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A unitized approach to regenerative solid polymer electrolyte fuel cells

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In this work on regenerative fuel cells, the initial part deals with water electrolysis using a cell design that closely resembled that of a solid polymer fuel cell. The electrolytes were Nafion® 117 and the Dow experimental membrane. The electrodes were Pt-on-C and Pt/Ir-on-C gas diffusion electrodes on the oxygen side and Pt-on-C on the hydrogen side. Fuel cells were built with the above mentioned electrodes and membranes. These cells were run to obtain fuel cell and electrolysis data. Data for a maximum of five regenerative cycles were obtained. The current–potential data in the regenerative electrolysis were characterized by a gradual decay with time. The fuel cell data were very stable. The membrane–electrode assemblies were found in very good condition, and no visible corrosion of electrodes was evident.

1. Introduction

The solid polymer fuel cell (SPFC), also known as the solid polymer electrolyte (SPE®) fuel cell, promises to be useful in many earth and space applications. In space applications and in some earth applications, it would better serve its purpose if it were regenerative, i.e. perform both as a fuel cell and an electrolyser. Such versatility would be convenient because a solar array could provide power during the sunlight portion of the orbit of a space vehicle or a space station; the same device could then function as a fuel cell to generate power from hydrogen and oxygen during the dark portion of the orbit.

In the design of a regenerative fuel cell two approaches may be taken: (i) the fuel cell and electrolysis units may be kept separate; and (ii) only one unit functions as a fuel cell and an electrolyser. In the present state of the technology, an SPFC can only provide power and cannot function as an electrolyser. Indeed, if by chance the unit is polarized to split water, it results in the failure of the fuel cell. The present work, nevertheless aims to identify those conditions permitting the same unit to function as both a power producer and also as an electrolyser, in other words as a 'unitized regenerative fuel cell'.

Solid polymer electrolysis technology has demonstrated [1–5] high efficiency and current density capabilities and is considered a promising method for large scale hydrogen production. The electrocatalyst is directly deposited on to the membrane in this approach.

SPFC technology has progresssed considerably [6–12] in recent times: the catalyst loading level has decreased and the performance level has increased. One important area of concern in this technology is that the efficiency of catalyst utilization in the fuel cell remains very low, about 10–20% [6,7] compared to approximately 100% [13] in a phosphoric acid fuel cell. Attempts are being made to increase the catalyst utilization by increasing the three-dimensional reaction zone in the electrode. An increase in utilization efficiency of platinum in an SPFC would be equivalent to depositing a layer of platinum on top of the membrane, and thus this may also favour water electrolysis in an SPFC. Therefore, it would be appropriate to make parallel investigations on the capability of an SPFC also functioning as an electrolyser.

Both the electrolysis and fuel cell reactions can be represented as follows:

$$H_2O \rightleftarrows \tfrac{1}{2}\,O_2 + H_2$$

2. Experimental details

2.1. *Choice of cell design and cell description*

Since an objective of this work was to use a cell design similar to that of a solid polymer fuel cell, the initial work on electrolysis was carried out in a cell of the form shown in Fig. 1. The design is based on the fuel cell technology developed by Ticianelli, Srinivasan and their coworkers [6,7] using porous gas diffusion electrodes, The water reservoir for electrolysis was placed inside the cell in contact with the membrane. An alternative choice for the water reservoir would be to bring the water in contact with the back of the porous gas diffusion electrodes. But that choice would flood the porous electrodes during the electrolysis mode, and then the electrodes would be totally unsuitable in the fuel cell mode.

