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Recent developments in the technology of sulphur dioxide depolarized electrolysis

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The use of sulphur dioxide as an anode depolarizer in the electrolytic production of hydrogen can considerably reduce the electrical energy input to the electrolyzer. The present work deals with developments in the technology of SO_2-depolarized electrolysis. Recent achievements in electrode fabrication techniques and optimization of cell configuration have resulted in substantial improvements in both cell potential and performance stability. While operating in 50 wt% sulphuric acid at 50° C and 1 atm, the measured cell potentials at 200 and 400 mA cm^{-2} were $\sim$ 0.77 and 1.05 V (including ohmic losses), respectively. A cell endurance test, performed at a constant current density of 100 mA cm^{-2}, indicated that a stabilized cell potential of $\sim$ 675 mV was achieved after 80 hours of continuous operation. The resulting gas from the test cell contained 98.7 vol% hydrogen. The effect of acid concentration in the range 10–60 wt% on the performance characteristics of an SO_2-depolarized electrolyzer was also investigated. Experimental results revealed that the optimum acid concentration for operating SO_2-depolarized electrolyzers is approximately 30 wt%. The observed cell potential was only 0.71 V at 200 mA cm^{-2}.

1. Introduction

Hydrogen is a key industrial chemical. At the present time, most hydrogen gas is produced either by the steam reforming of natural gas or the partial oxidation of oil. The large-scale hydrogen market is mainly in fertilizer, petrochemical, metallurgical, semiconductor, pharmaceutical and food processing industries. In recent years, hydrogen has also attracted attention as a potential energy carrier of the future. Hydrogen can possibly be used, in large quantities, as a clean fuel for fuel cells, for gas turbines and for providing thermal energy (e.g. supplementation of natural gas). According to some estimates, the expanding hydrogen market in the United States will result in a demand for hydrogen at the end of the century at least 3 times higher than the current hydrogen supply [1].

With the continued increase in costs and dwindling availability of oil and natural gas, the development of alternative techniques for hydrogen generation, using non-fossil energy sources, is of crucial importance in meeting the anticipated increasing demands for hydrogen. More recently, a number of currently available methods and advanced concepts have been proposed for bulk hydrogen production. Water electrolysis is technically well developed and can use energy derived from a wide variety of non-fossil primary sources, such as nuclear (fusion), solar, ocean thermal and wind energy, through the intermediate generation of electricity. Recent significant achievements in the development of this technology have been thoroughly discussed elsewhere [2–4]. Due to the limitation of the thermodynamic reversible potential for the electrochemical decomposition of water, high electrical energy is needed (i.e. about 1.8–2.0 V at a practical current density of 200 mA cm^{-2}). Consequently, the production cost of electrolytic hydrogen is presently 2 to 3 times higher than that of hydrogen derived from fossil fuels.

The electrical energy input can be considerably reduced by using sulphur dioxide as an anode depolarizer [5]. In 50 wt% H_2SO_4 at 25° C, for example, the reversible cell potential of an SO_2-depolarized electrolyzer is only $\sim$ 0.29 V as compared to 1.23 V for water electrolysis [6]. More

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precisely, the electrolytic production of hydrogen by depolarized electrolysis theoretically utilizes ~ 24% of the electrical energy required in the conventional water electrolyzers. In fact, SO_2-depolarized electrolysis is the first step of a hybrid thermochemical–electrochemical hydrogen production process [7]. Sulphuric acid produced in the cell is concentrated, using thermal energy from a high-temperature source, then catalytically decomposed to form sulphur dioxide, oxygen and water. Finally, the sulphur dioxide is returned to the electrolyzer to complete the cycle.

