

## EVALUATION OF ELECTRODE MATERIALS FOR VANADIUM REDOX CELL

M RYCHCIK and M SKYLLAS-KAZACOS\*

*School of Chemical Engineering and Industrial Chemistry, University of New South Wales, P O Box 1, Kensington, NSW 2033 (Australia)*

(Received May 26, 1986, accepted in revised form July 11, 1986)

### Summary

Several electrode materials have been evaluated for their suitability as positive electrodes in a new, all-vanadium redox cell. Cyclic voltammetry and charge/discharge experiments have been performed to determine electrochemical performance and stability of these materials during charging. Graphite plates perform well as negative electrodes, but undergo chemical and mechanical disintegration after several cycles when used as positive electrodes, as do some carbon cloths and fibre material

An iridium oxide-coated, dimensionally stable anode has shown excellent electrochemical characteristics and stability over several charge/discharge cycles. Charging current efficiencies of over 90% can be achieved. The cell can be discharged between 10% and 90% state-of-discharge with the cell voltage varying from 1.22 V to 1.16 V. The charged electrolytes are stable for several months over the temperature range  $-5^{\circ}\text{C}$  to  $60^{\circ}\text{C}$  and the open-circuit cell voltage remains constant at 1.3 V for over 3 days with negligible rate of self-discharge.

---

### Introduction

A new all-vanadium redox cell with excellent charge/discharge characteristics has recently been reported [1, 2]. The cell employs V(II)/V(III) and V(IV)/V(V) redox couples in  $\text{H}_2\text{SO}_4$  as the negative and positive half-cell electrolytes, respectively. Graphite plates are used for electrodes. The advantage of this system over other redox cells [3 - 6] is that it employs the same metal on both sides of the cell and thus eliminates any problems of cross-contamination of solutions by diffusion of metal cations across the ion exchange membrane. Although NASA has recently used [4] premixed solutions, this has introduced other difficulties such as the need to use lower concentrations of reactants to avoid crystallization, a reduction in the open-circuit voltage, and the presence of large quantities of inactive materials in

---

\*Author to whom correspondence should be addressed.

each half-cell. Although cation diffusion still needs to be minimised in the all-vanadium cell to prevent self-discharge, any cross-mixing is simply overcome by recharging the solutions.

Charge/discharge coulombic efficiencies of over 90% are exhibited by laboratory-scale, all-vanadium cells [2]. Furthermore, cells can be cycled between 15 and 85% state-of-charge with only 0.1 V shift in the charge or discharge voltage. Thus, at a discharge current density of  $6 \text{ mA cm}^{-2}$ , the voltage decreased from 1.22 V to 1.16 V when the cell was approximately 90% discharged

The only problem that has been identified to date in laboratory-scale, all-vanadium cells is the deterioration of the positive carbon electrode during the charging cycle. Although graphite shows acceptable reaction rates for the vanadium species, this material is not resistant to the oxidising solution during charging and undergoes mechanical disintegration. The negative electrode, however, shows good stability even after several months' use. A number of electrode materials have been tested in our laboratory to determine both their electrochemical behaviour and stability during cell operation. These results, together with data from several charge/discharge experiments, are presented here

## Experimental

The electrochemical performance and stability of a number of electrode materials were evaluated using both cyclic voltammetry and charge/discharge experiments. For both purposes, the electrolyte consisted of a solution of  $\text{VOSO}_4$  (BDH Chemicals Ltd, Poole, England) in  $\text{H}_2\text{SO}_4$  (Ajax Chemicals Pty. Ltd., Australia).

For cyclic voltammetry, glassy carbon (area =  $0.03 \text{ cm}^2$ ), gold ( $0.007 \text{ cm}^2$ ) and lead ( $0.38 \text{ cm}^2$ ) electrodes were employed, as well as a Dimensionally Stable Anode, DSA, consisting of iridium oxide on titanium ( $0.4 \text{ cm}^2$ ) and manufactured by Diamond Shamrock Ltd (Cleveland, U.S.A.). Apart from the DSA, the electrodes were polished with 1200 grit silicon carbide paper, rinsed in distilled water and cleaned ultrasonically in distilled water for 15 min using an Ultramet III Sonic Cleaner (Buehler Ltd., Evanston, U.S.A.). In the case of the DSA, all experiments were performed on electrodes that had been soaked in 2 M  $\text{H}_2\text{SO}_4$  for 30 min and rinsed in distilled water. Cyclic voltammograms were obtained with a Pine RD3 potentiostat (Pine Instrument Co, Grove City, Pennsylvania, U.S.A.) and a Model D-72PB Riken Denshi X-Y recorder. All potentials were measured using a saturated calomel electrode (SCE) as reference and are reported with respect to SCE in this paper. A graphite rod was used as a counter electrode. Voltammograms always started from the value of the static potential and the first sweep was conducted in a direction towards more positive potentials.

