Development of high-surface area Ni-alloy catalysts
for anion exchange membrane water electrolysis

M. Bates, S. Mukerjee
Northeastern University Center for Renewable
Energy Technology
Northeastern University
Boston, MA 02115, USA

Anion exchange membranes (AEMs) open an exciting door for the development of non-Pt group metal (PGM) catalysts in fuel and electrolysis 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. At a certain performance barrier, the cost per kgH_2 will undoubtedly out-compete PGM electrocatalysts. 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".

Ni-alloy-oxide thin films have recently shown high performance for oxygen evolution in alkaline electrolytes[1]. Ni-alloys also have a long history of moderate performance for hydrogen evolution in alkaline media[2] (as compared to Pt electrocatalysts). More recent studies have shown significantly increased alkaline HER performance from Raney Ni-Mo electrodes.[3]

Recent experiments indicate that Ni-alloys may even out-perform the standard IrO_2 catalysts for oxygen evolution in terms of activity and stability. RDE results show ~30A/g at η=370mV for initial Raney Ni-alloy oxide samples and up to 220A/g for Ni-alloy oxides on commercial Raney Ni supports. However, initial cell testing indicates significant mass-transport and utilization issues requiring optimization of catalyst layer fabrication on gas diffusion electrodes. Thus, synthesis efforts for anode catalysts have begun to optimize conditions for high-surface area Raney Ni-alloy oxides. Anode studies will target structure-activity relationships for OER on the mixed-phase oxide samples and evaluate the OER activity as a function of pH.

Research efforts on cathode development involved RDE screening of binary & ternary carbon-supported Ni-alloys. XRD analysis of initial promising catalysts revealed Ni fcc & metal oxide crystallite phases. These results indicate possible H_{ads}-spillover effects theorized for materials with highly reversible oxidation states described in the literature for Ti,Nb,W &Ta bronzes in acidic media[4], but possibly applicable to TM-oxides in alkaline media. Cell testing for the highest RDE-performance Ni-Cr/C materials showed poor HER performance, so investigations are being conducted into electro-deposited Raney Ni-alloy films for AEMWE cathodes.
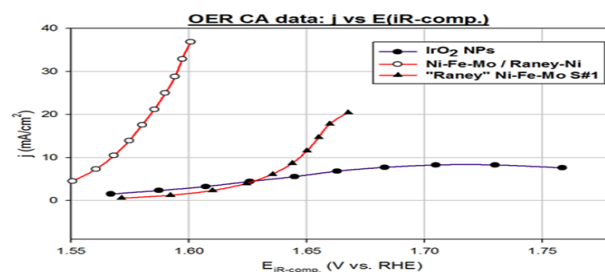

Figure 1 – iR-corrected steady-state polarization data for OER catalysts in RDE cell. 50μg(metal)/cm^2 loading on polished GC disk in 0.1M KOH @50°C.
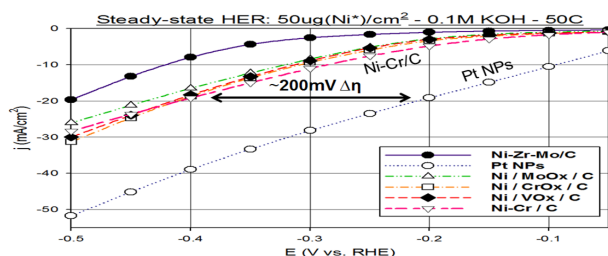

Figure 2 – –Steady-state polarization data for HER catalysts in RDE cell. 50μg(metal)/cm^2 loading on polished GC disk in 0.1M KOH @50°C.
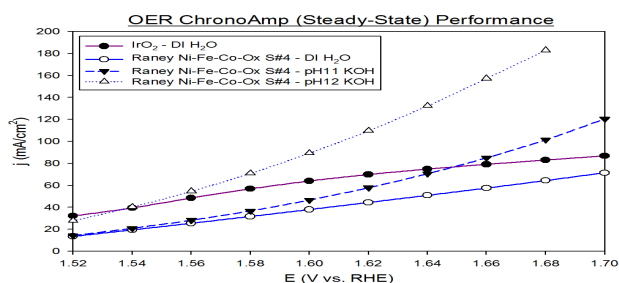

Figure 3 – 6.25cm^2 ½ cell testing: Pt GDE cathode, Tokuyama A201 membrane, Raney Ni-alloy anode @50C, 100mL/min H_2O(w/ & w/out KOH) anode fuel, 100mL/min $H_{2(g)}$ @ 100% RH cathode fuel. Data from steady-state chronoamp. 20mV step, 1min hold.
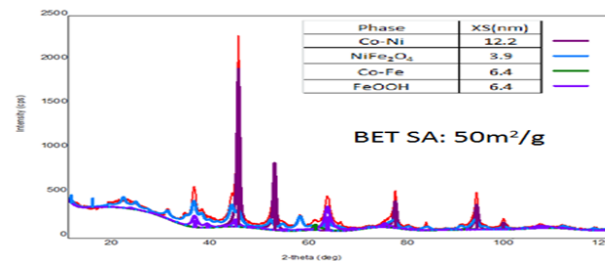

Figure 4 - – XRD data (red) & phase fitting from Rigaku PDXL software. Crystallite size (XS) calculated from Scherrer Eq. using whole powder profile fitting procedure in PDXL. BET surface area from Monosorb single-point analyzer.

References:
(1) Li, X.; Walsh, F. C.; Pletcher, D., *Physical Chemistry Chemical Physics* **2011,** *13* (3), 1162-1167.
(2) Fan, C.; Piron, D. L.; Sleb, A.; Paradis, P., *Journal of The Electrochemical Society* **1994,** *141* (2), 382-387.
(3) Lasia, A., Birry, L. *Journal of Applied Electrochemistry* **2004,** *34*, 735-749.
(4) Jaksic, J. M.; Labou, D.; Papakonstantinou, G. D.; Siokou, A.; Jaksic, M. M., *Advances in Physical Chemistry* **2011,**