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Study of SO_2-Depolarized Water Electrolysis

Anu Lokkiluoto, **Michael Gasik**, **Tuomo Kuikka**, Aalto University Foundation
School of Science and Technology, Finland

1 Introduction

Hydrogen is a promising energy carrier, which has the potential to replace fossil fuels used as power source of vehicles. There is, however, no large scale, cost-effective, environmentally attractive hydrogen production process available for commercialization today. One of the best alternatives of hydrogen production is the so-called hybrid sulphur cycle (HyS), which is also known as Westinghouse process. The Nuclear Hydrogen Initiative of The US DOE has identified the hybrid sulphur cycle together with sulphur-iodine cycle as the first priority cycles [1]. According to the calculations carried out within the IEA HIA Task 25, of these two processes, the HyS is the more favourable one.

In the low-temperature part of the HyS, sulphur dioxide depolarized electrolysis (SDE) is used, where hydrogen and sulphuric acid are produced as products of the reaction between water and dissolved SO_2. The advantage of the SDE is based on the fact that the reversible voltage E^o of the net reaction (1)

$$SO_2\,(aq) + 2H_2O \rightarrow H_2SO_4\,(aq) + H_2\,(g) \qquad (1)$$

is only 0.158 V at 25 °C [2], versus the theoretical $E^o = 1.23$ V needed for conventional water electrolysis (alkaline or PEM). In laboratory scale tests, the realized cell voltage has been 0.5-1.2 V depending on the current density versus 1.85 – 2.05 V of the commercial alkaline electrolysis. Thus the HyS process takes only 30 - 40% of the electric energy needed for direct water splitting by conventional electrolysis. A review by O' Brien et al. concerning the electrochemistry of oxidation of SO_2 in SDE was published recently. [3]

Research groups at the Savannah River National Laboratory (SRNL) and at the University of South Carolina (USC) have studied recently the SDE. Both research groups have used PEM electrolyser with carbon bipolar plates/flow channels and Pt/C electrodes (MEA structure). These were the materials used also by the original Westinghouse group. [4] At SRNL, SO_2 dissolved in H_2SO_4 is used as the anolyte, and water is fed to the cathode. [1] The electrolyser has been operated also in dry cathode mode. [5] At USC, they have used gaseous feed of SO_2 to the anode, while liquid water is fed to the cathode. [6]

The aim of this study was to identify the possible technical obstacles in respect to materials stability in production process of H_2 by SO_2-depolarized electrolysis. Metallic materials have good strength to weight ratio, are easily formed and joined and have good heat transfer properties. For engineering purposes, it is usually desirable to use metal alloys whenever possible. From the materials point of view, the SDE is very challenging due to the corrosiveness of the electrolytes used (mixtures of sulphuric acid and SO_2). Compared to the time of the original Westinghouse studies, new metallic corrosion resistant alloys exist nowadays.

A bench-scale flow-through electrolysis cell with an active area of 0.01 m^2 and a test facility with necessary auxiliary equipment were built. With this facility, one-week-long tests were carried out. In addition to these tests, corrosion resistance testing of the coated electrode materials was carried out in a dedicated autoclave. The electrochemical behaviour of the possible bipolar plate/electrode materials was investigated also with linear sweep voltammetry.

The materials studied included uncoated stainless steel 904L and TiN- and gold coatings on steel 904L. Stainless steel 904L has good corrosion resistance in sulphuric acid solutions. The corrosion resistance of stainless steels is due to the formation of dense, protective passive layer. All metals, which corrosion resistance is based on their passive behaviour, have also high surface resistance. For bipolar plates/electrodes, high surface conductivity would be beneficial. Coatings can be used to modify surface properties, and conductive coatings like TiN and gold have been widely studied for PEM fuel cell applications. [7]

2 Experimental Methods and Materials

The materials studied included uncoated stainless steel 904L and TiN- and gold coatings on steel 904L. Disc-shaped samples (~15 mm x 2mm) were used both in linear sweep voltammetry and autoclave experiments. The samples were polished first with SiC paper, grades 240, 400 and 1200, and after that with 6, 3 and 1 µm diamond pastes. TiN and gold-coatings were then manufactured using proprietary low-temperature PVD-method. Thickness of the TiN coating was ~1 µm and thickness of the gold coating was 50±20 nm. A bulk gold electrode with the same dimensions as the samples was prepared from a commercial (24K - 999) gold sheet. The same coating process was used also for the electrodes of the bench-scale electrolyser.

3 Linear Sweep Voltammetry

Linear sweep voltammetry (LSV) is a versatile electrochemical method, which enables simultaneous study of the effects of applied potential, solution composition and temperature. In LSV, the potential applied of the sample is changed, and the current response is recorded. The resulting voltammogram (i-E-curve) shows the electrochemically active and passive potential regions.

