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Charge storage in cells of the type gold/solid electrolyte/gold

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Significant amounts of charge, 0.1–50 C g^{-1}, can be stored in cells of the type Au/solid electrolyte/Au after charging at 400–700° C and 1.5 V. Solid electrolytes that give this effect include Li_4SiO_4, $Na_3Zr_2PSi_2O_{12}$, single crystal and polycrystalline β-alumina. Highest storage was found with Li_2TiO_3. These amounts of charge are 6–8 orders of magnitude larger than are to be expected if gold is behaving as a normal blocking electrode. Possible applications are in novel types of thermal battery.

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1. Introduction

Gold is frequently used as a blocking electrode for a.c. measurements on solid electrolytes. For cationically conducting solid electrolytes, discharge apparently does not occur at low charging voltages and the gold–solid electrolyte interface behaves as a double layer capacitance of 10^{-6}–10^{-7} F cm^{-2} [1]. We have found recently that at high temperatures, cells containing β-alumina as the solid electrolyte behave completely differently [2]. For example, after applying a d.c. potential of 1.5 V across the cell, Au/β-alumina/Au, for 24 h and at 400–700° C, charge totalling 10^{-2}–10^{-1} C g^{-1} was stored in the cell, as shown by measuring the current–time behaviour on subsequent discharge. This charge is about 5 to 6 orders of magnitude larger than expected from double layer phenomena. The present paper reports an extension of this work to cells that contain a variety of solid electrolytes.

2. Experimental

Solid electrolytes were prepared by conventional solid state methods using oxide or carbonate reagents of analar or reagent grade. Mixtures were fired in electric muffle furnaces in Pt crucibles or Au foil boats at temperatures in the range 600–1200° C, depending on composition. Completeness of reaction was checked by powder X-ray diffraction using a Philips diffractometer or a Hägg focusing camera, CuKα_1 radiation. Cylindrical pellets were cold pressed from finely ground solid electrolyte at 50 000–100 000 p.s.i. and then sintered at 1000–1200° C for a few hours. Pellet diameters were 9 mm and thicknesses 1–5 mm.

Gold electrodes were attached to opposite pellet faces by applying Hanovia liquid gold paste followed by a strip of Au foil. The pellet, with electrodes attached, was gradually heated up to ~ 500° C and held at that temperature for 30 min in order to decompose the organo-gold paste and harden the metallic gold residue. The Au foil strips were wrapped around the ends of Pt wires which were threaded through ceramic spaghetti and the whole arrangement was suspended in a vertical tube furnace so that the pellet was located in the hot zone of the furnace (Fig. 1). A chromel alumel thermocouple (not shown) was threaded through an adjacent piece of spaghetti and placed in close proximity to the pellet. After the jig and furnace had reached thermal equilibrium, the furnace temperature stayed constant to within ± 1° C.

A constant voltage d.c. source was used to apply a potential difference across the electrodes in the range 0.1–30 V. The current which passed through the cell was measured using the following arrangement. A standard resistor (usually 10 Ω) was placed in series with the cell and the voltage drop across R was measured by a Honeywell-Brown recording millivoltmeter. The current passing through R, and therefore through the cell, was determined from the millivoltmeter reading and the total charge passed determined from the area

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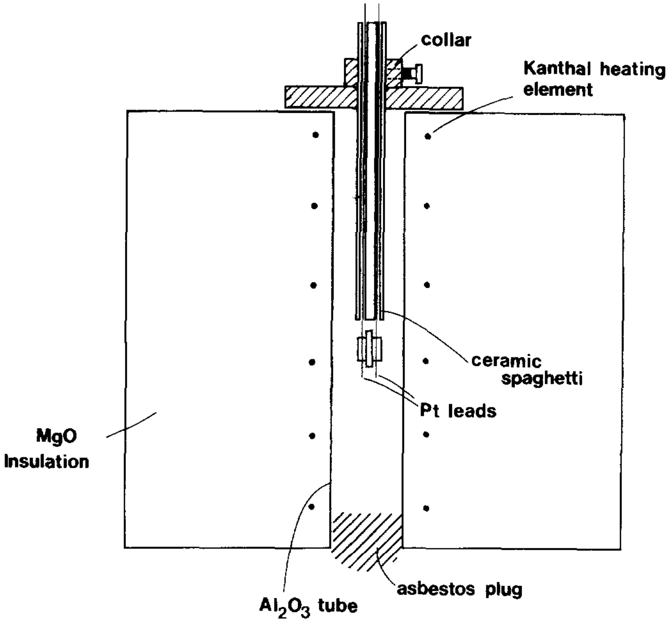

