

Alloy Oxide Electrocatalysts for Regenerative Hydrogen-Halogen Fuel Cell

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ABSTRACT

Stable, catalytically active, and inexpensive halogen electrodes are essential for the success of the regenerative hydrogen-halogen fuel cell as a competitive means of large-scale electricity storage. We report the synthesis and electrochemical testing of two novel electrode materials — ruthenium-cobalt and ruthenium-manganese alloy oxides. These alloys were fabricated by wet chemical synthesis methods as a coating on a titanium metal substrate and tested for chloride and bromide oxidation and for chlorine and bromine reduction. These alloy oxides exhibit high catalytic potency and good electrical conductivity good stability, while having a significantly reduced precious metal composition compared to commercial chloride oxidation electrodes made of the oxide of a ruthenium-titanium alloy. We tested alloys with Ru content as low as 1% that maintained good electrochemical activity. Stability tests indicate immeasurably small mass loss.

INTRODUCTION

There are many means of storing electrical energy, but only a few are feasible for the power levels, costs, and energy storage capacities required to support grid scale intermittent renewable energy production and use. Among these are flow battery systems that involve hydrogen-halogen, vanadium redox, and zinc bromine chemistries.

We expect the hydrogen-halogen flow battery or regenerative fuel cell to become a competitor because of the low overpotentials afforded by the halogen electrode, leading to very high roundtrip efficiencies at reasonable current densities; the high energy density; and the inexpensive reactants. The corrosive halogen and hydrohalic acid environment provides a materials challenge, however. Making low cost, high performance, durable electrodes is essential for the success of the technology.

Commercial chloride oxidation electrodes are based on DeNora's Dimensionally Stable Anode (DSA), which is an oxide of the Ru_xTi_{1-x} alloy, with x typically greater than 30% [1]. DSAs have superb electrocatalytic properties for chloride oxidation at highly anodic potentials. The DSA electrode kinetics of the chlorine oxidation reaction have been studied extensively [2-5].

Hydrogen-halogen based regenerative fuel cell electrodes require an inexpensive electrocatalyst for *both* oxidation and reduction reactions that is a good electron conductor with a surface that is stable below a pH of 0. Hydrogen-halogen based regenerative fuel cells from the 1980s employed comparable electrode materials to DSAs [7]; other carbon-supported and noble metal containing oxide catalysts have also been investigated [8]. The hydrogen electrode is similar to hydrogen-oxygen PEM fuel cells; hence we expect the attainable precious metal loading on the hydrogen electrode to be similar to optimal loadings in hydrogen-oxygen fuel cells [9].

Hydrogen-halogen cells were studied beginning in the 1970s for utility and military energy storage applications. Areas of study included membrane properties, electrode kinetics, and cell design [6-8,10-14]. While these cells were deemed enabling for missile defense (MX missile program), interest waned at the end of the cold war as needs for large-scale energy storage diminished. Studies have shown that DSAs perform well for electrocatalysis of halide oxidation and reduction processes [10]. Unfortunately, the Ru precious metal loading is high, making DSAs an expensive electrode choice for a halogen-based electricity storage technology. Reducing the Ru loading without significantly compromising the electrocatalytic and other desirable properties would be very valuable.

This present investigation shows that a significant decrease of Ru metal content (down to 1 at%) by alloying with inexpensive metals can be achieved without compromising catalytic activity or stability. Two alloy constituents that are particularly promising are cobalt and manganese. Results on two specific electrode materials, $\text{Co}_{0.89}\text{Ru}_{0.11}\text{Oxide}$ and $\text{Mn}_{0.99}\text{Ru}_{0.01}\text{Oxide}$, are presented. This significant decrease of Ru content does not diminish halogen redox performance compared to pure RuO_2 or commercially available DSAs. Stability is also maintained.