The electrochemical reactions in an SO_2-depolarized electrolyzer are illustrated in Fig. 1. During electrolysis, sulphur dioxide dissolved in the electrolyte is electrochemically oxidized at the anode, producing sulphuric acid, hydrogen ions and electrons:

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e. \qquad (1)$$

The hydrogen ions move in the electrolyte toward the cathode, then recombine with electrons which pass via an external circuit to form hydrogen gas:

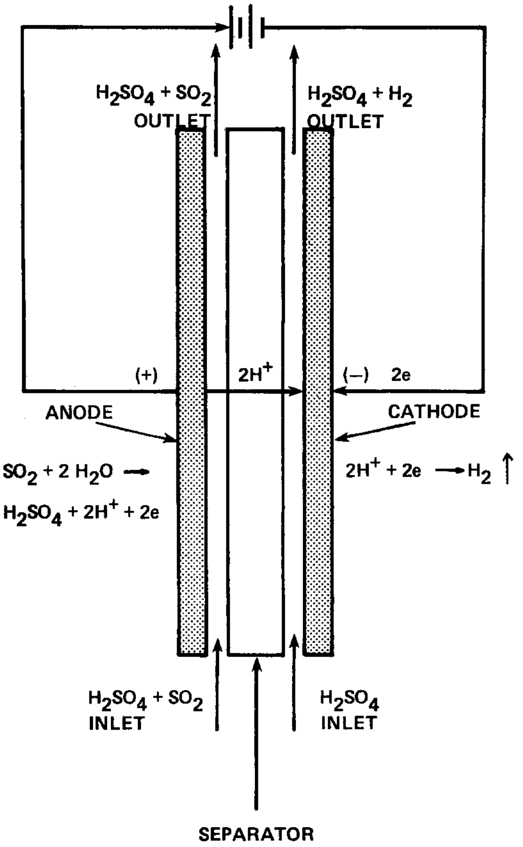

Fig. 1. Schematic diagram of a sulphur dioxide depolarized electrolyzer.

$$2H^+ + 2e \rightarrow H_2. \qquad (2)$$

Thus the overall reaction in an SO_2-depolarized electrolyzer may be represented by an equation of the form:

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2. \qquad (3)$$

During testing the sulphur-dioxide saturated electrolyte is circulated over the anode at a reasonably high flow rate to remove waste heat and sulphuric acid product.

The main purpose of the current electrolysis technology programme at Westinghouse is to develop effective, inexpensive and long-life cell components for SO_2-depolarized electrolyzers. Major efforts have focused on the development of electrode fabrication techniques, electrochemical characterization of fabricated electrodes and improved cell configuration, investigation of the long-term performance stability and study of electrolyte concentration effects on the cell performance. This paper summarizes the significant progress that has been recently accomplished.

2. Experimental

2.1. *Preparation of test electrodes*

Two different kinds of porous carbon plates, obtained from the Pure Carbon Company, have been evaluated as catalyst supports. The two substrates, designated P7620 and FC13, have specific surface areas of ~ 1 and ~ 450 $m^2 g^{-1}$, respectively. In the preparation of a test electrode, a grooved carbon plate was activated by oxidizing it in concentrated nitric acid (13.5 N) at 80° C for 4 hours. Due to the formation of soluble mellitic acid, $C_6(COOH)_6$, the oxidation process increased the pore void volume and roughened the wall of each micropore.

An appropriate amount of an aqueous solution of $Pt(NH_3)_4Cl_2$ or H_2PtCl_6 was applied to the surface of the pretreated carbon plates by a vacuum filtration method and an *in situ* heat treatment (~ 40° C) using an infrared lamp. The carbon plate, coated with a uniform layer of Pt-containing chemical, was then thermally decomposed in a quartz-tube furnace under a hydrogen atmosphere at 600° C. This process resulted in the formation of a uniformly distributed and well-bonded catalyst layer on the surface of the grooved carbon plate. The resulting electrodes had an active surface area of approximately 20 cm^2, and platinum catalyst loading in the range 5–10 $\mathrm{mg\,cm}^{-2}$.

In addition, carbon cloth-backed electrodes were prepared following a proprietary manufacturing process [8]. These electrodes were only evaluated as anodes in the electrolysis cells.