Fig. 1. Cell and furnace arrangement.

under the *I* versus *t* curve. In order to discharge the cell, the d.c. source was removed from the circuit and the leads to the solid electrolyte cell reversed. The discharge current was then measured in the same way as the charging current. In some experiments, an additional load of 10^4 Ω was placed in series with the cell.

3. Results and discussion

A variety of solid electrolytes, with Au electrodes, were charged and discharged, initially over a wide range of temperatures and charging voltages. For several of the materials studied, significant charging and discharging currents were observed,

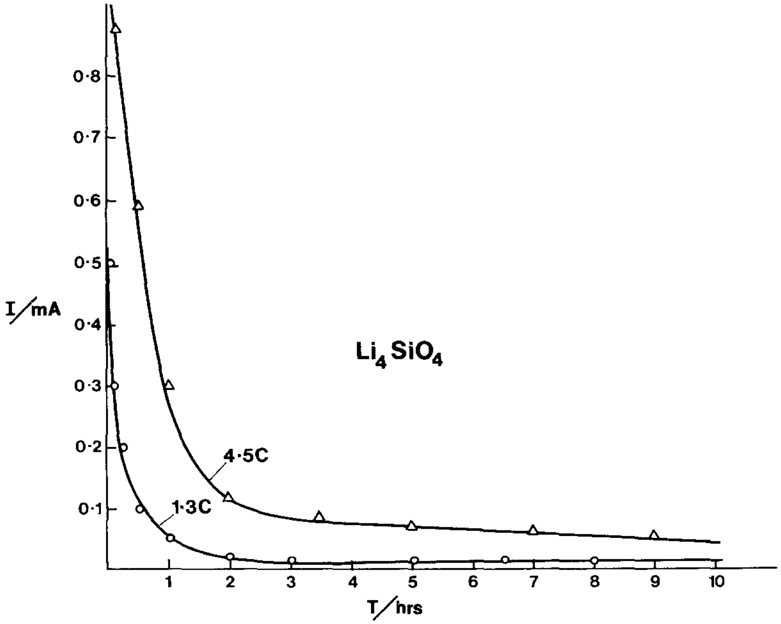

Fig. 2. Li_4SiO_4, 525° C, electrode area (*A*) = 0.25 cm^2, thickness of electrolyte pellet (*l*) = 0.2 cm, charging voltage (V_{ch}) = 1.5 V, mass of pellet (*m*) = 0.257 g. Δ Charging, ○ discharging.