The cell shown in Fig. 1 was constructed from two 7.6 cm × 7.6 cm × 1.3 cm Plexiglas plates that served as endplates of the cell. The cell was designed to facilitate easy evaluation of electrodes without any arrangements for gas collection. The membrane and electrode (M&E) assembly, containing a slightly oversized solid polymer electrolyte membrane, was placed

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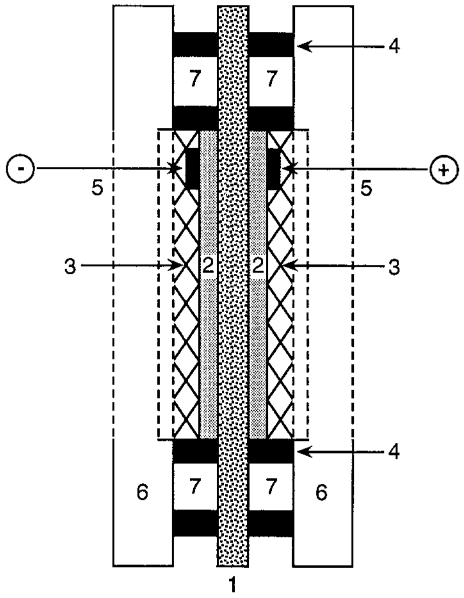

Fig. 1. A vertical cross-sectional view of the electrolysis cell with a solid polymer membrane. (1) Membrane, (2) porous Pt/C electrodes, (3) plastic wire nets, (4) thick gaskets, (5) current collectors, (6) thick Plexiglass ends, and (7) water in contact with membrane.

between the endplates. The central part of each endplate held an electrode in a depression of dimensions 0.16 cm depth and 6.5 cm^2 area. This part also had holes going through the endplates for gas removal. The latter served to keep the membrane and electrode assembly pressurized against the current collector. A platinum-coated nickel screen, equal in dimension to the electrode and spot-welded to a 0.064 cm diameter nickel wire, served as a current collector. Behind the current collector were also placed several layers of plastic wire nets that helped to fill up the space and removed the evolved gas. The water reservoir remained inside the cell in between two 0.16 cm thick silicone rubber gaskets and around the electrodes. The water was introduced into the cell with the help of a syringe.

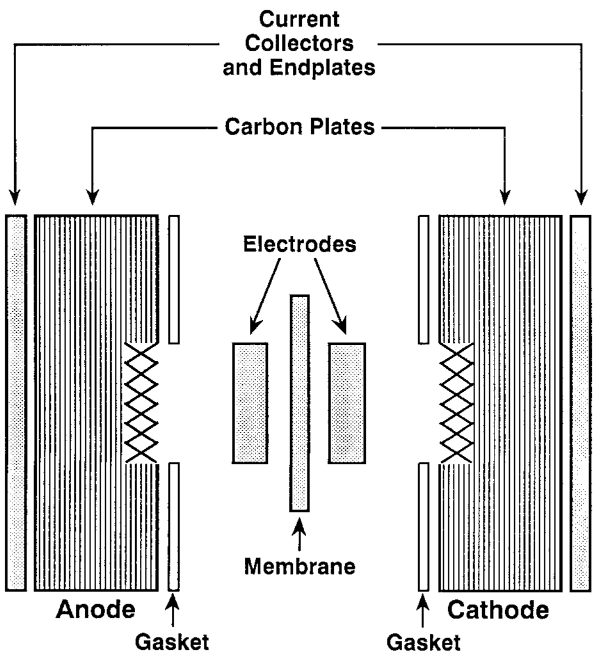

Fig. 2. Cell parts for single fuel cell assembly.

Water electrolysis was practised in the temperature range 30–80 °C. The cell was placed in a 5·0 cm × 8.9 cm × 25.4 cm vessel and immersed in a water bath whose temperature was controlled by a heater and a thermostat. The temperature could be controlled to ± 1 °C.

For the regenerative fuel cell data collection, the cell in Fig. 2 [6,7] was adapted to serve both as a fuel cell and an electrolyser. Two pieces of gasket on each side of the membrane (as in Fig. 1) made room for the water reservoir. Behind the electrodes and on top of the gas channels on the carbon plates were placed several layers of nickel screen, so that when the cell was assembled with the gaskets, the electrodes were in good contact with carbon plates that also served as current collectors. Water was introduced into the reservoir with a syringe.