2.2. *Electrochemical cell*

Fig. 2 illustrates the details of an improved cell configuration designed for operation in a flow-by mode. The electrolyzer was constructed of lucite using O-ring seals. A microporous rubber diaphragm was employed as the gas separator. Platinum-catalyzed, carbon-plate electrodes were evaluated as both anode and cathode. A spacer was incorporated between the separator and a test electrode to obtain sufficient electrolyte flowing over the electrode surface. On the back of each current collector, a pressure pad was placed to assure good electrical contact at the electrode/collector interface and to reduce the inter-electrode spacing.

2.3. *Electrolysis test assembly*

The electolysis test assembly is shown in Fig. 3. During an experiment, anolyte and catholyte were circulated at flow rates of about 700 and 300 $\mathrm{cm}^3\,\mathrm{min}^{-1}$, respectively. The anolyte was pre-saturated with sulphur dioxide before it flowed into the cell. A hydraulic overpressure was maintained between the cathode and anode compartments of the electrolyzer to prevent the migration of SO_2-containing species through the separator. In each compartment, a Hg/Hg_2SO_4 reference electrode was connected to study the electrochemical behaviour of the anode and cathode.

2.4. *Electrochemical measurements*

Electrochemical studies on candidate electrodes and improved cell configurations were conducted in 50 wt% sulphuric acid at 50° C and atmospheric pressure. A constant current was applied through a test electrolyzer using a Heath Model SP-2730 power supply. Simultaneously, the overall cell potential, ohmic loss and polarization potentials of anode and cathode were investigated as a function of the current density, which was increased in steps from 10 to 400 $\mathrm{mA\,cm}^{-2}$. In general, the readings were taken after 6 min of equilibration at

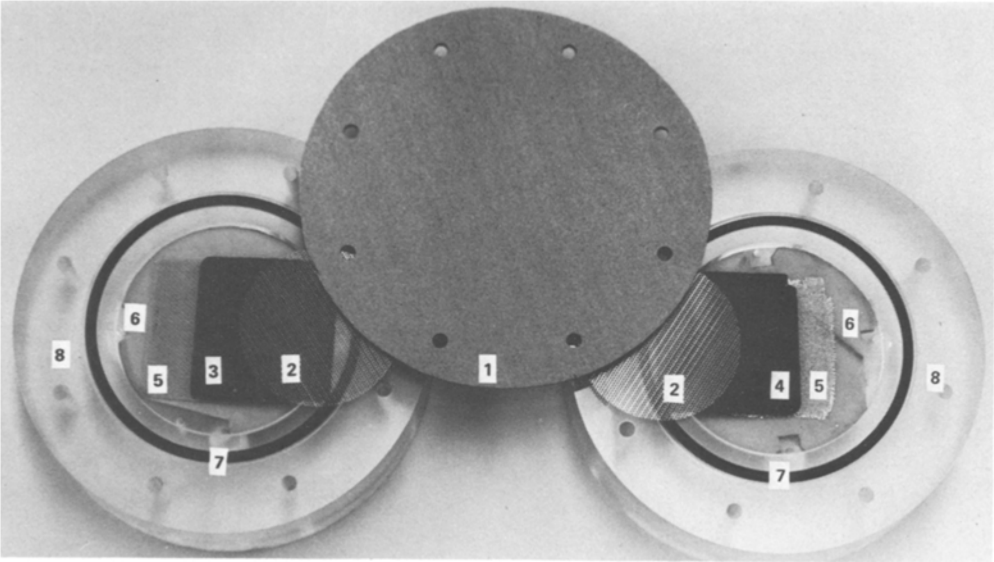

Fig. 2. Details of an improved lucite cell. 1, Separator; 2, spacer; 3, anode; 4, cathode; 5, current collector; 6, pressure pads; 7, O-ring seal; 8, cell frame.