Figure 1 shows the design of the cell used for most of the charge/discharge experiments. The cell was constructed from 5 mm perspex sheets, this material being chemically resistant to the sulphuric acid as well as to the

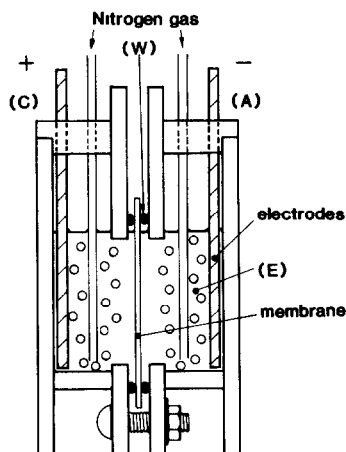


Fig 1 Schematic of laboratory redox cell A, anode, C, cathode, E, electrolyte, W, washers, N<sub>2</sub>, nitrogen inlets

oxidising and reducing agents used in the tests. A graphite plate was used as the negative electrode. It functioned well over a large number of cycles with only slow rates of hydrogen evolution when the cell was over 85% charged.

The following materials were tested as positive electrodes:

- (i) Graphite rods and plates
- (ii) Carbon fibre material (CTF-3000, Alhstroem, Finland)
- (iii) Carbon cloth (GF-20, Nikon Carbon Co. Ltd., Japan)
- (iv) Platinised titanium sheets
- (v) Iridium oxide DSA (Diamond Shamrock, Cleveland, U.S.A.)

A wide range of VOSO<sub>4</sub> concentrations, from 0.1 M to 2 M in 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M H<sub>2</sub>SO<sub>4</sub> was employed. The stability of these solutions at -5 °C, at room temperature and at +60 °C was tested and no noticeable change was observed over a period of nine months

The positive-electrode compartment was separated from its negative-electrode counterpart by an ion-selective membrane which was sealed with rubber washers. Two types of membrane were employed in the cell; namely, a sulphonated polyethylene, anion-selective membrane and a polystyrene sulphonic acid CMV cation-selective membrane (Asahi Glass Co. Ltd., Tokyo, Japan). Nitrogen was bubbled through both compartments, both to enhance mass transport and to maintain an inert atmosphere in the negative half-cell compartment (to prevent air oxidation of the V(II) species in the charged cell). The cell was charged using a BREMI BRS-41 d.c. power supply and discharged across various loads.

The average experimental conditions for charging were as follows

Electrolyte: 0.1 - 2 M VOSO<sub>4</sub> in 1 M or 2 M H<sub>2</sub>SO<sub>4</sub>

Temperature: 20 °C, 40 °C

Electrode area: 15 cm<sup>2</sup> (3 cm × 5 cm)

Current density approximately 10 mA cm<sup>-2</sup>

Voltage: 2.2 - 2.9 V for full charge

## Results and discussion

### *Cyclic voltammetric studies*

The cyclic voltammetric studies were conducted on a number of electrode materials in solutions of  $\text{VOSO}_4$  in  $\text{H}_2\text{SO}_4$  in order to determine the suitability of the materials as positive electrodes in a vanadium redox cell. The behaviour of glassy carbon, gold, and lead is shown in Fig 2. The V(IV)/V(V) redox couple (peaks A and B in Fig. 2) is seen to be electrochemically irreversible at both glassy carbon and gold electrodes (Fig 2(a) and (b), respectively). On the other hand, the lead electrode (Fig 2(c)) is passive over the potential range in which V(IV)/V(V) reactions would be expected to occur, and is therefore unsuitable as a positive electrode for the vanadium cell. Like lead, titanium was also found to be passive in the potential range of interest, with formation of a highly resistant surface layer. Platinised titanium did not exhibit this problem and showed good reversibility for both the V(IV)/V(V) and V(II)/V(III) redox couples. As with gold, however, the high cost of this material would be prohibitive for large-scale applications in redox cells.