In the electrolysis mode, the evolved gases exited through the channels in the carbon plates, and in the fuel cell mode, the reactant gases entered the cell through the same channels.

2.2. *Electrodes and electrolytes*

The electrodes were of the Pt-on-C type with Pt : C ratio of 20 : 80. The platinum loading was 1 mg cm^{-2}; the electrode backing material was Torray carbon paper. Electrodes with carbon cloth backing performed poorly in the electrolyser mode. Hence, electrodes with Torray carbon paper were used to collect electrolysis and regenerative fuel cell data. Electrodes with Torray carbon paper backings were obtained from ElectroChem. Inc. (Boston, MA).

It was observed that Pt/Ir-on-C electrodes performed better than Pt-on-C electrodes in the electrolysis mode. Thus, some Pt/Ir-on-C electrodes were prepared by depositing iridium on to the Pt-on-C electrodes from an iridium compound and reducing it with sodium borohydride. The iridium content was approximately 20% of platinum. The required amount of hexachloro iridium was dissolved in 0.1 ml of 80% aqueous methanol solution. The entire solution was then painted on to the catalytic side of a Pt-on-C electrode with a small brush. The electrode was then dried at 60 °C for a few minutes. A 5% solution of sodium borohydride in 80% aqueous methanol was then brushed on to the electrode, which was finally washed in 20% aqueous methanol and then dried.

The solid polymer electrolytes were Nafion® 117 of thickness 0.018 cm and the Dow experimental proton exchange membrane (Type XUS 13204.10) of thickness 0.01 cm.

The area of an electrode was 5 cm^2. Electrodes were impregnated with 5% Nafion® solution (Aldrich Chemical Company) following procedures described in the literature [6,7]. Approximately 0.5 mg cm^{-2} of Nafion® in the dry state was deposited on an electrode. The electrodes and the membrane were then

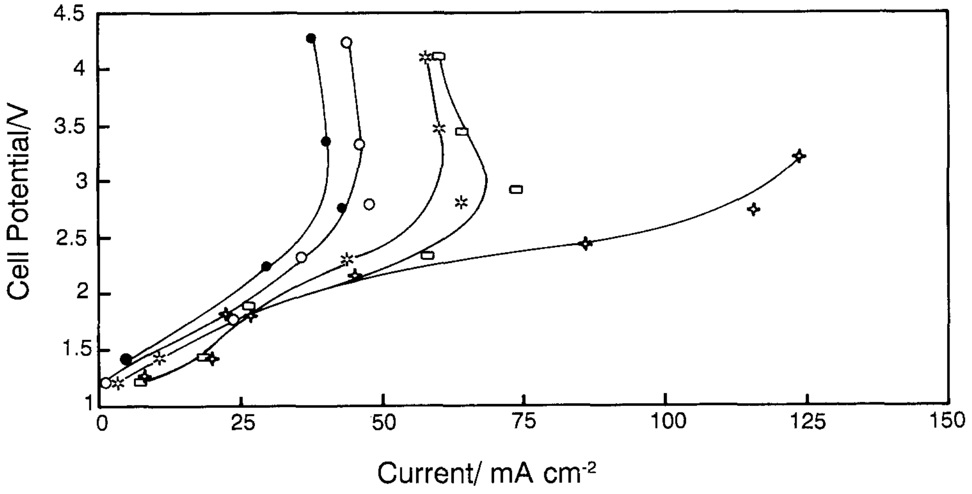

Fig. 3. Current–potential data showing effect of water addition on cell peformance with Nafion® membrane. Both anode and cathode: Pt-on-C with Torray paper backings. Key: (●) 30 °C, (○) 50 °C, (*) 65 °C, (□) 80 °C, and (+) 30 °C with water.

hot-pressed at 130 °C for 90 s under a pressure of 70 kg cm^{-2}.