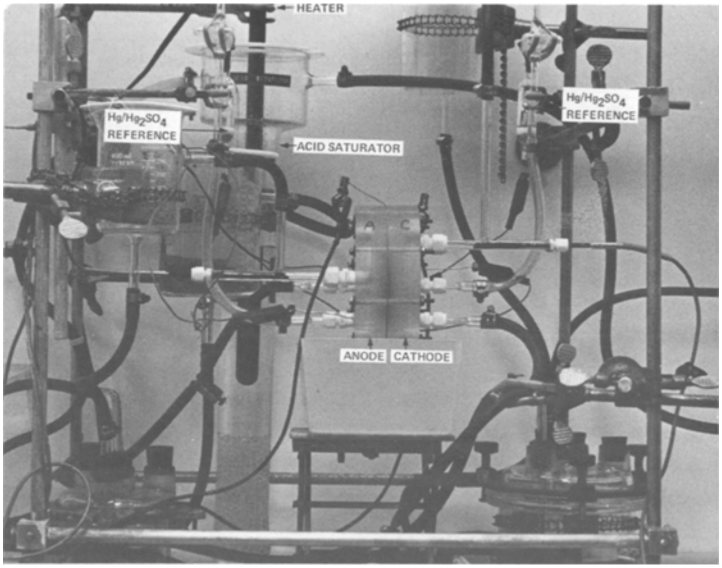

Fig. 3. Electrolysis test assembly.

each current density. Short-term performance stability measurements were also made on each test electrolyzer by monitoring the cell potential at a constant current density of 100 mA cm^{-2} as a function of time up to 2.5 hours.

A cell endurance test was carried out on an intermediate electrolyzer, designated NC-4, using 50 wt% sulphuric acid at 50° C and 1 atm. By operating the cell continuously at 100 mA cm^{-2}, the cell potential, anodic overpotential, cathodic overpotential and ohmic loss were measured as a function of time. During the test, the gradual increase of acid concentration in the anolyte resulted in a detectable effect on the anodic overpotential and cell potential. Therefore, make-up water was introduced to the anolyte at an appropriate rate to maintain a constant concentration. Because of a double pump failure, the endurance test was terminated after ~ 173 hours of operation, which was slightly shorter than the planned operating time of 200 hours.

The dependence of cell performance on acid concentration was also studied in electrolyzer NC-4 at 50° C and atmospheric pressure. The cell potential–current density relationships were determined in sulphuric acid of concentration 10–60 wt%.

2.5. *Chemical analyses*

During the endurance test, the gas from the cathodic compartment of the electrolyzer was collected and then analyzed by mass spectroscopy. The chemical compositions on the surface of the cathode were identified using electron spectroscopy for chemical analysis (ESCA).

3. Results and discussion

3.1. *Electrochemical characterization*

Table 1 summarizes the cell components and performance characteristics of key experimental cells constructed and tested over the period 1979–80. The performance of a lead-frame electrolyzer (designated OC-1), devised for the evaluation of cell components in the earlier work, is considered as the baseline for comparison. A Pt-catalyzed, carbon-plate anode and a briquetted carbon cathode (both of loading ~ 10 mg cm^{-2}) were incorporated in this cell. It should be noted that the porous carbon plate (designated P7620) used in the fabrication of the anode had a low specific surface area of only ~ 1 m^2 g^{-1}. At 200 mA cm^{-2}, the initial cell potential of OC-1 was measured at ~ 1.22 V, including the ohmic loss. While operating continuously at a constant current density of 100 mA cm^{-2} for 2 hours, the observed cell potential increased at a rate of ~ 16 mV h^{-1}.

