Novel Non Precious Metal Catalyst for PEMFC Applications

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Introduction

Proton Exchange Membrane (PEM) fuel cells are electrical power generators. PEMFCs are the best choice for a wide range of portable, stationary and automotive applications because of their high power density and relatively low temperature operation. Though PEMFCs are on the verge of commercialization, the major impediment to the commercialization of this technology is the cost involved. Presently Pt and Pt alloys are widely used as anode and cathode materials. Despite a cathodic overpotenital loss of 20%, Pt and its alloys are still preferred for their resistance towards corrosion in acidic media. Pt however, being an expensive metal of low abundance, it is of interest for researchers to develop a corrosion resistant non noble metal substitutes. Development of selective oxygen reduction non noble catalyst is also of interest for Direct Methanol Fuel Cells (DMFC), where methanol cross over and oxidation of methanol at the cathode remains an impeding factor for its commercialization.

In the last few years, several transition metal compounds have been proposed as oxygen reduction reaction (ORR) selective catalyst. Prominent among them are macrocycle based metal containing porphyrin system, chevrel phase type compounds (e.g., $Mo_4Ru_2Se_8$) and other transition metal chalcogenides. Generation of a $M\text{-}N_4$ type moiety is known to be the active catalytic site for oxygen reduction. Other than macrocycles, these $M\text{-}N_4$ moiety can be generated from low cost precursors. Ingredients necessary to generate a catalyst are: (i) a transition metal, (ii) a source of nitrogen (e.g NH_3, Acetonitrile) and (iii) high temperature pyrolysis. Adsorbing metals on the carbon support followed by heat treatment to yield a catalytic site allows the investigation of various non noble transition metals as catalysts for oxygen reduction. In the present work, non noble transition metals such as Fe, Co and Cr were studied for oxygen reduction. The performance of these catalyst are based on three main criterion; (i) activity towards oxygen reduction; (ii) Oxygen reduction pathway (two electron pathway/ four electron pathway; (iii) amount of hydrogen peroxide generated. The amount of peroxide generated is crucial to estimate the performance of a catalyst towards oxygen reduction.

Experimental

Non noble metals such as Cr, Fe and Co were impregnated on high surface area ketjen black carbon. 10 wt % of non noble metal were impregnated from aqueous solution of metal salts ($[M^{2+}]$ = 0.2 g/ml) followed by several heat treatments to obtain oxygen reduction catalysts. These catalysts were tested by half cell measurements using a rotating ring disc electrode (RRDE) setup. 8 mg of the catalyst was dissolved in 1 ml of isopropyl alcohol in a ultrasonic mixer. 15 microlitres of this catalyst ink was pipetted on a glassy carbon rotating disc electrode followed by 5 microlitres of 5 wt% nafion in alcohol - water (1:25) solution. RRDE measurements were performed at room temperature in a three electrode, single compartment cell containing 0.5 M H_2SO_4 solution. Hg/Hg_2SO_4 was used as the reference electrode in the study. All potentials in this study are referred with respect to the reference hydrogen electrode (RHE). Electrochemical studies were done using Scribner Associates Corrware Software with EG&G Princeton applied Model 273 potentiostat/galvanostat

Results and Discussion:

Electrochemical half cell studies using a RRDE set up were performed for Co, Cr and Fe catalyst prepared under various heat treatments. Table 1 summarizes the electrochemical results obtained for Co, Cr and Fe catalyst obtained from a NH_3 based heat treatment. The value of half wave potential is an indication of the catalytic activity of the catalyst towards oxygen reduction. From the table it can be observed that Co shows high activity towards oxygen reduction followed by Cr and Fe ($E_{1/2}$ = Co>Cr>Fe). However, the % peroxide produced on Co is relatively high compared to that on Cr and on Fe. As shown in Table 1, the Cr catalyst exhibits the smallest peroxide generation, followed by Fe. In addition, the number of electrons exchanged on the Cr catalyst is close to four, suggesting a four-electron pathway for the oxygen reduction reaction. Similar studies were performed for transition metal catalysts prepared under various heat treatments. The optimal heat treatment and the potential transition metal based catalyst for PEMFC application will be identified. Also few alloy combinations to increase the performance of the catalyst will be studied. Results from the above studies will be presented and discussed in the presentation.

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Catalyst	Ep (V *vs.* RHE)	$E_{1/2}$ (V *vs.* RHE)	Avg. no. of electrons	% H_2O_2 (at 0.6 V RHE)
Co	0.499	0.4635	2.9	54.52
Fe	0.406	0.399	3.27	36.49
Cr	0.5	0.4336	3.59	20.29

Table1. Summary of electrochemical results obtained for Cr,Co and Fe catalyst prepared from NH_3 treatment.