Although graphite rods and plates exhibited acceptable reaction rates for the vanadium species, previous work [2] showed that this material is not resistant to the oxidising solution during the charging cycle and undergoes

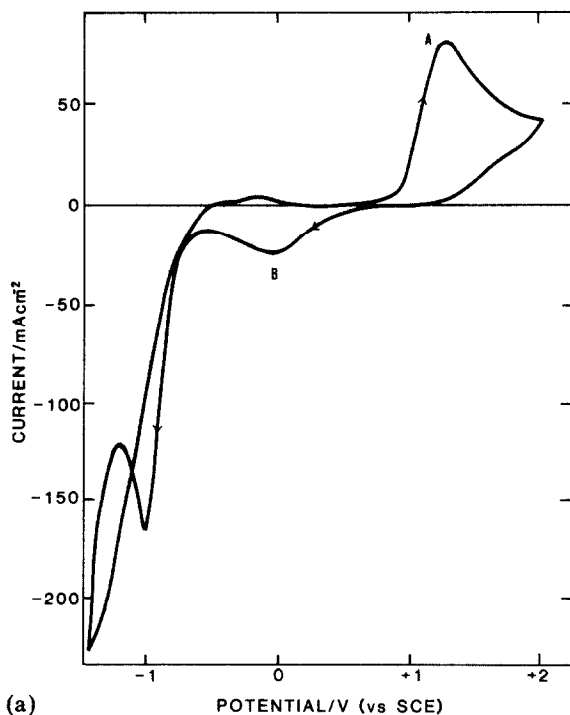


Fig 2(a) (For Figure legend please see facing page )

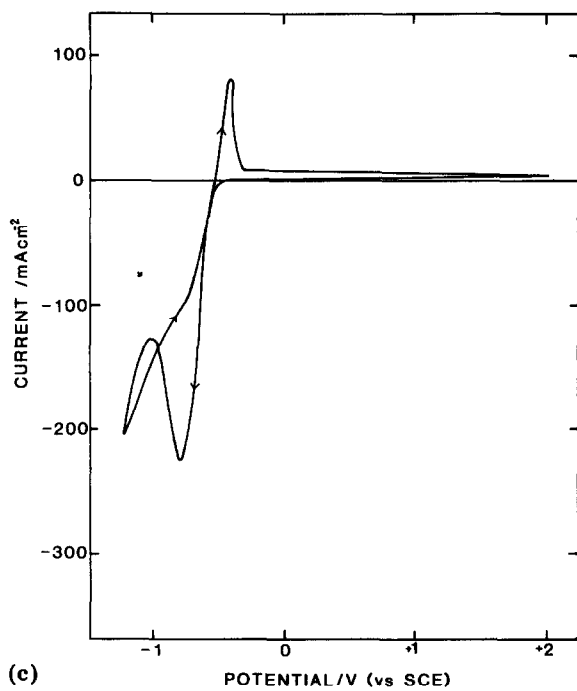
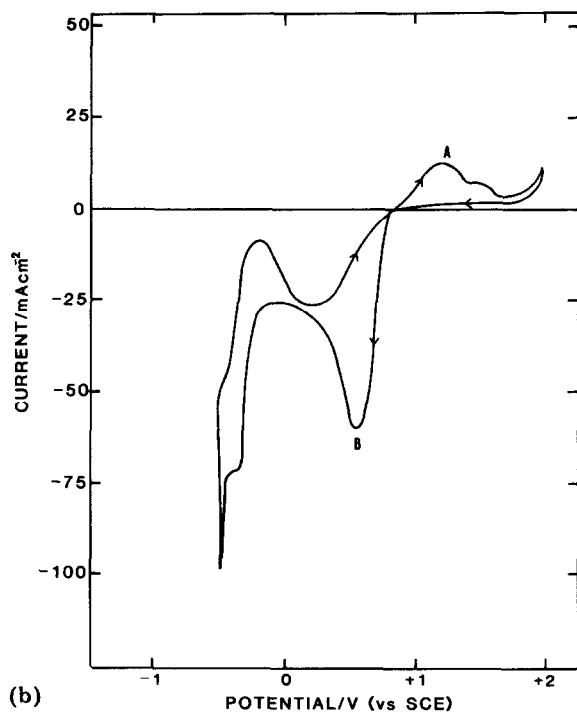