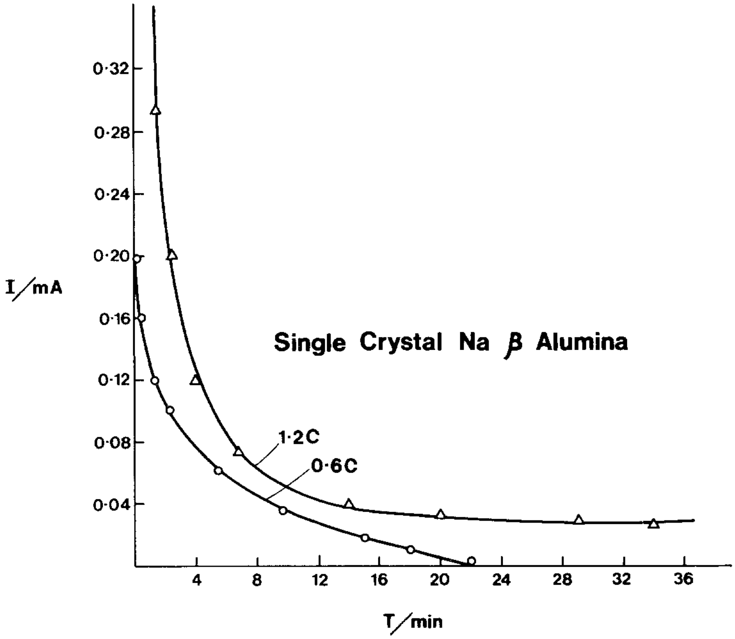

Fig. 3. Single crystal β-alumina, 600°C, $A = 0.14\ \mathrm{cm}^2$, $l = 1.4\ \mathrm{cm}$, $V_{ch} = 1.5$ V, $m = 0.358$ g. △ Charging, ○ discharging.

over the range of temperatures between 400 and 700° C. The main objective was to maximize the charge that could be stored and subsequently released for each solid electrolyte and most experiments were made in the temperature range ~ 500–600° C. The charging voltage was usually 1.5 V although significant charging occurred at voltages as low as 0.5 V. Increasing the voltage to 30 V did not greatly affect the charge stored although an increased charge was often passed during the charging cycle. These experiments were carried out in air.

Typical results are given in Figs. 2–6 for Li_4SiO_4, single crystal Naβ-alumina, polycrystalline β-alumina, $Na_3Zr_2PSi_2O_{12}$ and Li_2TiO_3. All were obtained with 10 Ω as the load resistance;

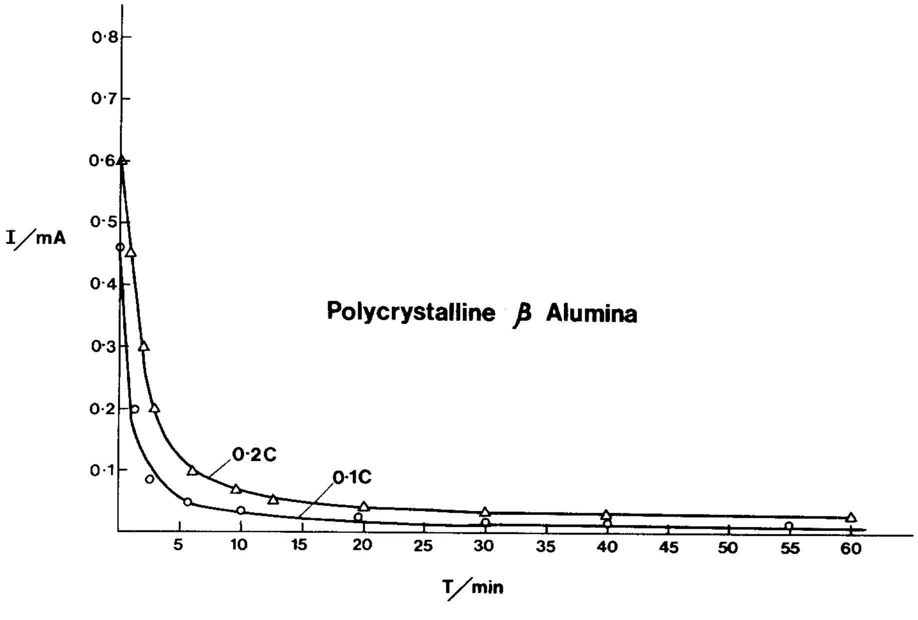

Fig. 4. Polycrystalline β-alumina, 745° C, $m = 0.23$ g, $A = 0.9\ \mathrm{cm}^2$, $l = 0.1$ cm, $V_{ch} = 1.5$ V. △ Charging, ○ discharging.