2.3. *Electrolysis measurements*

During the trial of electrolysis in the cell shown in Fig. 1, 30 min were allowed for the temperature to equilibrate. The cell was polarized to a constant voltage with a d.c. power supply. At each potential, 1 min was allowed for the current to stabilize. In many instances, a fairly stable current was obtained, but also in many cases, the current continued to drift downward. The reason for this downward drift of current was thought to arise from improper gas removal that contributed to a time-dependent buildup of ohmic resistance at the electrode – membrane interface. The current decay was observed at all levels of current and was of lesser magnitude during the initial few minutes of polarization.

At the completion of measurements, the cell was disassembled and membrane and electrodes examined. Generally, the contacts between the electrode and membrane were found to be very good. Also, no corrosion of the anode side of the cell was evident. This is because water does not come in direct contact with the polarized anode: the electrode is in contact with the solid electrolyte.

2.4. *Regenerative fuel cell measurements*

As the object was not to obtain optimized fuel cell performance but to see if a unitized regenerative fuel cell would be feasible, only a comparative data collection was emphasized. It is well-known that in solid polymer electrolyte measurements the cell needs to be conditioned for a few days by running it under extreme conditions to attain the highest level of fuel cell performance. In the present study, the fuel cell was conditioned only for 2–3 h at a high temperature (80 °C) and pressure (35 N cm^{-2}) before data collection at several temperatures and at the atmospheric pressure.

For the regenerative fuel cell measurements in the cell type shown in Fig. 2, the fuel cell data were first collected. Water was then introduced into the reservoir, and a time period 10–15 min was allowed for

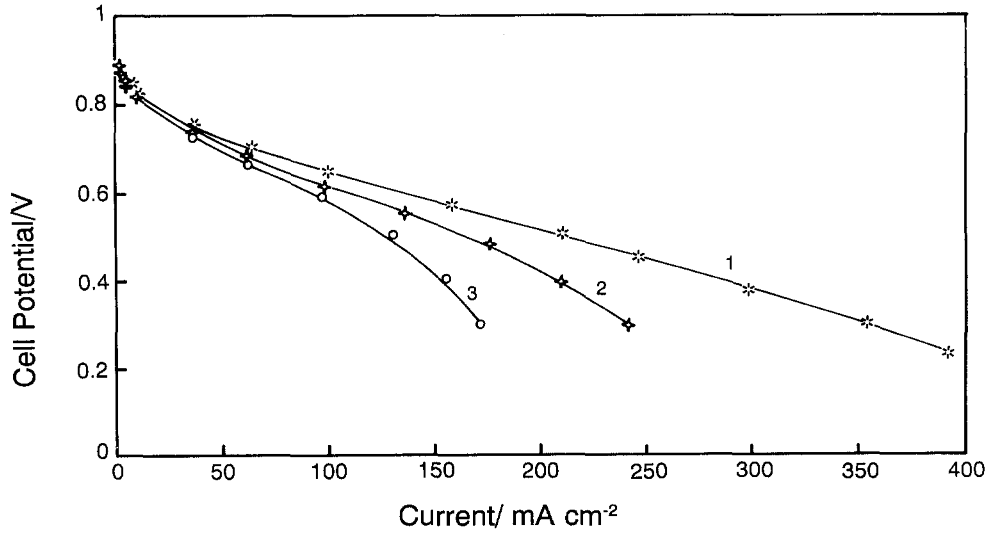

Fig. 4. Regenerative fuel cell performance with Pt/Ir-on-C electrode as the oxygen electrode. Electrode backing: Torray carbon paper. Membrane: Nafion®. Key: (*) Cycle 3, 50 °C, (+) cycle 2, 50 °C, (○) cycle 1, 50 °C.