Fig 2. Cyclic voltammograms for various electrode materials in solution of 2 M VOSO<sub>4</sub> + 2 M H<sub>2</sub>SO<sub>4</sub> (a) glassy carbon, (b) gold, (c) lead electrode Sweep rate = 4 V min<sup>-1</sup>

mechanical disintegration. Coating the carbon with a conductive polymer such as polyaniline [7], may be one way of stabilising the positive electrodes in a redox cell. In the present study, therefore, polyaniline thin films were electrodeposited onto platinum and the cyclic voltammetric behaviour examined in the  $\text{VOSO}_4$  solution. As shown in Fig. 3, polyaniline itself undergoes oxidation and reduction (peaks C and B) in the potential range of  $\text{V(VI)/V(V)}$  redox couple. However, the magnitudes of the corresponding voltammetric peaks decrease with each cycle, and after four cycles examination of the electrode revealed that the polyaniline film had completely dissolved from the platinum surface. Polyaniline is thus unsuitable, but further work in evaluating a wide range of other conductive polymer materials is currently in progress

The poor stability of carbon anodes in many industrial electrochemical processes, has resulted in the widespread use of DSA materials. Figure 4 gives the cyclic voltammogram obtained on an iridium oxide DSA in  $\text{VOSO}_4$  solution. To avoid the possibility of reducing the oxide, the voltammogram was not taken below 0 V. A dramatic improvement in the reversibility of the  $\text{V(IV)/V(V)}$  was observed, and the current density was also higher than on a glassy carbon electrode. After several cycles, there was no evidence of disso-

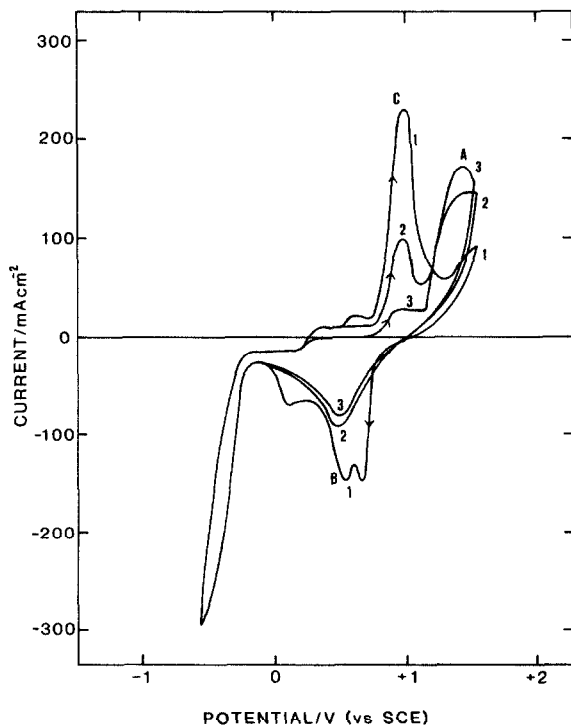


Fig 3 Cyclic voltammograms for polyaniline layer on platinum in 2 M  $\text{VOSO}_4$  + 2 M  $\text{H}_2\text{SO}_4$  first(1), second(2) and third(3) cycles Sweep rate =  $4 \text{ V min}^{-1}$

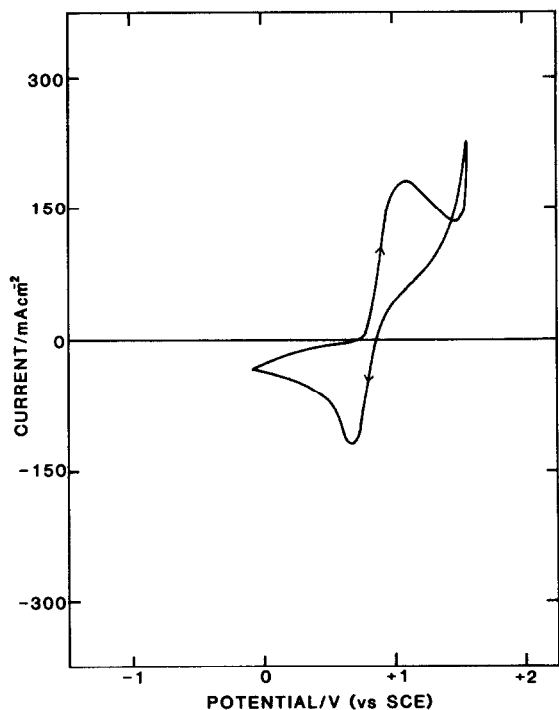
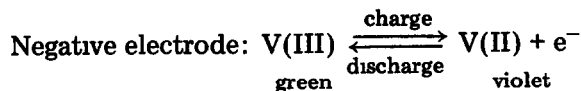
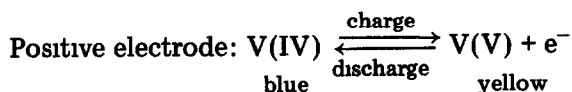