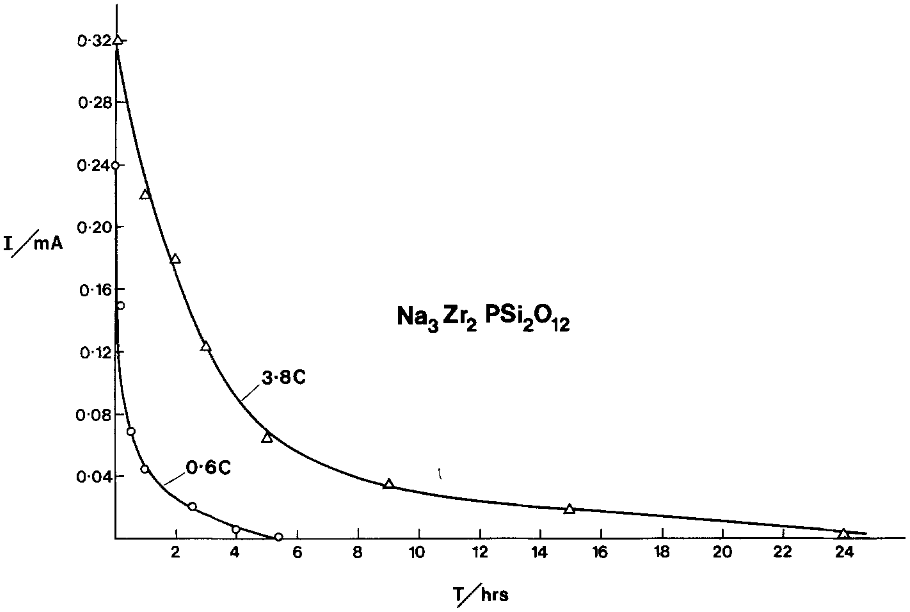

Fig. 5. $Na_3Zr_2PSi_2O_{12}$, 612°C, $m = 0.395$ g, $A = 0.36$ cm^2, $l = 0.3$ cm, $V_{ch} = 1.5$ V. Δ Charging, ○ discharging.

additional results for Li_2TiO_3 with a $10^4\ \Omega$ resistor in the circuit are given in Fig. 7. The material that gave the highest storage was Li_2TiO_3; 1–10 C were stored for pellets of mass ~ 0.25 g. It is interesting that Li_2TiO_3 is not a particularly good solid electrolyte, since $\sigma\,(500°\mathrm{C}) \simeq 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, as determined by a.c. measurements over the frequency range 10^2–10^5 Hz. This means that any search for cells with improved storage characteristics need not be restricted to those containing highly conducting solid electrolytes; indeed, the storage obtained for β-alumina was lower than that of most other materials studied. The open circuit voltage (OCV) of a cell contain-

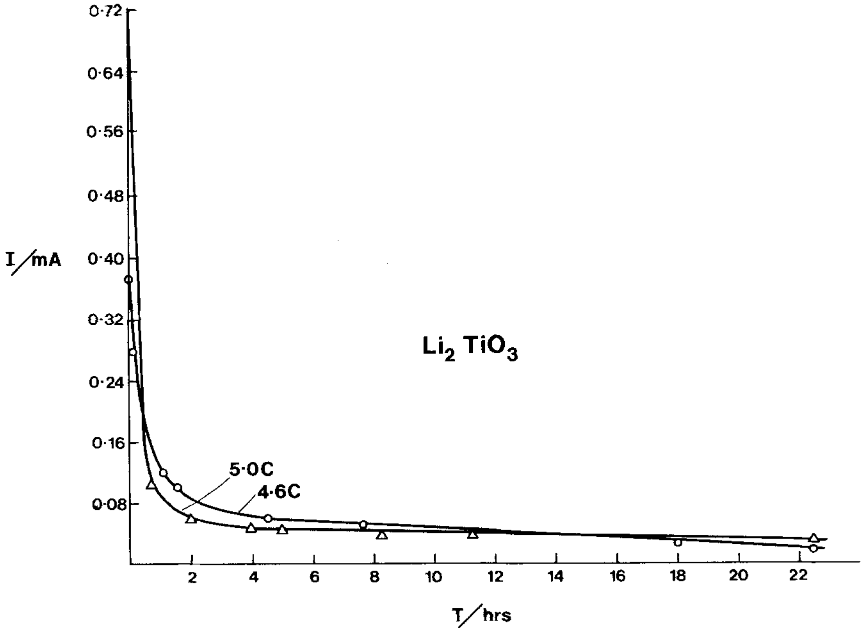

Fig. 6. Li_2TiO_3, 602°C, $A = 0.30$ cm^2, $l = 0.25$ cm, $m = 0.202$ g, $V_{ch} = 1.5$ V. Δ Charging, ○ discharging.