In the improved cell configuration NC-1, which used lucite frames, cell components similar to those in OC-1 were evaluated. At 200 mA cm^{-2},

Table 1. Cell components and performance characteristics of key electrolyzers†

Electrolyzer	*Anode*	*Cathode*	E_{cell} *at 200 mA cm*$^{-2}$ (mV)	*Improvement*‡ (mV)	$\mathrm{d}E_{\text{cell}}/\mathrm{d}t$ § (mV h^{-1})
OC-1	Pt/C-plate (P7620) 10 mg cm^{-2}	BCE¶ 10 mg cm^{-2}	1220	–	16
NC-1	Pt/C-plate (P7620) 10 mg cm^{-2}	BCE 10 mg cm^{-2}	1150	70	4
NC-2	Pt/C-plate (FC13) 10 mg cm^{-2}	BCE 10 mg cm^{-2}	930	290	4
NC-3	Pt/C-plate (FC13) CCE (EC-9885)‖ 12 mg cm^{-2}	Pt/C-plate (FC13) 10 mg cm^{-2}	840	380	< 1
NC-4	Pt/C-plate (FC13) CCE (EC-9885) 7 mg cm^{-2}	Pt/C-plate (FC13) 10 mg cm^{-2}	830	390	< 1
NC-5	Pt/C-plate (FC13) CCE (MBI-303-8) 7 mg cm^{-2}	Pt/C-plate (FC13) 10 mg cm^{-2}	770	450	$\ll 1$

† Testing conditions: 50 wt% H_2SO_4 at 50° C and atmospheric pressure; anolyte flow rate 700 cm^3 min^{-1}; microporous rubber diaphragm used as a separator.

‡ Achievable improvement in cell potential in comparison with electrolyzer OC-1.

§ Performance degradation rate after operating at a constant current density of 100 mA cm^{-2} for 2 hours.

¶ BCE = briquetted carbon electrode.

‖ CCE = carbon cloth-backed electrode.

the measured cell potential was ~ 1.15 V, showing an improvement of only 70 mV over OC-1. However, the use of the lucite-cell configuration resulted in a substantial reduction of performance degradation from 16 to 4 mV h^{-1}. Starting with electrolyzer NC-2, a high-surface-area carbon plate (designated FC13) was used to substitute for P7620 as the catalyst substrate. As illustrated in Table 1, this cell exhibited an overall cell potential of ~ 930 mV at 200 mA cm^{-2}. In comparison with NC-1 the significant improvement in the cell performance is essentially due to the more uniform distribution of catalyst particles on the highly porous anode substrate.

In late 1979, a carbon cloth-backed anode loaded with 2 mg cm^{-2} of platinum was developed and incorporated between the diaphragm and the spacer in electrolyzer NC-3. The electrode layer on the cloth was prepared from a mixture of Engelhard catalyst (designated EC-9885) and polytetrafluorethylene binder. Note that a Pt-catalyzed, carbon-plate electrode, rather than a briquetted carbon electrode, was used as a cathode in NC-3. As shown in Table 1, the incorporation of the carbon-cloth anode and the catalyzed carbon-plate cathode resulted in a distinct reduction in the cell potential and a substantial improvement in the performance stability (the observed degradation rate decreasing from ~ 4 mV h^{-1} to less than 1 mV h^{-1}).

Attempts were also made to reduce the noble metal content in the test electrodes. At the anode of cell NC-4 (see Table 1), an intentional reduction of platinum loading from 12 to 7 mg cm^{-2} caused no significant variation in the cell potential and performance stability, as compared to cell NC-3. More recently, a new catalyst (designated MBI-303-8) has been obtained to replace EC-9885 for preparing carbon cloth-backed anodes. As shown in Fig. 4, fine platinum particles in this catalyst are supported on black pearls. Further studies by transmission electron microscopy revealed that the mean particle size of the platinum was approximately 10 nm. The catalyst MBI-303-8 was evaluated electrochemically in the electrolyzer NC-5. As seen from Table 1, the measured cell potential at 200 mA cm^{-2} is as low as 770 mV. After operating continuously at

