site, which remains stable and active in a harsh environment where even Pt dissolves. We present a comprehensive investigation of the immunity towards halide ion adsorption using a combination of in situ synchrotron x-ray absorption spectroscopy (XAS), electrochemistry, and density functional theory (DFT) based first-principles calculations.

2. Materials and methods

All experiments reported in this study were carried out on Fe-N_x-C catalysts (poly-FeN_xC) developed in-house by high temperature pyrolysis of a polymer-N/Fe network, using crosslinked and complexed polyethylene imine (xPEI) supported on carbon black (see Supplementary information for details). *In situ* x-ray absorption spectroscopy was employed to identify the various structural and electronic forms of iron centers present in the investigated catalysts. Data collection and analysis of the extended (EXAFS) and near (NEXAFS) XAFS structure, including Delta-Mu ($\Delta\mu$), is described in the Supplementary information. All electrochemical measurements were performed at room temperature using rotating ring-disk electrode (RRDE) equipment purchased from Pine Instruments connected to an Autolab (Ecochemie Inc., model-PGSTAT 30) bipotentiostat. The 1 M $HClO_4$ and 1 M and 5 M HCl electrolytes were prepared from 70% double distilled perchloric acid (GFS Chemicals) and 34% hydrochloric Acid (Alfa Aesar), respectively. A 30% Pt/C catalyst from BASF-ETEK (Somerset, NJ) and 30% Rh_xS_yC from De Nora Tech (Concord, OH) were used as received. Catalyst inks were prepared by ultrasonically dispersing the catalyst powder in a 1:3 (by volume) ratio of water/isopropanol solution. The typical Fe-N_xC catalyst loading employed was 600 $\mu g/cm^2$ ($\sim$15–20 $\mu gFe/cm^2$) and 15 $\mu g/cm^2$ of metal in case of Pt/C and Rh_xS_y/C, respectively, on a 0.196 cm^2 glassy carbon disk. Reversible hydrogen electrode (RHE) generated using the same electrolyte as the bulk was used as the reference electrode for the Cl^- dosing study, and Ag/AgCl was used with 1 M HCl as electrolyte. All current values are normalized to the geometric area of the glassy carbon disk unless otherwise stated. All potentials are referred to the RHE scale. Removal of the surface bound iron nanoparticles present in the xBPEI-Fe catalysts was achieved by boiling the catalyst in hot (100C, 2 h) 5 M hydrochloric acid solution saturated with chlorine gas. Procedure this was chosen to simulate a harsh corrosive environment, worst case scenario, which can occur in situation of flooding of the cathode with hot (55–60 °C) concentrated (up to 5 M) HCl and saturated with chlorine evolved during the electrolysis process.

Theoretical calculations were performed using the Vienna Ab initio Simulation Package (VASP) code [27–29] for two different model clusters: FeN_4C_{10} (Fig. 5a) representing Fe-N_4 centers in a perfect graphene plane; and, Fe-N_4-C_8 (Fig. 5b) simulating Fe-N_4 centers within defective pores at the edge of the carbonceous scaffold. A 4×6 graphene supercell containing 26 carbon atoms was generated using a hexagonal graphene unit cell of 2 atoms. The Fe-N_4 cluster was embedded by creating a carbon divacancy [30]. All the outer carbons in the model clusters were passivated with hydrogen atoms [31]. The Fe-N_4-C_8 model was built by the removal of the two next near neighbor carbon atoms of the Fe site, followed by geometry optimization. These simulations create a fragment Fe-N_4-C_8 similar to the model utilized by Kattel et al. [30]. The core electrons were described by the projector augmented wave (PAW) basis [32] using a cutoff energy of 400 eV to describe the valence electrons. For electronic exchange-correlation effects, we used generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof (PBE) parametrization [33] GGA functionals are crucially important in order to describe correctly properties of iron [34]. The DFT calculations were performed with full relaxation of ionic positions until two consecutive relaxations reached an energy difference of less than 0.1 meV. The geometry optimization was carried out using a $2 \times 2 \times 1$ Monkhorst-Pack k-space grid [35]. Spin polarization was included in electronic density of states (DOS) and binding energy calculations. DOS was computed using a denser k-point mesh of $8 \times 8 \times 1$ and a smearing parameter $\sigma = 0.1 eV$.

3. Results and discussion

3.1. Effect of Cl^- on ORR polarization curves (RDE)

Fig. 1 presents comparative polarization curves (Fig. 1a), including results after mass transport correction (Fig. 1b), of Fe-N_x-C catalyst derived from a cross-linked network of branched polyethyleneimine complexes, hereafter referred to as poly-FeN_xC, with and without the presence of Cl^-, compared with Pt/C (BASF-ETEK, NY) and Rh_xS_y/C (Denora Tech, OH).

The two noble metal catalysts represent current state-of-the-art for oxygen consuming materials in PEM fuel cells and HCl electrolyzers, respectively [11,16,18]. The rotating disk response (I–V curves normalized to disk geometric area) to ORR without the presence of chlorides displays the expected superiority of the Pt/C and Rh_xS_y/C catalysts over the non-noble metal materials. This is expected in the acidic pH with the performance difference falling within 150 mV in half-wave potential, $E_{1/2}$, (see Supplementary information, Table S1) as reported earlier [20,22,26]. However, addition of Cl^- results in drastic increase of the ORR overpotential for both Pt/C and Rh_xS_y/C, the former being negatively affected to a greater degree. On the other hand, the poly-FeN_xC material shows high resistance against poisoning (Figs. 1a–b). A detailed analysis of the RDE data including the Tafel analysis is provided as Supplementary data (Table S1). The poisoning of the supported noble metal electrocatalyst surface (i.e., Pt/C) by halide ions has been previously studied by Arruda et al. [8]; using an *in situ* XAS/$\Delta\mu$ – XANES technique, a 3-fold bonded Cl^- was shown to poison the surface at