The samples were studied at both oxidizing (anodic) and reducing (cathodic) potentials in H_2SO_4-SO_2-solutions at room temperature. The cathodic scans without SO_2 correspond to the cathode side of the SDE cell, and the anodic scans with SO_2 correspond to the anode side. The counter electrode was a platinum flag. The reference electrode was an SCE protected with a special glass jacket in a separated compartment connected with the main cell by a salt bridge. The 1000 ml cell was made of glass, and it had a gas-tight Teflon-lid, the test equipment is shown in figure 1.

Testing was carried out in 15 and 40 wt-% sulphuric acid with and without S(IV) additions. The solution was de-aerated prior experiments with instrument grade N_2 at least for 30 min.

Magnetic stirring was used during the experiments and de-aerating. The amount of SO_2/HSO_3^- was analysed by iodometric back-titration.

The sweep rate was 20 mV/s. The potential ranges of the experiments were -300…+1900 mV (anodic scans without SO_2), +200…+1900 mV (anodic scans with SO_2), and -800…0 mV vs. SCE (cathodic scans). The anodic scan with SO_2 was started at 0.2 V vs. SCE to avoid reduction of SO_2. The open circuit potential (OCP) was measured at the beginning of each experiment mostly to check the connections.

Figure 1: Three-electrode cell used in LSV test.

4 LSV Results

In figure 2, the behaviour of gold coated electrodes is shown on hydrogen scale. The cathodic side (without SO_2) corresponds to the cathode of the SO_2 depolarized electrolysis, and the anode side (with SO_2) corresponds to the anode. In a process corresponding to figure 2, the cell voltage would be ca. 0.8 V.

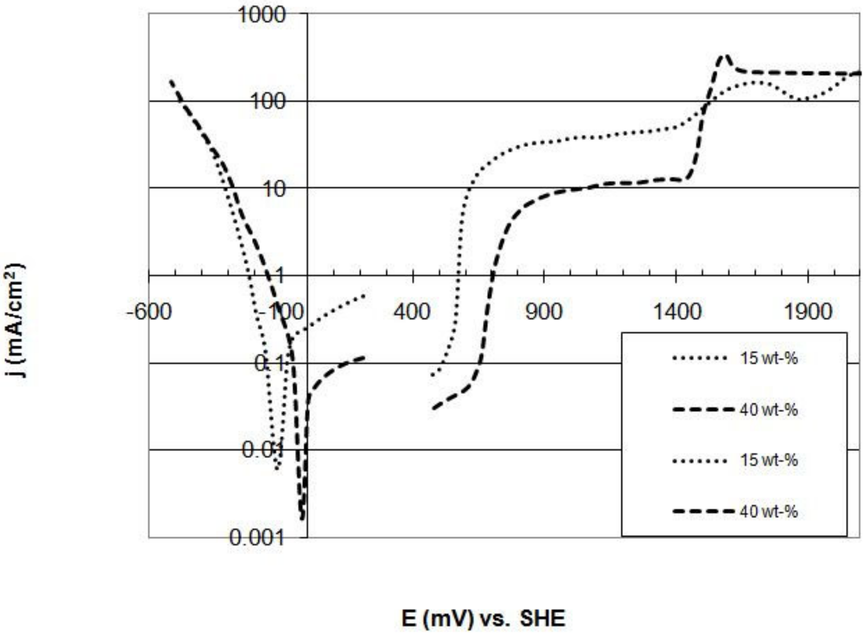

Figure 2: **Au-coated 904 L. T= 25 °C, 15 and 40 wt-% sulphuric acid, v=20 mV/s.**

5 Autoclave Materials Stability Tests

The autoclave corrosion testing was realized in parallel [8]. A special autoclave system was retrofitted and adapted to monitor the parameters listed below. Test equipment is shown in figure 3.

Atmosphere: N_2 <10 bar, SO_2 <2.8 bar

Temperature: RT to 100 °C

Stirrer: RPM from 40 upwards with 16 specimens

Total volume: 30 litres

Material: Special coatings + plastic in-bag for vessel protection.

Two test series were performed in the autoclave. The first series was performed in a sulphuric acid - nitrogen environment and the second in a sulphuric acid - sulphur dioxide environment. The sulphuric acid concentrations were 50 and 80 wt-% and test temperatures were 30 and 50 °C. These conditions are expected to be the most severe for the TiN coating and extreme conditions of the electrolyser.

Each test consisted of 8 specimens, which included duplicate samples of all the specimen types, with duration of two weeks.

