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SELECTION AND EVALUATION OF MATERIALS FOR ADVANCED WATER ELECTROLYZERS

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Abstract

Efforts are being made to find better and more stable (i) anode electrocatalysts for solid polymer electrolyte water electrolyzers and (ii) cell components (e.g., electrodes, separators) for advanced alkaline water electrolyzers. Of several mixed oxides of ruthenium examined as anode electrocatalysts in 1 N H_2SO_4, the ternary system (Ru-Ir-Ta) shows most promise. Most of these mixed oxides, prepared by the thermal decomposition method, exhibit low Tafel slopes for oxygen evolution. As with Pt and Ir, multicycling of a Ru-Ir electrode in H_2SO_4 produces a thick oxide layer, as ascertained ellipsometrically, with enhanced electrocatalytic activity for oxygen evolution. High surface area nickel or mild steel and nickel whisker electrodes reduce cell potentials for water electrolysis in alkaline electrolyte by about 100 mV. Composite barrier structures show prospects of improving chemical and mechanical stabilities of separators in alkaline electrolyte. The FY 1980 projects will consist of (i) assembly of LEED-Auger-ESCA system and development of methods to correlate electrocatalytic activity and surface properties; (ii) examination of promising ruthenium based mixed oxide electrocatalysts in single cells; (iii) electrochemical-ellipsometric investigation of Ru-Ir and Ru-Ir-Ta alloys; (iv) elucidation of role of hydrogen permeation in metals on time variation of hydrogen overpotential; (v) improvement of electrode configuration to lower overpotential losses; and (vi) examination of composite barrier materials.

1. Introduction

The activities at BNL during the year were concentrated in two areas: (i) finding better and more stable anode electrocatalysts for the General Electric Solid Polymer Electrolyte (SPE) Water Electrolyzer and (ii) evaluation of some materials as electrocatalysts or separators for advanced alkaline water electrolyzers. The Hewlett-Packard Data Acquisition System was programmed to collect and plot the results of current-potential measurements in four cells simultaneously. This included half and single cell measurements. The slowness of the oxygen electrode reaction is the major cause of efficiency losses in water electrolyzers(1). The overpotential for this reaction is at least 300 mV during acid or alkaline water electrolysis at desired current densities. A second problem, needing solution, is the increase of cell potential for water electrolysis with time. In acid electrolytes, this phenomenon is due to increase of oxygen overpotential with time while in alkaline electrolyte it is predominantly due to an increase of hydrogen overpotential(2). Efforts are in progress to elucidate the mechanism of time variation of overpotential and develop methods for its inhibition at BNL and the University of Virginia (UVA).

2. Anode Electrocatalysts for Solid Polymer Electrolyte Water Electrolyzers

2.1 Ruthenium Based Mixed Oxides

With the aim of stabilizing ruthenium based electrocatalysts for SPE water electrolyzers(3), mixed oxides of ruthenium with Ta, Zr, Hf, Ir, W, La, Mn, Pb and Sr were prepared by the thermal decomposition method on a titanium substrate and were examined as oxygen evolution electrocatalysts in 1.0 N H_2SO_4 at 25°C. With some of these oxides, the current-potential plots, obtained using the slow potential sweep technique, exhibit hysteresis, as shown in Figure 1 for $WRuO_x$. This behavior is characteristic of electrodes at which there is a time variation of overpotential. The mixed oxide $LaRuO_x$ behaved in a similar manner while the hysteresis was not observed with the other mixed oxides. The current-potential relations for oxygen evolution on RuO_x, IrO_x, $IrRuO_x$, $TaRuO_x$, $Ta_{0.5}Ir_{0.5}RuO_x$ and $TaIr_{0.5}Ru_{0.5}O_x$ were obtained using steady state techniques and the Tafel lines are shown in Figures 2 and 3. The time variation of overpotential at a constant current density of 50 mA cm^{-2} is considerably less on the binary and ternary oxides than on RuO_2. Elucidation of the mechanism responsible for improving and stabilizing the electrocatalytic activity of ruthenium by alloying with tantalum and iridium oxide awaits a detailed study of both the surface states and phase diagram of the TaIrRu oxide system.