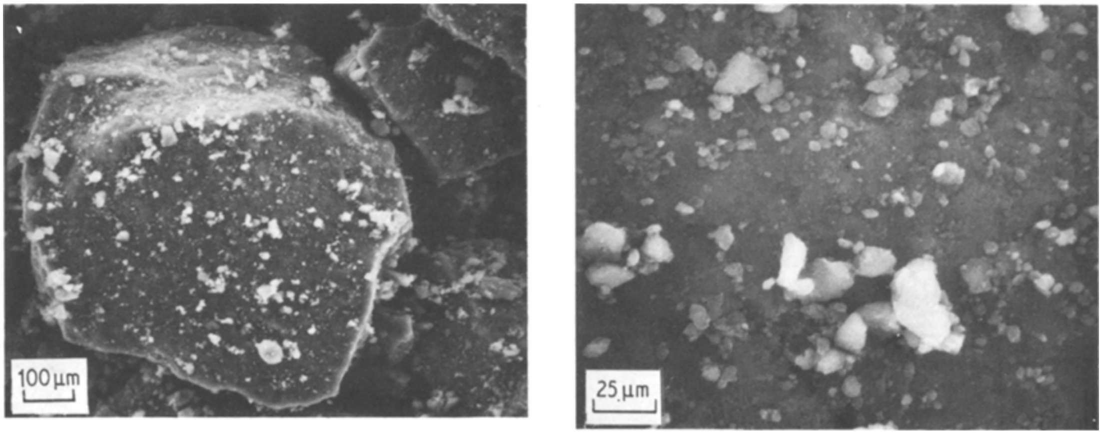

Fig. 4. Scanning electron micrographs of a carbon-supported platinum catalyst (designated MBI-303-8).

100 mA cm^{-2} for 2 hours, the cell performance was very stable with essentially no detectable degradation.

Fig. 5 presents achieved and projected cell performances for SO_2-depolarized electrolyzers. Recent progress in electrolysis technology has resulted in substantial improvements in both voltage efficiency and performance stability of electrolyzers. At a current density of 200 mA cm^{-2}, for example, the cell potential achieved was reduced from 1.22 V in mid-1979 to about 770 mV in February of 1980. It should be noted that, in the most recently developed cell, the observed cell potential is only 1.05 V at 400 mA cm^{-2}. The performance goal of the development programme is to obtain a stable cell potential of less than 600 mV at a current density of 200 mA cm^{-2}. The electrolyzer will operate at a temperature of ~ 100° C and a pressure in the range 5–20 atm, using sulphuric acid solutions of concentration 50–60 wt%.

3.2. *Cell endurance test*

With a view to evaluating the long-term stability of an SO_2-depolarized electrolyzer, an intermediate cell (NC-4) was tested continuously at a constant current density of 100 mA cm^{-2} for over one weak. Fig. 6 depicts variations of the observed cell potential and anodic overpotential with time.

During the first three days, the cell potential increased from an initial value of 644 mV to ~ 675 mV, showing an average decay rate of 10 mV day^{-1}. The gradual increase of cell potential

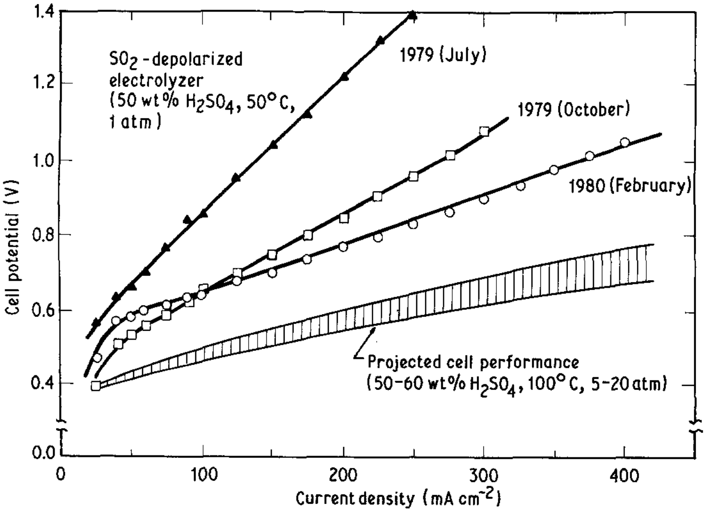

Fig. 5. Measured and projected cell performances of sulphur dioxide depolarized electrolyzers.