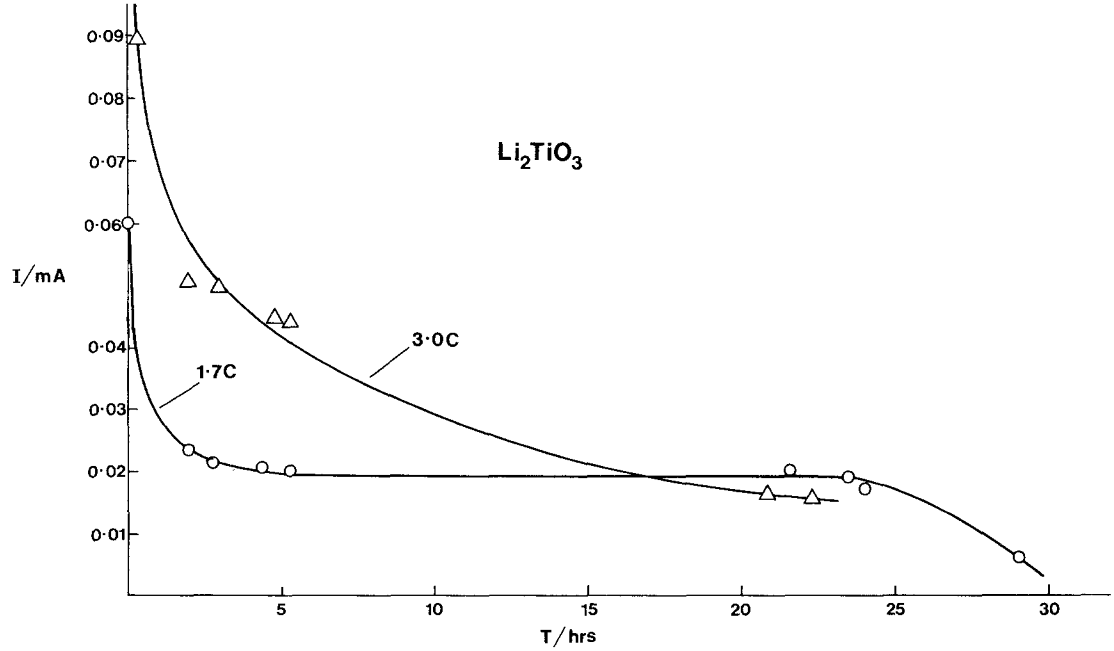

Fig. 7. Li_2TiO_3, 563°C, $A = 0.30\ cm^2$, $l = 0.25$ cm, $V_{ch} = 1.5$ V; Δ charging; o discharging. Charging and discharging circuit contained a load resistance of $10^4\ \Omega$.

ing Li_2TiO_3 is shown in Fig. 8. The cell had been charged at 1.5 V for 24 h and 563°C. The initial OCV, immediately after removal of the d.c. source, was high, approaching 1.4 V but it fell rapidly and obtained a constant value of 0.47 V after 24 h.

The processes involved in the charging and discharging of the cells are only poorly understood. It appears to be essential that the product(s) of the charging reaction remain at or close to the electrodes. The oxide ion conductor, CaO-stabilized zirconia, behaved in a completely different manner to the other solid electrolytes and no storage or discharge current could be obtained with it. On