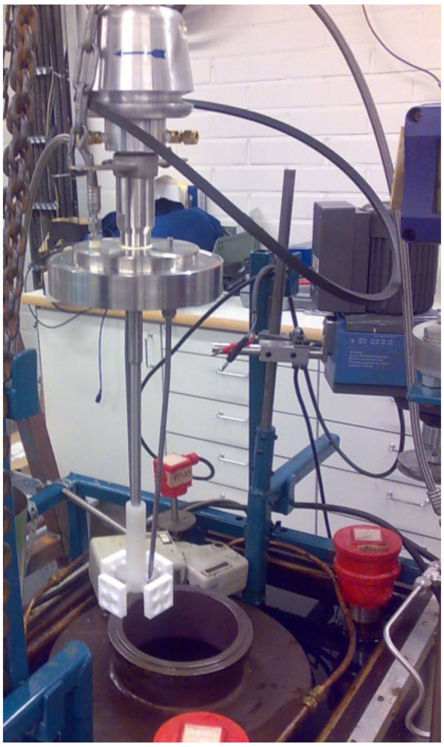

Figure 3: Photograph of the autoclave test equipment.

6 Autoclave Results

Samples were studied by optical and SEM microscopy. Also reference samples of both coatings and bare 904L were analyzed. All specimens were weighed before and after the experiments, but mass losses were not significant enough for any conclusions to be made. In figure 4, optical micrographs of gold coated samples tested in 50 wt-% sulphuric acid are shown.

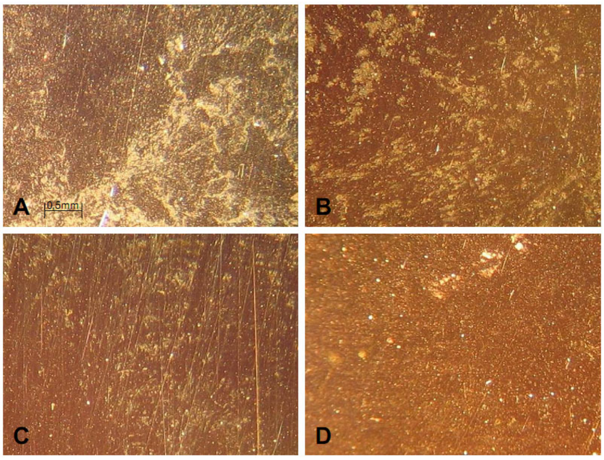

Figure 4: Au-coated 904L in 50 wt-% sulphuric acid. A=30 ºC, N_2; B=30 ºC, SO_2; C=50 ºC, N_2 and D=50 ºC, SO_2.

The gold coating showed no signs of corrosion when studied by optical microscopy.

7 Bench-scale Electrolyser

The bench-scale electrolyser test facility can be seen in figure 5. The active area of the electrolyser is 0.01 m^2. It was purchased from ElectroCell [9].

Figure 5: The bench-scale electrolyser test facility.

Two longer time-scale galvanostatic experiments were carried out at room temperature with current of 10 A, which corresponds 1 kA/m^2. The electrolyte flow rates were 60 – 80 l/h.

The first test was started by adding approximately 80 g/l of SO_2 to the anolyte, of which 70% was readily dissolved. No SO_2 was added during the experiments, so the test was carried out in a batch mode. The amount of SO_2 added corresponded to the solubility of SO_2 in sulphuric acid solution of that concentration and temperature and the test was continued until nearly all the SO_2 was consumed.

8 Bench-scale Electrolyser Results

The depolarization effect of SO_2 was ~0.65 V with gold-coated electrodes, similar to one observed in LSV experiments (figure 2).

9 Conclusions

The corrosion performance of all of the tested materials was better in sulfuric-acid with SO_2 than in pure sulphuric acid solution. This is most likely caused by the reducing nature of SO_2 under these particular conditions.

The corrosion resistance of 904L can be enhanced with gold coating. Thin gold coatings were stable in the conditions of SO_2 depolarized electrolysis at least in the short time scale (up to 14 days) of these experiments. Novel TiN-coatings tested do not seem to be suitable for SO_2 depolarized electrolysis, but they had a good corrosion resistance against sulphuric acid, compared to the older crystalline TiN-coatings. This was the case at low temperatures and lower acid concentrations used in the tests.

In the SO_2 depolarized electrolysis tests, the depolarizing effect of SO_2 was 0.6 - 0.7 V with gold coated 904 L electrodes. The gold coated anode showed catalytic activity towards SO_2 oxidation. With gold coatings, it might be possible to avoid the use of Pt catalysts in the SDE.

Acknowledgements

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