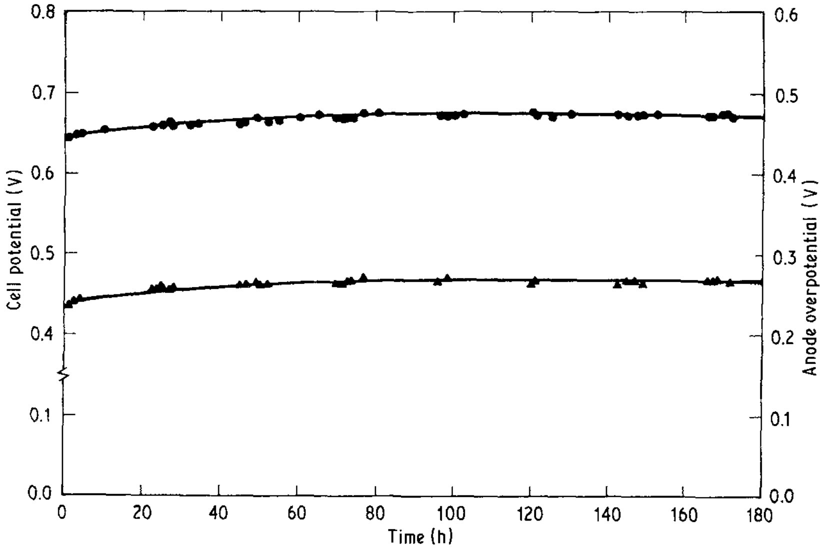

Fig. 6. Variations of the cell potential (●) and anodic overpotential (▲) with time in electrolyzer NC-4 during a cell endurance test. 50 wt% H_2SO_4, 50° C, 1 atm; microporous rubber diaphragm. Operating current: 100 mA cm^{-2}; anolyte flow rate: 700 cm^3 min^{-1}.

shown in Fig. 6 is obviously due to performance degradation at the anode. After 80 hours of continuous operation, the cell performance became essentially invariant with time. The stabilized cell potential and anodic overpotential were ~ 675 and ~ 265 mV, respectively. The observed cathodic overpotential and ohmic loss (being ~ 50 and ~ 60 mV, respectively) remained nearly constant throughout the course of the endurance test. The resulting gas from the cathodic compartment of NC-4 was collected and then analyzed by mass spectroscopy. The purity of hydrogen gas evolved in the electrolyzer was as high as 98.7 vol%. The detectable impurities included H_2S and SO_2. In addition, ESCA studies indicated that a small amount (~ 2.7 at%) of sulphide ions, rather than elemental sulphur, were present on the surface of the tested cathode.

3.3. *Effect of acid concentration on cell performance*

The dependence of the performance characteristics of an SO_2-depolarized electrolyzer on the acid concentration in the range 10–60 wt% was also investigated in the NC-4 cell. Fig. 7 presents experimental data on the cell performances in sulphuric acid of various concentration. In sulphuric acid of concentration over 30 wt%, the measured cell potentials increased significantly with increasing concentration, essentially due to the enhanced reversible cell potential and decreasing conductivity in the electrolyte.

It is noted [9] that the reduction of the activity of water molecules with acid concentration results in a significant enhancement of the reversible cell potential. As seen from Fig. 7, the electrolyzer NC-4 exhibited the lowest cell potentials in 30 wt% sulphuric acid, these being about 0.57, 0.71 and 0.82 V at current densities 100, 200 and 300 mA cm^{-2}, respectively. In 60 wt% sulphuric acid, the observed cell potentials increased drastically with increasing current density. Along with the increase of acid concentration from 50 to 60 wt%, considerable enhancements in the overall cell potentials were observed at various current densities.