Fig 4. Cyclic voltammogram for DSA in 2 M  $\text{VOSO}_4$  + 2 M  $\text{H}_2\text{SO}_4$ . Sweep rate = 1  $\text{V min}^{-1}$

lution of the oxide film. The stability of the DSA was further evaluated in a series of charge/discharge experiments, the results of which are presented in the following section.

#### Charge/discharge experiments

Initial charging of the cell was performed in two stages: (i) V(IV) was oxidised to V(V) in the positive compartment, while V(IV) was reduced to V(III) in the negative compartment; (ii) the positive electrolyte was replaced by fresh  $\text{VOSO}_4$  solution and the charging continued. During the second stage, the fresh V(IV) was oxidised to V(V), while the V(III) was reduced to V(II) in the negative half-cell. Subsequent charge/discharge reactions, would be:



The colour changes served to indicate the progress of the reactions.

The use of 2 M  $\text{VOSO}_4$  allows V(V) solutions to be prepared, approximately ten times more concentrated than the reported saturation solubility of  $\text{V}_2\text{O}_5$ , which is given as 0.245 M in 3 M  $\text{H}_2\text{SO}_4$  [8]. The higher concentration gives a considerable increase in the energy density of the electrolytes. Over 40 A h can be obtained per litre of solution, assuming only a 75% use of its capacity.

In concentrated solutions (1 M or more), strong absorption of light results in very intense, almost black solutions. As noted in the Experimental Section, high purity nitrogen was continuously bubbled through the solutions to avoid reoxidation of V(III) to V(II) in the negative half-cell, as well as to stir the solution to reduce concentration polarisation.

When using graphite rods and plates as positive electrodes, a suspension of carbon particles began to appear in the solution towards the end of the first charging cycle. Inspection revealed that the electrodes had undergone partial disintegration, thus indicating that graphite is not resistant to the oxidising conditions during charging and undergoes chemical and mechanical attack. The carbon fibre and carbon cloth electrodes also exhibited similar breakdown after one or two charging cycles. Platinised titanium sheets performed well, however, and showed no signs of chemical attack during charging experiments.

With each of the above electrodes, only minor amounts of oxygen and hydrogen were evolved during charging, so that average coulombic efficiencies of over 90% were obtained for a charge/discharge cycle. Figure 5(a) shows a typical charging curve at 20 °C for a cell employing a sulphonated polyethylene membrane, and a graphite positive electrode.

The stability of the open-circuit cell voltage was also examined and was found to remain constant at  $1.3 \pm 0.05$  V for 72 h. A subsequent discharge

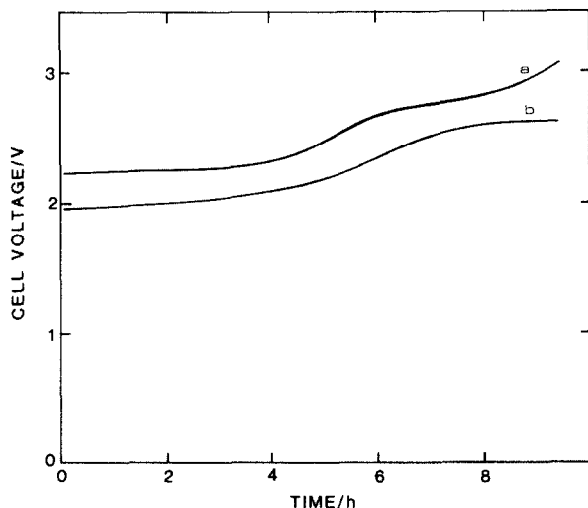


Fig 5 Effect of increase in electrolyte temperature on charging voltage (a) 20 °C, (b) 40 °C. Charging current =  $10 \text{ mA cm}^{-2}$ .



experiment indicated that approximately 10% self-discharge had occurred over the 72 h period when using this particular membrane material. By increasing the temperature to 40 °C, a considerable decrease in the charging voltage was obtained, as shown in Fig. 5(b). In both cases, however, the positive half-cell electrolyte was unstirred so that considerable concentration polarisation is evident from the rise in cell voltage.