MATERIALS AND METHODS

The electrodes were fabricated via traditional wet chemical oxide synthesis techniques [1]. Varying proportions of Ru and Co or Mn salts were mixed to form a precursor for the oxide electrode material, which was then painted on a titanium foil substrate. All of the following chemicals were purchased from Alfa Aesar. The Ru salt was ruthenium(III) chloride hydrate, with a purity of 99.9% (PGM basis), Ru 38% min. The Mn salt was manganese(II) chloride tetrahydrate, with a purity of 99% (metals basis). The Co salt was cobalt(II) chloride, with a purity of 99.7% (metals basis). The titanium foil substrate was 0.127 mm thick, with a purity of 99.99% (metals basis).

To obtain a solution of Mn and Ru, MnCl_2 and RuCl_3 were dissolved in a mixture of isopropanol and HCl(aq) . To obtain a solution of Co and Ru, CoCl_2 and RuCl_3 were dissolved in the same solvent.

The titanium foil substrates were first abraded with emery cloth followed by rinsing with soap water and sonication in isopropanol for 10 minutes. They were then acid-dipped for 20 min. in 2 M HCl(aq) at 80 °C. The substrates were rinsed thoroughly with 18.2 MΩcm water several times. The clean Ti substrates were placed on a piece of tissue paper inside a clean petri dish. The top surfaces of the substrates were also covered with tissue paper to protect the clean surface, and the substrates were left to dry in air before coating.

A clean Ti substrate was then coated with one of the mixed salt solutions with a paint brush. After the coating, the solvent was evaporated by placing the coated electrode on a hot plate at 60 °C for 15 to 20 minutes. The dried salt crystals were then oxidized in an air-atmosphere furnace at 470 °C for 15 to 20 minutes.

We also fabricated three other pure oxide electrodes for comparison. Oxides of pure ruthenium, cobalt, and manganese were synthesized with the above procedures, except that, instead of a mixed cation salt solution, we used only one salt containing the respective cation.

Electrochemical testing of the electrodes was performed using a BASi Epsilon potentiostat with a three electrode cell. The fabricated oxide electrode was the working electrode. The counter electrode was a 0.5 mm diameter by 3 cm long Pt wire, and the reference electrode was a BASi RE-5B Ag/AgCl electrode (stored in 3 M NaCl(aq), 0.196 V vs. NHE). All potentials reported are with respect to this reference electrode. The working electrodes were covered with non-conductive nail polish everywhere except where we exposed to the electrolyte a particular, readily measured active area. The electrodes were pushed through a piece of parafilm covering a small glass beaker, which was filled with a dissolved halogen-containing electrolyte.

For the chlorine redox experiments, the electrolyte was ~80 mL of 1 M HCl(aq) + 4 M NaCl(aq). We electrochemically generated Cl₂ gas bubbles by cycling the electrode for 110 cycles from 1.0 V to 1.6 V at a scan rate of 10 mV s⁻¹. During this time, the electrolyte was stirred with magnetic pellet. Cl₂ gas dissolved into the electrolyte and turned the solution a very light yellowish color.

For the bromine redox experiments, the electrolyte was ~80 mL of 1 M HBr(aq) which had initially been purged with argon. We electrochemically generated Br₂(aq) by cycling the electrode for 110 cycles from 1.0 V to 1.4 V at a scan rate of 10 mV s⁻¹. During this time, the electrolyte was stirred with a magnetic pellet. The solution became dark yellow due to the generation of dissolved Br₂, but the Br₂ solubility limit was not reached.

Linear sweep voltammetry polarization curves were measured to assess electrocatalytic activity (Fig. 1). For the chlorine redox experiments, the voltage was swept from 1.0 V to 1.6 V at a rate of 10 mV s⁻¹. For the bromine redox experiments, the voltage was swept from 0.7 to 1.4 V at a rate of 10 mV s⁻¹. Both the chlorine and bromine experiments were performed in an unstirred, still solution.

Endurance testing was performed by applying an oxidation current of 250 mA/cm² for 10 hr. to the (Co,Ru) oxide electrode in the chloride and bromide containing electrolytes described above. The time-dependence of the potential was monitored.

Preliminary compositional analysis was performed using energy dispersive X-ray analysis (EDAX) in a Zeiss EVO-50 scanning electron microscope. Spectra were compared to simulations using the STRATEGEM software package. The EDAX data were obtained from 6-7 different spots on each sample using different electron accelerating voltage. This analysis permitted the relative concentrations of the metals to be determined but we have not yet determined the exact oxidation state of the alloys.