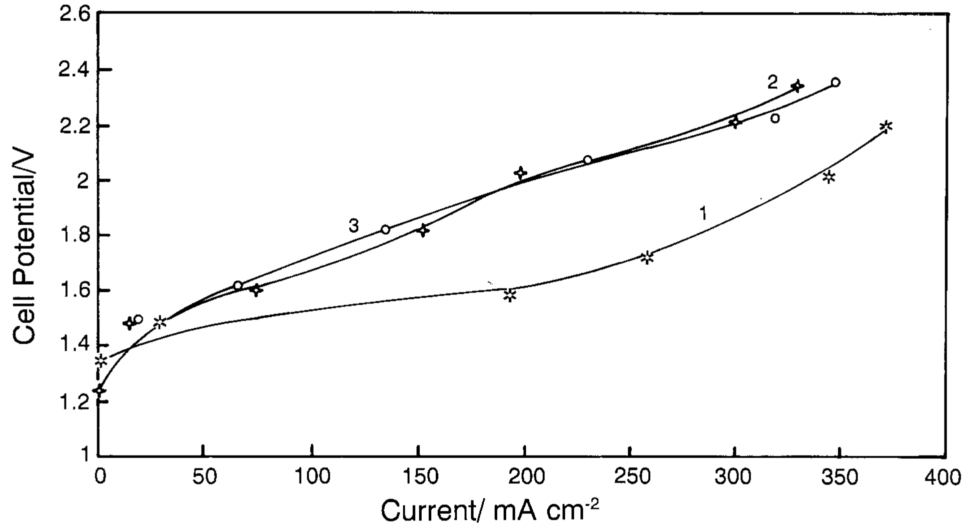

Fig. 5. Regenerative electrolyser performance at 65 °C with Pt/Ir-on-C electrode in the same cell of Fig. 4. Key: (○) Cycle 3, 65 °C, (+) cycle 2, 65 °C, (*) cycle 1, 65 °C.

stabilization of conditions. The cell was then run as an electrolyser, in which mode the hydrogen electrode in the fuel cell produced hydrogen and the oxygen electrode, oxygen. A current instability, similar to that observed earlier, was also observed while running the fuel cell in the electrolysis mode. At each potential, a period of 1 min was allowed for stabilization of the electrolysis current. After data collection in the electrolysis mode, the cell was immediately connected as a fuel cell passing the reactant gases through channels in the carbon plates of the cell (cf. Fig. 2). A reasonable current (100 mA cm^{-2}) could be immediately drawn from the cell. A period of 2–3 h was again allowed for cell conditioning at 50 °C and 0 N cm^{-2} pressure. This was followed by data collection as a fuel cell. The cycle of fuel cell–electrolyser was then repeated. Unlike the electrolysis current, the fuel cell current remained very stable.

3. Results and discussion

In the cell design chosen for this work, water does not come in contact with the electrodes directly, but indirectly through absorption on the membrane.

It was thus necessary to establish that water was being absorbed on the membrane covering the electrodes. For this purpose, electrolysis experiments were performed at temperatures 30, 50, 65 and 80 °C without the addition of any water into the reservoir. The initial temperature was 30 °C, then temperature was increased for collection of data at higher temperatures. The cell was then cooled, water introduced, and polarization measurements taken. The 30 °C data with water addition and the data at four temperatures without any water addition are presented in Fig. 3. When no water was added, the cell potential increased dramatically and limiting currents reached at low values. The limiting currents even tended to decrease with increasing potentials. With addition of water into the reservoir (cf. Fig. 1), a much higher current was reached. These results indicated that the chosen cell design was suitable for water electrolysis with the solid polymer electrolyte.

The rationalization of the temperature effect on the limiting current is related to the diffusion layer thickness of the reactant, water. The limiting current is inversely proportional to the diffusion layer thickness.

