CALCIUM/$Ca(AlCl_4)_2$–THIONYL CHLORIDE (TC) CELL. EFFECT OF TEMPERATURE AND CELL PARAMETERS ON PERFORMANCE

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Summary

The $Ca/Ca(AlCl_4)_2$–TC cell has very high power and energy densities. A C-size cell can deliver 1 A continuously over a temperature range of −40 to +80 °C. The cell capacity increases (at all rates) with increase in the carbon cathode porosity from 82 to 88%, and with decrease in the Teflon binder content from 12 to 6%. The addition of 10% (v/v) of SO_2 to the electrolyte increases its conductivity by 40 - 50% over a temperature range of −40 to +50 °C. This should increase both the power and energy density of the cell.

Introduction

The increasing interest in safe, high power, high energy density batteries has encouraged research on the Ca/TC system [1 - 9]. A very powerful laboratory prototype, C-size, $Ca/Ca(AlCl_4)_2$–TC/C cell has been developed recently in our laboratory [4, 7, 9]. It exhibits, at room temperature, an energy density and power density similar to that of the Li–SO_2 battery, but has much better safety features. It successfully resists 25 V charging and reversal abuses [4, 7, 9], and almost no calcium was deposited during these tests.

The goal of this work was to study the effect of temperature and cell parameters on its performance.

Experimental

Laboratory prototype C-size cells with electrode areas of 100 or 130 cm^2 were constructed and tested. The electrolyte was 0.95M $Ca(AlCl_4)_2$. In some cases it contained 10% (v/v) of SO_2. These solutions were saturated with SO_2 by bubbling Matheson 99.9% SO_2 gas at room temperature for about 10 min. Details concerning materials, solution preparation, and cell construction are described in refs. 3, 4 and 9. The procedure for conductivity

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measurements is described in ref. 10. The discharge tests were performed in a temperature-controlled chamber (Associated Environmental Systems) by loading the cell with a suitable power resistor. Data were collected and processed using an IMS 8000 microcomputer.

Results and discussion

The optimal structure and porosity of the cathode-current collector in soluble-cathode lithium batteries depend, among other things, on the type of reactions taking place on this collector [11, 12]. The optimal porosity for low rate Li/TC cells is about 80% [11, 12]. The Teflon content of the cathode is typically 10% [13]. We chose this composition of Teflon-bonded Shawinigan Black cathode-current collector as a baseline for our work. However, it appeared that this is not the optimal composition for the Ca/TC cell.

It can be seen in Fig. 1 that the capacity per gram of carbon (for 12% Teflon cathodes) increases with the porosity at all rates from 50 mA to 1200 mA, while at low rates the effect is more pronounced. The increase in porosity results from the decrease in the carbon content of the cathode. Therefore, at a certain stage, a further increase in porosity, although improving the capacity per gram of carbon, results in a decrease of cell capacity.

The effects of the Teflon content and the porosity of the cathodic-current collector, as well as the effect of the active electrode area on cell performance, are shown in Fig. 2. The combination of increasing the electrode