2.2 Electrochemical and Ellipsometric Studies on Ru-Ir Alloy

A combined electrochemical-ellipsometric method was used with the aim of (i) drawing correlations between electrocatalytic and optical properties of oxide films formed on surfaces and (ii) elucidating the mechanism of the time variation of overpotential. Investigations were made on a Ru-Ir alloy (50-50 atomic percent) in 1.0 M H_2SO_4. Preliminary results showed that oxygen evolution kinetics can be improved by multicycling of the electrode between 0.1 to 1.5 volts vs DHE. Similar effects were observed with multicycling of Pt and Ir electrodes(4,5). A Tafel slope of 60 mV/decade was obtained, as shown in Figure 4. The performance improvement is attributed to the growth of oxide layer with thickness of about 30 Å. This layer is enriched in $Ir(OH)_3 \cdot XH_2O$ due to preferential dissolution of Ru. The oxide layer dissolved when oxidized at higher anodic potentials (say 2.1 volts vs DHE) and the resulting oxide layer is a poorer electrocatalyst. A Tafel slope of 80-85 mV/decade was observed on this oxide layer. In contrast to the oxide formed on Ir metal, this oxide layer on the Ru-Ir alloy cannot be reduced completely even at high cathodic potential which indicates the presence of ruthenium oxide. However, the composition of Ru in the oxide layer is lower than that in the bulk material.

DISCLAIMER

3. Materials for Advanced Alkaline Water Electrolyzers

3.1 Anode and Cathode Electrocatalysts

During the reporting period, beryllium copper nickel alloy (0.44 Be, 30.25 Ni, 69.31 Cu), obtained from Kawecki Berylac Industries (KBI), high surface area nickel deposited on mild steel (from International Nickel Company-INCO) and nickel whisker electrodes with a high surface area deposited on mild steel from UVA were evaluated as electrocatalysts. The beryllium copper nickel alloys exhibited higher anodic and cathodic overpotentials than nickel. The high surface area nickel electrodes from INCO and from UVA were tested only as anodes. The deposited electrodes should be on nickel screens to be evaluated as cathodes. These high surface area nickel electrocatalysts showed a lowering of activation overpotential and merit further investigations at BNL in small cells and at Teledyne Energy Systems (TES) in the 5-cell test rig. The whisker electrodes showed a peculiar behavior in that there was a lowering of hydrogen overpotential, which further decreased with time. This was attributed to the observation that black deposits of nickel were found on the cathode. This process could have occurred only by disintegration or dissolution of the nickel particles from the high surface area whisker anodes and subsequent deposition of the nickel ions or particles in the electrolyte on the cathode.

3.2 Separators

There was a modest effort to develop sandwich barrier materials of asbestos coated on both sides with Teflon bonded potassium titanate. This type of approach may serve a two-fold purpose - mechanically stabilize Teflon bonded potassium titanate and chemically stabilize asbestos - in advanced alkaline water electrolyzers operating at temperatures above 100°C. A Mallory suggestion of asbestos sandwiched between Permion 300 showed a high electric resistance. Tin hydrosol treated asbestos from UVA increased the cathode overpotential. Polybenzimidazole (PBI), although acceptable as far as electrolyte resistance is concerned, showed poor physical stability.

4. Proposed Studies for FY 1980

The major tasks in FY 1980 will be (i) the assembly of the LEED-Auger-ESCA system and (ii) the development of methods using this instrument for identifying the chemical nature of metallic and nonmetallic electrocatalysts before and after electrolysis and for elucidation of effects of crystallite size, orientation and alloying on electrocatalytic activities. A detailed electrochemical-ellipsometric investigation on Ru, Ru-Ir and Ru-Ir-Ta will be made to draw correlations between the electrocatalytic activities for oxygen evolution and optical properties of the oxide films formed on these substrates in the potential region for oxygen evolution in acid electrolytes. The promising ruthenium based mixed oxide anode electrocatalysts will be tested in acid electrolyte single cells at BNL. Recommendations will be made to the General Electric Company for further evaluation of these materials in SPE water electrolyzers. Investigations will be initiated to screen and evaluate low cost membranes as substitutes for the expensive Nafion in SPE water electrolyzers. Efforts will be made to elucidate the role of hydrogen permeation in metals (e.g., nickel) on the mechanism of time variation of hydrogen overpotential in alkaline electrolyte. The prospects for reduction in overpotential losses in alkaline water electrolyzers by changes in electrode configuration will be examined. Composite barrier materials will be further developed and tested in this electrolyte medium.