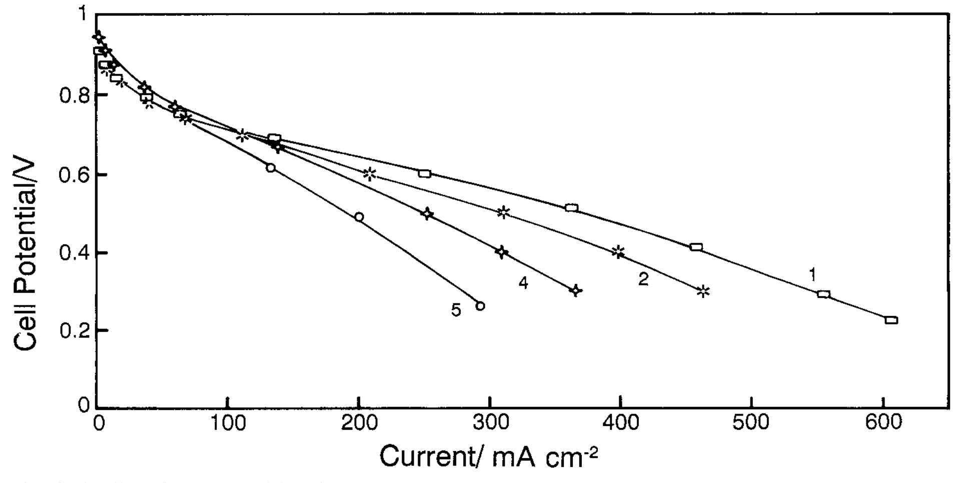

Fig. 6. Regenerative fuel cell performance with Pt/Ir-on-C as the oxygen electrode and Dow membrane. Electrode backing: Torray carbon paper. Key: (○) Cycle 5, 50 °C, (+) cycle 4, 50 °C, (*) cycle 2, 50 °C, (□) cycle 1, 50 °C.

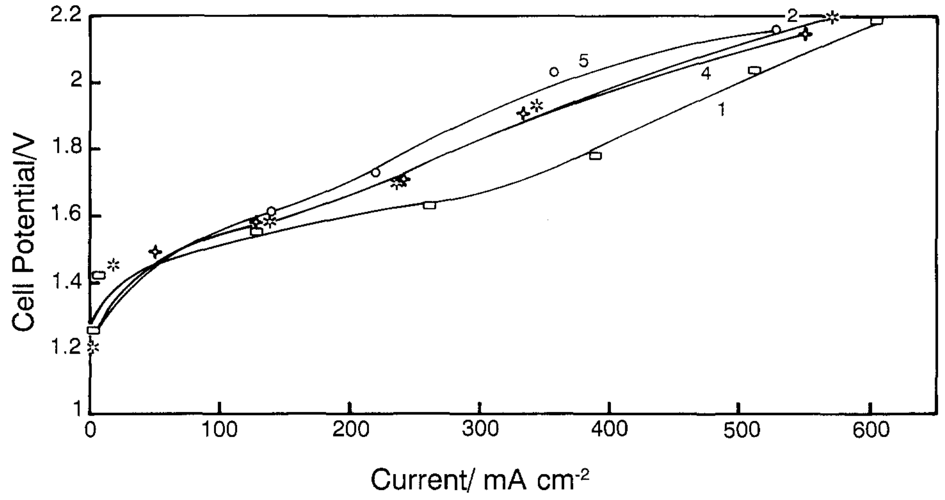

Fig. 7. Regenerative electrolyser performance at 65 °C with the same cell as used in Fig. 6. Key: (o) Cycle 5, 65 °C, (+) cycle 4, 65 °C, (*) cycle 2, 65 °C, (□) cycle 1, 65 °C.

With increasing temperature, the diffusion layer thickness decreases making more reactants available at the electrode surface. Thus, at a higher temperature a higher limiting current was obtained. After the limiting current was reached, the current even tended to decrease with a further increase of potential. This is indicative of the fact that a solid polymer electrolyte was involved, and its diffusion layer thickness is more clearly defined than that for a liquid electrolyte, and the availability of reactant is sharply decreased.

