

Investigation of the alkaline interface for non-PGM electrocatalysts in AEM water electrolysis

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Recent research has proven that totally PGM-free water electrolysis cells can achieve high performance using anion-exchange membranes¹. However, current non-PGM AEMWEs require the use of very high catalyst loading to reach reasonable performance targets. Furthermore, it is believed that the primary failure mechanism is the degradation of the interface between the catalyst layer and the AEM. Therefore, a robust understanding of the alkaline interface is required to engineer high-performance, low cost and durable AEMWE cells.

Operation in alkaline media enables overcoming the “stability criterion” problem of the acid analog, which restricts its use to PGM catalysts. AEMs allow the use of inexpensive transition metal (TM) catalysts for both hydrogen and oxygen evolution reactions (HER/OER). Activity of TM electrodes relative to PGM is a function of several factors including inner/outer sphere charge transfer, changes in coverage of spectator species and changes to the nature of the transition state. The low cost and abundance of TM catalysts should pave the way for the commercialization of modular water electrolysis systems and facilitate the construction of regional “hydrogen highways”.

A major challenge in the development of AEM systems is the significantly decreased HER/HOR kinetics in alkaline vs. acidic media². However, this problem can be addressed by combining adjacent metal & metal-oxide catalytic sites. Markovic et al. have recently proposed that TM-oxide-decorated Pt electrocatalysts should mitigate the issues of decreased HER/HOR kinetics in alkaline media³. Research is underway at NUCRET investigating the relationship between nickel and various metal oxides for the development of non-PGM alkaline electrodes. Initial studies show that Ni/Cr-Ox is very active for the HER and approaches the activity of a Pt black benchmark. Furthermore, the Ni/Cr-Ox outperforms a Ni/Mo-Ox, indicating that the type of TM-oxide plays a crucial role in HER activity (Fig1). This work will screen combinations of Ni/TM-oxide systems to identify descriptors for HER/HOR enhancement.

Fuel or electrolysis cells which utilize anion exchange membranes necessitate the use of anion-exchange ionomers (AEIs) to provide a bridge for the conduction of hydroxide ions between the solid polymer electrolyte and the catalyst layer. However, AEIs have a significant inhibitory effect on Pt electrocatalysts. RDE studies at NUCRET have shown in the case of Pt black, a loss of 80% of electro-active surface area (EASA) in the presence of AEI as compared to the EASA in the presence of the traditional Nafion ionomer (Fig2). This loss of EASA results in a loss of HER activity. Ni-alloy electrocatalysts have no clear descriptor for EASA, but they show an increase in HER activity in the presence of AEIs (Fig3).

RDE studies have identified linear trends of charge versus loading in Ni redox peaks (Fig4) and CPE values from EIS testing. We hope to develop relevant metrics for EASA for the HER & OER reactions for TM electrocatalysts. Continued research at NUCRET will investigate the effect of AEIs and the synergism between metals and metal oxides for the hydrogen and oxygen evolution reactions.

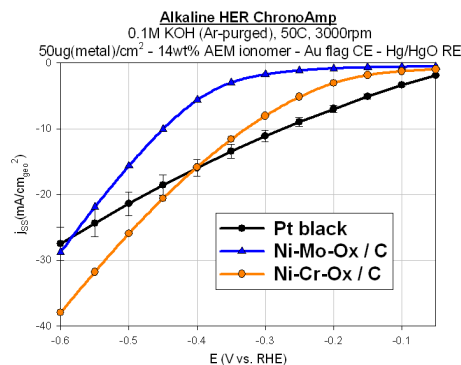


Figure 1 – Steady-state polarization data for HER catalysts in RDE cell. 50 $\mu\text{g}(\text{metal})/\text{cm}^2$ loading on polished GC disk in 0.1M KOH @50°C.

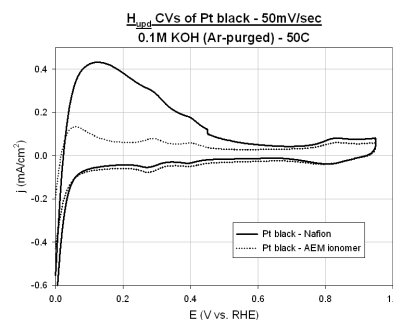


Figure 2 – 50 $\mu\text{g}(\text{Pt})/\text{cm}^2$ loading on polished GC disk in 0.1M KOH @50°C. Catalyst inks contained 50 μL of 5wt% ionomer in 10mL ink volume, resulting in ~14wt% (w.r.t. Pt) ionomer in the catalyst layer.

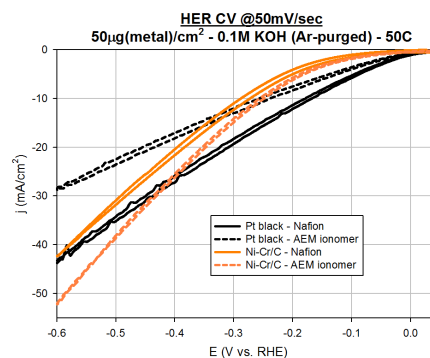


Figure 3 – HER CV scans @50mV/sec for Pt black versus Ni-Cr/C electrocatalysts with AEM and Nafion binder. 14wt% ionomer content in the catalyst layer (w.r.t. metal LD).

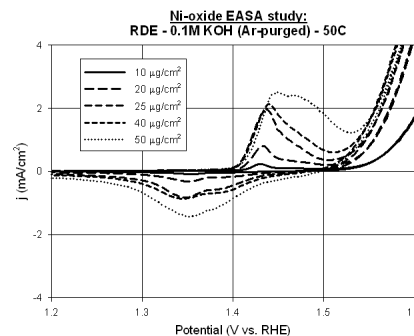


Figure 4 – Increase of Ni^{2+/3+} redox peaks with loading on GC RDE tip. CV scans at 20mV/sec.

Acknowledgement:

Authors gratefully acknowledge the project management and financial support from Proton On-Site as part of an ARPA-E grant.

References:

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- (2) Gasteiger et al. *JECS*. **2010**, 157, B1529-B1536
- (3) Markovic et al. *Nature Chemistry*. **2013**, 5, 300-306