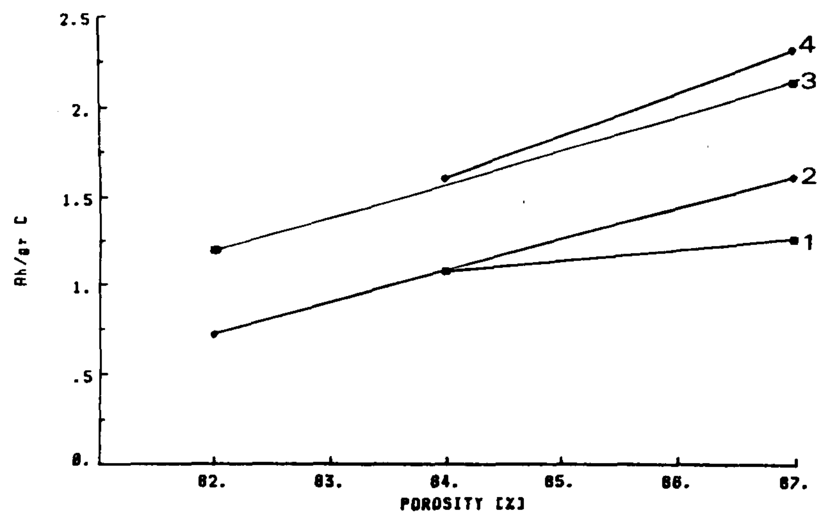

Fig. 1. A plot of capacity per gram of carbon as a function of electrode porosity: Electrode area, 130 cm^2; 0.95M $Ca(AlCl_4)_2$. Teflon content, 12%; 1, 1200 mA; 2, 500 mA; 3, 125 mA; 4, 50 mA.

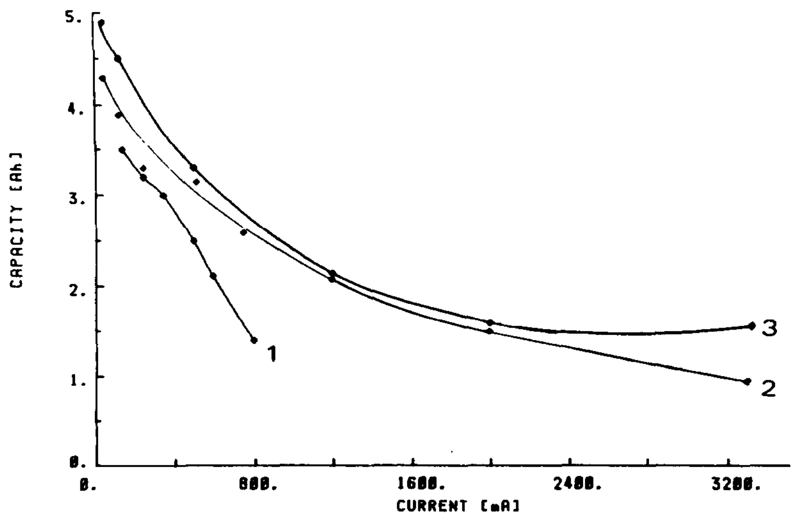

Fig. 2. A plot of cell capacity as a function of discharge rate at room temperature: 1, electrode area 100 cm^2, 12% Teflon, 82% porosity; 2, electrode area 130 cm^2, 12% Teflon, 86% porosity; 3, electrode area 130 cm^2, 6% Teflon, 87 - 88% porosity.

area from 100 to 130 cm^2 and increasing the porosity from 82 to 86%, markedly increases both the capacity and rate capability of the cell. A decrease in Teflon content, which results in a slight increase in porosity, further improved cell capacity at all rates from 50 to 3200 mA (Fig. 2).

Electrolyte conductivity greatly influences cell capacity and rate capability. It was found that the addition of 10% (v/v) of SO_2 to the electrolyte increases its conductivity by 40 - 50% over the temperature range −40 to +50 °C (Fig. 3). It should also be noted that the solutions are stable at −40 °C and no salt precipitation was observed. It seems that one of the major reasons for the flat discharge curve of the Ca–TC cell (and probably of the Li–TC cell also) is the generation of SO_2 during discharge. At low temperatures, the conductivity of the 0.7M solution is higher than that of 0.9M and 1.3M solutions, while above room temperature, the conductivity of the 1.3M solution is higher. For discharge tests we chose 0.9 - 1.0M solution as a compromise.

The Ca–TC cell can deliver 1 A continuously over a temperature range of −40 to +80 °C (Fig. 4). The discharge curves are reasonably flat except for a large voltage delay at −40 °C. This voltage delay is caused mainly by an initial, thick, passivating oxide layer which covers the anode. This can be eliminated, as is shown in Fig. 5, by rubbing the anode with sandpaper prior to assembling the cell.

The effect of temperature on capacity is shown in Fig. 6. At a medium rate of 125 mA, cell capacity drops from about 4.5 A h at 25 °C to 1 A h at −40 °C. At a high rate (1 A), the capacity is almost constant (2 A h) over the temperature range 0 - 80 °C and drops to 1 A h at −40 °C.