While collecting regenerative fuel cell data, a cycle consisted of collecting data first as a fuel cell and then as an electrolyser. The temperature was maintained at 50 °C and pressure 0 N cm^{-2} for both reactant gases. Both Pt-on-C and Pt/Ir-on-C electrodes were tested. Since the latter electrode showed better electrolyser performance, the data for this Pt/Ir-on-C electrode have been chosen for presentation here. The open circuit voltages of these electrodes were 15–20 mV lower than those obtained with the Pt-on-C electrodes. The o.c.v. for the latter ranged between 0.980 to 1.02 V, reflecting effect of temperature, pressure, and electrode variations. The fuel cell performances were thus slightly lower for Pt/Ir-on-C electrodes than those for Pt-on-C electrodes. Figures 4 and 5 present performances for a Pt/Ir-on-C electrode in combination with a Nafion membrane in the fuel cell mode at 50 °C and electrolyser mode at 65 °C, respectively. The electrolysis current reached to 350 mA cm^{-2} at 2.2 V, compared to 250 mA cm^{-2} at 2.4 V for the Pt-on-C electrode (not presented here).

The decline of cell currents with cycling in Figs 4 and 5 needs explanation. Note that during data collection in the fuel cell mode, the membrane was humidified by passing the reactant gases through water [6,7] at 60 °C. It is possible that the electrodes retained a portion of the humidification water. In fact, when the cell was disassembled after data collection, droplets of water were observed on the electrode backing, the carbon paper. The electrodes used had 30% PTFE contents in the backing layer. A 50% PTFE content would improve the situation with respect to fuel cell data, decreasing electrode wetting and hence increasing diffusion of reactant gases to the catalyst site. The higher currents observed in the regenerative electrolysis may be related to some degree of wetting of the electrode backing and to an increased water transportation to the catalyst site. The decline of performance with cycling for both fuel cell and electrolyser may be related to a combination of factors: entrapped gases at the membrane–electrode interface that may result in membrane ionomer drying, some loosening of the electrode from the membrane, and wetting of the carbon paper backing. However, from visual observations, after disassembly of the cell, the contacts between the membrane and electrodes were found to be very good.

The fuel cell and electrolyser data were also obtained with the Dow membrane and Pt-on-C and Pt/Ir-on-C electrodes. The performances with the Dow membrane were better than those with the Nafion® membrane. Again, the Pt/Ir-on-C electrode data have been chosen for presentation here. The fuel cell and electrolyser data are shown in Figs 6 and 7, respectively, for up to five cycles. At the end of the second cycle, after the electrolyser run, the cell was heated to 80 °C and electrolyser data taken again to see the temperature effect on electrolysis in the regenerative mode. This was considered equivalent to cycle no. 3, but without the associated fuel cell data. Hence, cycle no. 3 in these plots is missing. The temperature effect on the regenerative electrolysis, however, was not significant.

The electrolysis data in Fig. 7 represent the best electrolyser performances obtained in this work. The current reached to 600 mA cm^{-2} at 2.2 V. With cycling, the electrolyser current decay was minimal, and at the lower current ranges up to 150–200 mA cm^{-2}, the decay was smaller. At 200 mA cm^{-2} the cell potential was 1.7 V.

The higher currents with the Dow membrane are related to its lesser thickness, and hence to a lower electrolytic resistance. Another possible reason is its more hydrophilic characteristics, experienced by many workers [14,15]. The latter is borne out by the fact that there are more sulphonic acid groups per molecule in the membrane that accounts for its higher conductivity and better water retention characteristics [14,15]. However, the differences observed here with Nafion® and Dow membranes are less striking than what would have been expected, for example from fuel cell studies [14].

4. Conclusions

Unitized regenerative fuel cell data have been obtained with a cell having features of a fuel cell design, and using gas diffusion electrodes and solid polymer electrolytes usually used in fuel cells. There were some problems associated with the stability of electrolysis current output of the cell. The electrolysis current decreased with time. The fuel cell current was found to be very stable. However, both the fuel cell and electrolysis currents decreased with repeated cycling. This decrease was thought to be arising due to a combination of factors: entrapped gases at the membrane–electrode interface, possible drying of the interface during electrolysis, some degree of loosening of the membrane, and wetting of electrode backings.

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