RESULTS AND DISCUSSION

The results of the linear sweep voltammetry experiments are shown in Figure 1. Figure 1(a) shows chloride oxidation (negative) and chlorine reduction (positive) current densities as functions of potential for several different electrodes. Figure 1(b) shows bromide oxidation (negative) and bromine reduction (positive) current densities as functions of potential for several different electrodes.

Pure cobalt oxide is seen to exhibit a negligible current density, but once it is alloyed with Ru to become Co_{0.89}Ru_{0.11}O_x, the catalytic activity for bromine approaches that of pure RuO₂, and the activity for chlorine exceeds that of pure RuO₂. Mn_{0.99}Ru_{0.01}O_x also exhibits appreciable halide oxidation activity—a surprising result considering there is only 1 at.% of Ru present in the oxide. Clearly ruthenium plays a significant role in the catalysis, and the understanding of this role is the focus of future research.

During the endurance tests (holding 250 mA/cm²) on Co_{0.89}Ru_{0.11}Oxide for chloride oxidation, a steady voltage of 1.335 V was maintained for 10 hr. The same electrode in the bromine electrolyte maintained a steady voltage of 1.230 V. In the case of bromine oxidation, voltage fluctuations were observed during the experiment, but we observed no systematic trend upward or downward. Mass loss from the cobalt-bearing electrode after 10 hours of chloride oxidation was imperceptible, with an upper limiting error bar of 10⁻⁹ gm per coulomb.

In summary, we have synthesized Co-Ru and Mn-Ru alloy oxides with very low precious metal content that exhibit good catalytic activity and good stability in acidic electrolytes and halogen environments. These are expected to enable advances in the development of the hydrogen-halogen regenerative fuel cell.

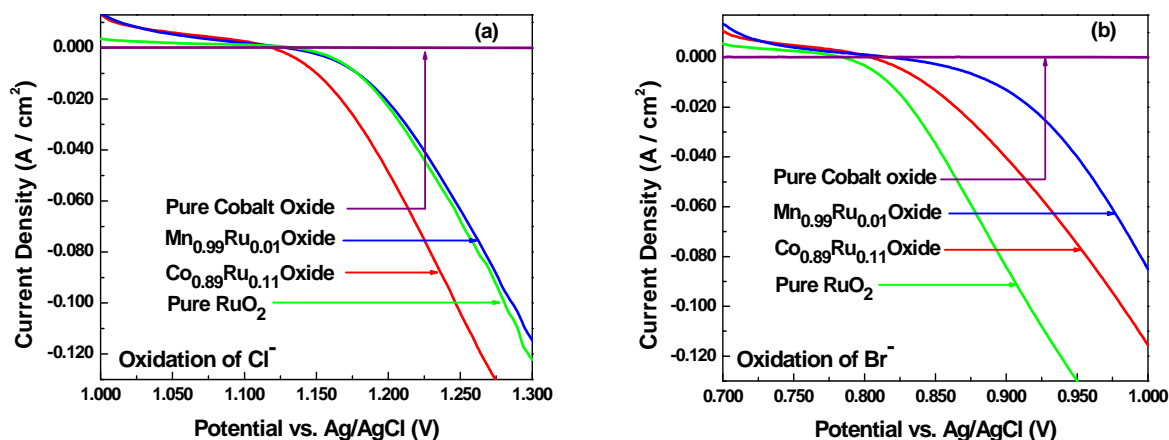


Figure 1. (a) Electrocatalytic activity of experimental electrodes for chloride oxidation and chlorine reduction. For the cobalt oxide electrode, the current density is four orders of magnitude lower than the others. (b) Results for bromide oxidation and bromine reduction show comparable slopes to those in (a).

ACKNOWLEDGMENTS

This research was supported by National Science Foundation grant NSF-IIP-0848366 through Sustainable Innovations, LLC. We thank Dr. Trent M. Molter for helpful discussions. Special thanks to David Lange, Harvard Center for Nanoscale Systems, for assistance in multi-energy EDAX analysis of the composition of the specimens.

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