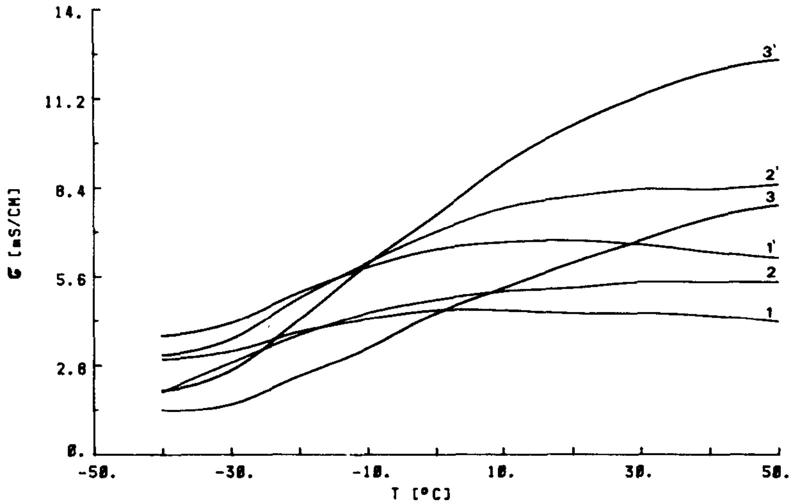

Fig. 3. The effect of temperature and SO_2 on conductivity of $Ca(AlCl_4)_2$ solutions: 1, 0.7M; 2, 0.9M; 3, 1.3M without SO_2. The superscript denotes electrolyte which contained 10% (v/v) SO_2.

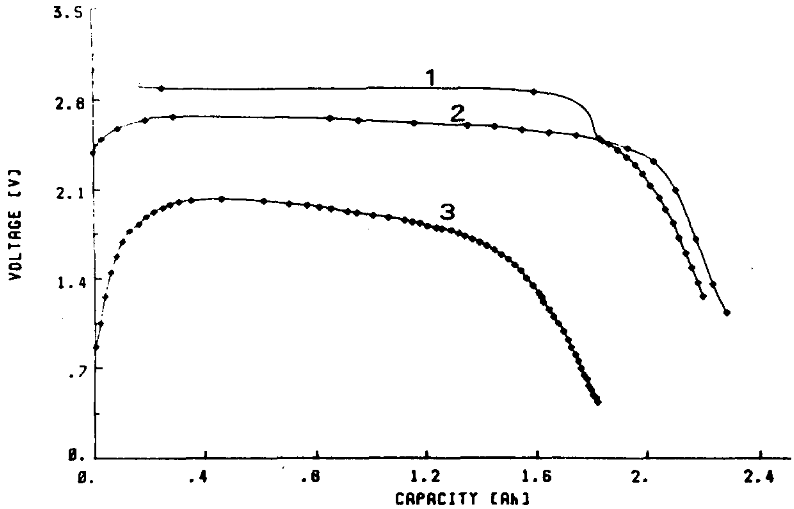

Fig. 4. The effect of temperature on discharge curves at about 1 A: electrode area 130 cm^2, 0.95M $Ca(AlCl_4)_2$, 88% porosity, 6% Teflon. 1, 2.5 Ω + 80 °C; 2, 2.2 Ω 25 °C; 3, 2.2 Ω −40 °C (3 contained 10% v/v SO_2).

The possibility of storing Ca–TC cells at high temperature was studied using small laboratory cells of 10 cm^2 electrode area [3]. It was found that they lost about 10% of their capacity after two weeks of storage at 70 °C. After this, they exhibited flat discharge curves with only minor voltage delay