Further improvement in the performance of the all-vanadium cell was achieved by replacing the sulphonated polyethylene amon-selective membrane (resistance  $1.2 \Omega \text{ cm}^2$ ) with a polystyrene sulphonic acid cation-selective membrane CMV (resistance  $0.43 \Omega \text{ cm}^2$ ) and by reducing the inter-electrode distance from 90 mm to 30 mm. Nitrogen was also bubbled into both the negative and positive half-cells to improve mass transport. As a result of the decreased cell resistance and concentration polarisation, the charging voltage dropped by 0.5 V while the discharge voltage increased by 0.1 V. Figure 6 shows the charge (curve a) and discharge (curve b) curves obtained with a graphite positive electrode and the polystyrene sulphonic acid membrane. By replacing the graphite with a DSA, however, curves a' and b' were obtained during charge and discharge at a current density of  $6 \text{ mA cm}^{-2}$ . Several charge/discharge cycles were carried out with the above cell and reproducible results were obtained. Furthermore, there was no noticeable change of the DSA surface, showing that this electrode is stable.

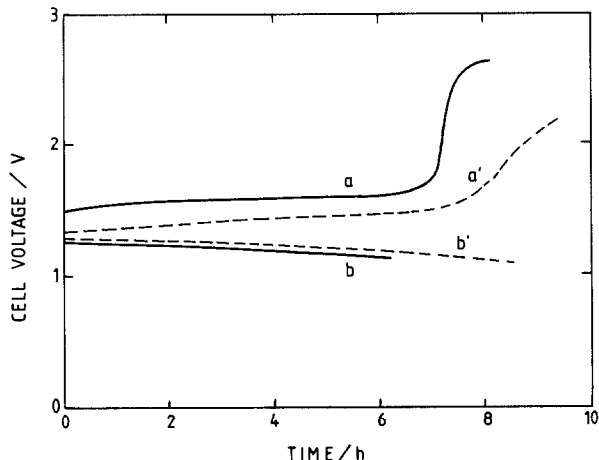


Fig. 6 Cell voltage vs time curves for third charge (curves a, a') and discharge (curves b, b') cycles. Charging current  $6 \text{ mA cm}^{-2}$ , membrane polystyrene sulphonic acid, positive electrodes graphite (curves a, b) and DSA (curves a', b')

## Conclusions

The above results have demonstrated that high coulombic and energy efficiencies can be achieved with the all-vanadium redox cell. The DSA showed the best electrochemical performance and stability during charging,

while the cation-selective polystyrene sulphonic acid membrane had the lower resistivity and showed no change in its characteristics, even after several charge-discharge experiments and several hundred hours of contact with the solutions

A larger-scale (2 W) flow cell has been constructed and its performance is currently being evaluated for various charge and discharge current densities, electrolyte flow rates, and temperatures, so that the optimum operating conditions for the all-vanadium redox flow cell can be established before progressing on to a multi-cell system.

### Acknowledgement

Support was provided under the National Energy Research Development and Demonstration Programme which is administered by the Australian Commonwealth Department of Resources and Energy.

### References

- 1 M Skyllas-Kazacos, R Rychcik, R Robins, A Fane and M Green, *J Electrochem Soc*, 133 (1986) 1057
- 2 M Skyllas-Kazacos and M Rychcik, in preparation
- 3 L H Thaller, *NASA TM-79143*, National Aeronautics and Space Administration, U S Dept of Energy, 1979, 8 pp.
- 4 R F Gahn, N H Hagedorn and J A Johnson, *NASA TM-87034*, National Aeronautics and Space Administration, U S Dept of Energy, 1985, 8 pp
- 5 D A Johnson and M A Reid, *J Electrochem Soc*, 131 (1985) 1058.
- 6 K Nozaki, H Kaneko, A Negishi and T Ozawa, *Proc Symp Advances in Battery Materials, Proc*, 84-4, The Electrochem. Soc, Princeton, NJ, 1984, p. 143
- 7 R Noufi, A J Nozik, J White and L F Warren, *J Electrochem Soc*, 129 (1982) 2261
- 8 Dong-gie Oei, *J Appl Electrochem*, 15 (1985) 231