

Oxygen Depolarized Cathode at M-N_x-C based Non- Noble Metal Centers for Electrocatalytic Recycling of Chlorine

Urszula Tylus, Robert J Allen and Sanjeev Mukerjee

Center for Renewable Energy Technology,
Department of Chemistry and Chemical and Biology
Northeastern University
317 Egan Center, 360 Huntington Avenue,
Boston, MA 02115

Chlorine is one of the most important products of the chemical industry and its production has risen enormously in the last decades. Its use in the production of polymers including polyvinyl chloride, polyurethanes and polycarbonate as well as chloroaromatics provides for a worldwide chlorine annual capacity of about 60 million tons [1].

Of the three electrolytic processes, diaphragm cell (Griesheim cell), mercury cell processor (Castner-Kellner cell) and the membrane cell, the latter offers the highest efficiency and safety. A general outline of a fully integrated electrolyzer process involves recycling the chlorine gas evolved in the anodic compartment of the cell for utilization as feedstock to the chemical plant. According to the latest technology, the cathode half involves oxygen reduction reaction, where development of the oxygen consuming gas diffusion electrode (GDE) technologies has tremendous impact on cost and energy savings due to much lower ORR overpotential [1-3].

Typical operation conditions of such cell involve aqueous solution of hydrochloric acid at maximum concentration of 20% (~5 M) and maximum temperature of 60 °C. This highly corrosive environment along with presence of halide ions calls for stable and non-sensitive oxygen reduction (ORR) catalyst. Current state of the art catalyst for ODC is rhodium based chalcogenite (Rh_xS_y/C) produced by DeNora, and it outperforms extremely ORR active Pt/C which is easily poisoned by chloride ions [4]. Rh_xS_y/C catalyst though not significantly more active compared to Pt/C possesses superior long term stability. However, as it involves precious metal, the cost is considered as a possible serious drawback [3, 5].

In the current work, we will present a novel non-precious metal-based catalyst (non-PGM) designed and synthesized in our laboratory that shows very promising OCD performance, which is not significantly affected by presence of chloride ions. Figure 1 includes polarization curves of our non-PGM catalyst (NEU-MNC) in acid electrolyte without and with presence of chlorides compared with Pt/C and the state of the art Rh_xS_y/C. As Figure 1 shows, this new catalyst shows relatively low overpotentials and high current densities in comparison to current state of the art carbon supported rhodium sulfide based chalcogenide (Rh_xS_y/C) as well as promising stability in presence of chloride ions (Cl⁻) even at high concentrations.

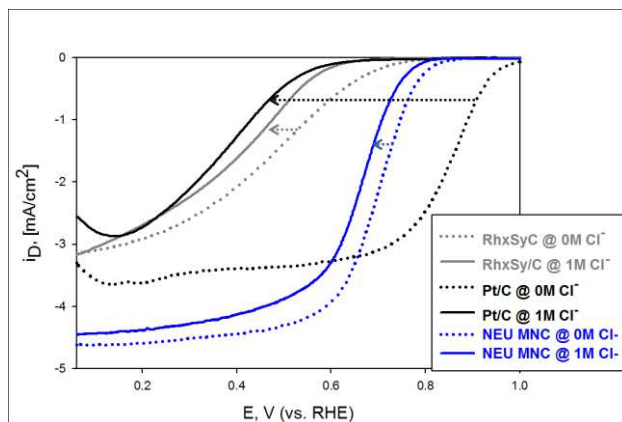


Figure 1: ORR polarization curves of NEU-MNC catalyst collected in 1M HCl (solid lines) and 1M HClO₄ (dotted lines), in comparison with state of the art Ru_xS_y/C (16ug Rh/cm²), and commercial Pt/C (14 ugPt/cm². (RDE@RT: 900rpm, 20mV-s, 0.247cm² GC, catalyst total loading 600ug/cm² (<=18 ugFe/cm²).

Unexpected shut-down of the HCl electrolyzer cell due to power outage at the plant may cause major problems that have to be accounted for, including a flooding of the cathode with high concentrations of HCl, up to 5M. This was a major reason for the highly active platinum-based ORR catalyst to be replaced by the current Rh_xS_y/C as the Pt catalyst undergoes irreversible dissolution when exposed to this highly corrosive environment [5]. Effect of long term exposure of the NEU-MNC catalyst on its activity is under current investigation and will be included in the presentation.

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References:

- [1] Education in Chemistry, 48 (2011) 48.
- [2] F. Federico, G.N. Martelli, D. Pinter, Gas-Diffusion Electrodes for Chlorine-Related (Production) Technologies, in: Modern Chlor-Alkali Technology, Blackwell Science Ltd, 2007, pp. 114-127.
- [3] J.M. Ziegelbauer, A.F. Gullá, C. O'Laoire, C. Urgeghe, R.J. Allen, S. Mukerjee, *Electrochimica Acta*, 52 (2007) 6282-6294.
- [4] T.J. Schmidt, U.A. Paulus, H.A. Gasteiger, R.J. Behm, *Journal of Electroanalytical Chemistry*, 508 (2001) 41-47.
- [5] A.F. Gullá, L. Gancs, R.J. Allen, S. Mukerjee, *Applied Catalysis A: General*, 326 (2007) 227-235.