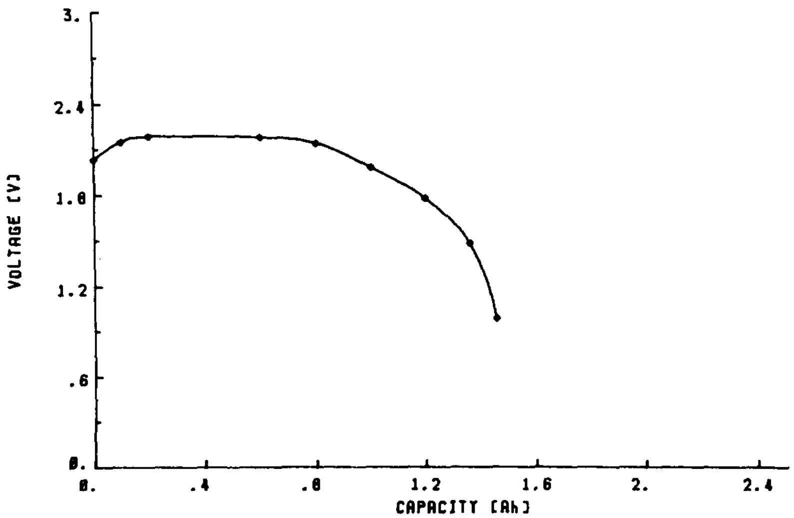

Fig. 5. Discharge curve at −20 °C: electrode area 100 cm^2, electrolyte: 0.95M $Ca(AlCl_4)_2$ +10% (v/v) SO_2, 88% porosity, 6% Teflon; load, 2.8 Ω. Anode was abraded with sandpaper prior to cell assembly.

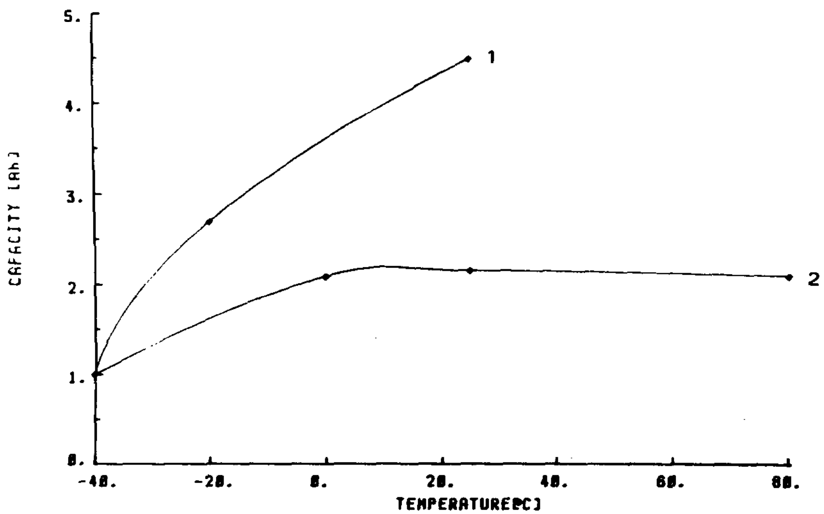

Fig. 6. The effect of temperature on cell capacity: 1, 125 mA, 2, 1000 mA. Cathode porosity: 88%; 6% Teflon.

(Fig. 7). Their minimum transient voltage at about 1.5 mA cm^{-2} was above 2 V.

It seems that the performance of the cell can be further improved by increasing the electrode area, optimization of electrolyte and SO_2 concentration, decreasing the Teflon content of the carbon electrode to 3 - 5%, and perhaps increasing the carbon electrode porosity to about 90%.

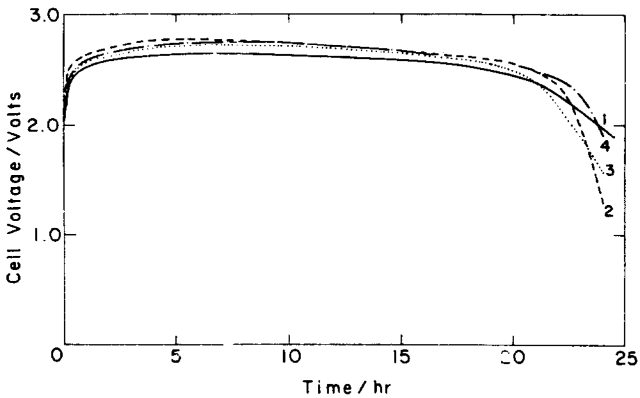

Fig. 7. Room temperature discharge of four, 10 cm^2 area cells at 1.45 mA cm^{-2} after 2 weeks of storage at 71 °C. The indices 1 - 4 denote the cell numbers.

Acknowledgement

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