ACKNOWLEDGEMENTS

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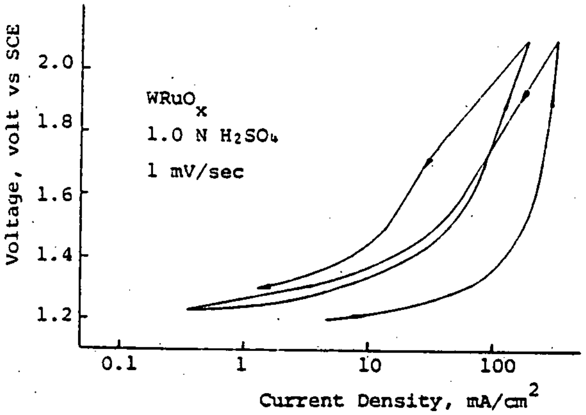

Figure 1. Voltage-current relationship for oxygen evolution reaction for $WRuO_x$ in 1.0 N H_2SO_4 at 25°C. Sweep rate: 1 mV/sec.

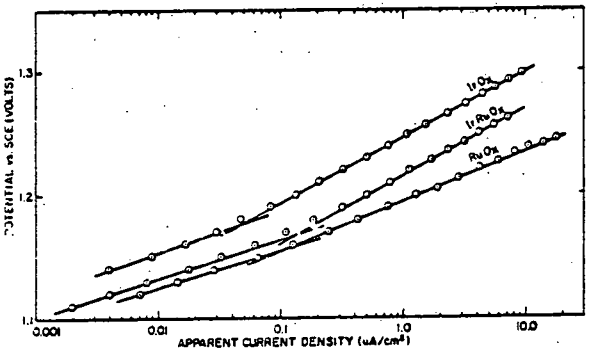

Figure 2. Tafel plots for oxygen evolution on IrO_x, $IrRuO_x$ and RuO_x in 1 N H_2SO_4 at 25°C.

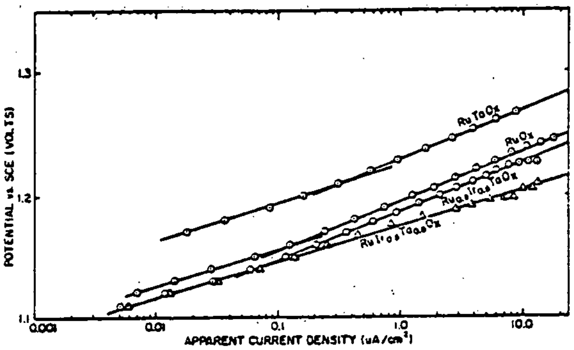

Figure 3. Tafel plots for oxygen evolution on RuO_x, $RuTaO_x$, $Ru_{0.5}Ir_{0.5}TaO_x$ and $RuIr_{0.5}Ta_{0.5}O_x$ in 1 N H_2SO_4 at 25°C.

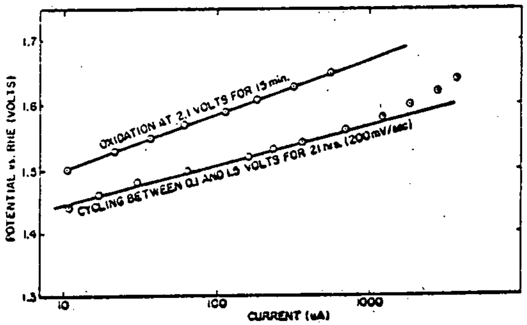

Figure 4. Tafel plots for oxygen evolution on oxides formed on Ru-Ir alloy in 1 M H_2SO_4 at 25°C.