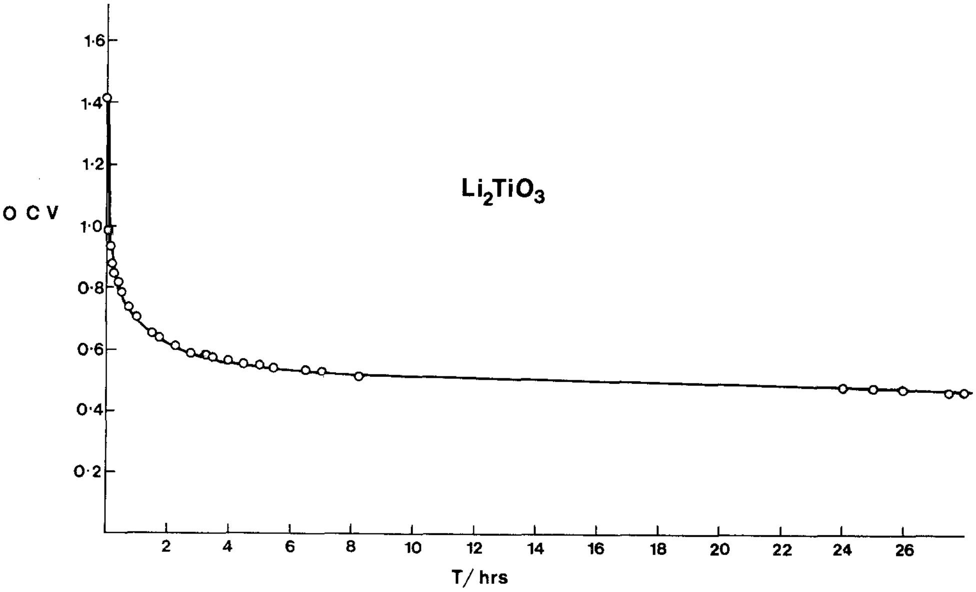

Fig. 8. Li_2TiO_3 cell, open circuit voltage after charging at 1.5 V and 563°C, $A = 0.60\ cm^2$, $l = 0.23$ cm.

charging, a current passed through the cell, Au/zirconia/Au, whose magnitude was independent of time and increased linearly with applied voltage, thereby showing that the cell obeyed Ohm's Law. At 630° C, the cell resistance was calculated as $\sim 7000\,\Omega$.

Stabilized zirconia is well known for its ability to act as an oxygen pump under an applied d.c. field, but because the cell in the present experiments was open to the atmosphere, no difference in O_2 activity at the two electrodes was allowed to build up. Hence no discharge current was possible. On the other hand the Na^+ and Li^+ containing materials were also charged open to the atmosphere and most gave large discharge currents. The inference is, therefore, that in the latter cells, the products of charging remain in the vicinity of the electrode–electrolyte interface and subsequently react when the cell is allowed to discharge.

Most of the cells studied contained polycrystalline solid electrolytes but an appreciable discharge current was also observed with a cell containing single crystal β-alumina. This rules out the possibility that the cell reaction is due in some way to processes occurring only at grain boundaries.

Further work is needed in order to understand better the processes involved. This includes experiments on: different electrode and electrolyte materials, the effects of pellet geometry, the electrode–electrolyte interface and the effects of atmospheric pressure and different types of atmospheres.

4. Applications

These cells have possible applications in a novel type of thermal battery, albeit rather expensive. They have the following characteristics. After charging a cell containing, e.g. Li_2TiO_3 at 500° C, the cell may be removed from the furnace and cooled to room temperature. It may be stored fully charged at room temperature, probably indefinitely (at least one month's storage has been tried without affecting the subsequent discharge). The cells are robust, without container problems and are inert to atmospheric attack. To activate them and recover the charge, it is necessary only to heat them. For Li_2TiO_3, discharge currents of 0.1–0.01 mA may be delivered over a period of up to several days depending on the size of the load resistance. The amount of charge stored in these cells is 0.1–1% of that stored in conventional cells. Alternatively, the cells may have applications as small, constant voltage sources at high temperatures.

The discovery of these cells also has implications for various aspects of electrode–electrolyte phenomena. For example, under what conditions does gold behave as a blocking electrode? How do other electrode materials such as Ag and Pt behave at high temperatures?

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References

[1] R. D. Armstrong, T. Dickinson and P. M. Willis, *J. Electroanalyt. Chem.* 67 (1976) 121.
[2] R. D. Armstrong and R. A. Burnham, *ibid* 72 (1976) 257.
[3] J. M. Aceves, B. G. Cooksley and A. R. West, *ibid* 90 (1978) 295.