According to the work by Appleby and Pichon [8], the anodic oxidation of sulphur dioxide in dilute sulphuric acid solutions takes place via the formation of dithionic acid ($H_2S_2O_6$):

$$SO_2 + H_2O \rightarrow H_2SO_3^+ + e \quad (4)$$

$$2H_2SO_3^+ \rightarrow H_2S_2O_6 + 2H^+ \quad (5)$$

$$H_2S_2O_6 \rightarrow H_2SO_4 + SO_2. \quad (6)$$

The combination of Equations 4 and 5 gives

$$2H_2SO_3 \rightarrow H_2S_2O_6 + 2H^+ + 2e. \quad (7)$$

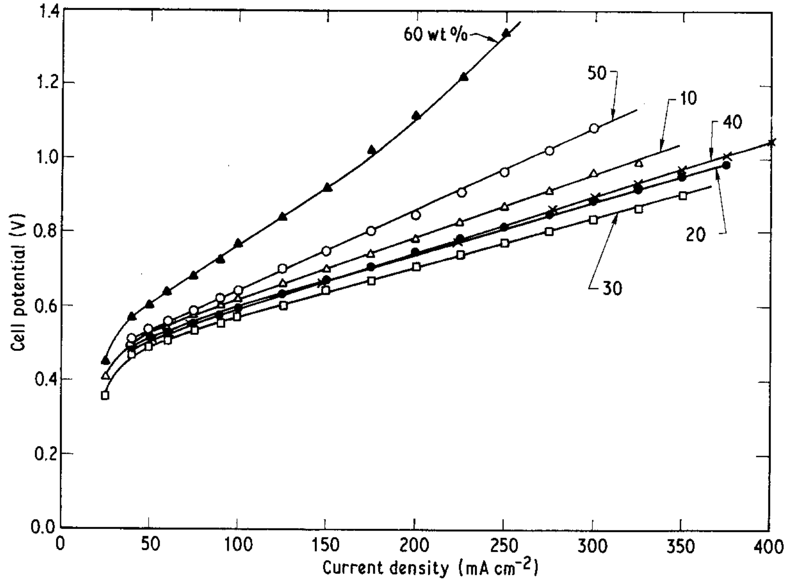

Fig. 7. Cell potential as a function of current density for electrolyzer NC-4 in sulphuric acid of concentration ranging from 10 to 60 wt%. 50° C, 1 atm; microporous rubber diaphragms.

As has been reported [10], the standard potential for Reaction 7 is as high as 0.564 V. By referring to Fig. 7, the measured cell potentials of NC-4 increased with decreasing acid concentration in sulphuric acid solutions of less than 30 wt%. The relatively poor performances in 10 and 20 wt% sulphuric acid is presumably attributed to the formation of the highly energetic dithionic acid as an intermediate and the decreasing activities of hydroxonium ions.

4. Conclusions

Manufacturing processes have been developed for preparing a platinum-catalyzed, carbon-plate electrode and a carbon cloth-backed electrode. The recent progress in the electrolysis technology has resulted in substantial improvements in both the voltage efficiency and performance stability of an SO_2-depolarized electrolyzer. In 50 wt% sulphuric acid solution at 50° C and atmospheric pressure, the most recently developed electrolyzer showed stable cell potentials of 0.77 and 1.05 V (including ohmic losses) at current densities of 200 and 400 mA cm^{-2}, respectively.

In an endurance test, the cell potential of an SO_2-depolarized electrolyzer became essentially stabilized, showing a cell potential of ~ 675 mV at 100 mA cm^{-2}. The purity of hydrogen gas evolved from the cathodic compartment of the electrolyzer has been verified to be as high as 98.7 vol%. The optimum acid concentration for operating an SO_2-depolarized electrolyzer is approximately 30 wt%; the observed cell potential in this acid is only 0.71 V at 200 mA cm^{-2}. In more concentrated acid solutions (40–60 wt%), the observed cell potentials increased significantly with increasing acid concentration, due essentially to reducing activity of water molecules as well as the decreasing conductivity of the electrolyte.

The next work in the programme will concentrate on (a) the reduction of noble metal loading on electrodes, (b) the further optimization of cell configuration, (c) the construction and evaluation of a pressurized electrolyzer and (d) the investigation and selection of improved separator materials.

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