Electrochemical Decomposition of Li_4SiO_4 and Li_2TiO_3 in Solid-state Thermal Cells

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Cells of the type Au|Li₄SiO₄|Au and Au|Li₂TiO₃|Au behave as secondary cells at high temperatures, $\gtrsim 400$ °C. The cell reactants are created *in situ* by charging the cells in air at *e.g.* 1.5 V. Electrochemical decomposition of the solid electrolytes occurs giving, as solid products, Li₂CO₃ at the negative electrode and Li₂SiO₃ and TiO₂, respectively, at the positive electrode. Under different charging conditions other products may be obtained with the Li₂TiO₃-containing cell. The products of charging form as a layer on the surfaces of the pellet and the gold electrodes appear to take no part in the reactions. The charged cells have open-circuit voltages in the range 0.4-0.5 V at *ca*. 500 °C and give discharge currents of *e.g.* 10-100 μ A through a 10⁴ Ω load resistance for several days.

Gold is commonly used as the electrode material for a.c. conductivity measurements on solid electrolytes and is assumed to be blocking to the discharge of cations. Thus, at room temperature, the gold/ β -alumina interface has been shown¹ to behave as a double-layer capacitance of size 3×10^{-7} F cm⁻². At higher temperatures, however, completely different behaviour is observed. For instance, the cell Au|Li₄SiO₄|Au may be charged and discharged above *ca*. 400 °C such that the quantity of charge passed in both directions is from 6 to 8 orders of magnitude larger than expected for double-layer phenomena.²⁻⁴ This quantity of charge is sufficiently large that the cells may have applications in novel types of thermal battery. It was found that similar charging–discharging phenomena occur with a variety of solid electrolyte materials, including single-crystal and polycrystalline β -alumina. It was suggested that the phenomena were caused by unidentified chemical reactions occurring at the electrode /electrolyte interface. In the present work, experiments have been carried out to identify the chemical reactions responsible for the charging and discharging and a more detailed study of the behaviour of two cells has been made.

Cells of the type Ag|RbAg₄I₅|graphite may be charged and discharged⁵ in a manner that, superficially, is similar to the thermal cells Au|solid electrolyte|Au. However, the former cells are, in fact, very large capacitors (*e.g.* of 50 F size) and can be charged and discharged at room temperature. The large capacitance values are achieved by greatly increasing the contact area between the electrode and the solid electrolyte. To do this, a powdered mixture of electrole and electrolyte is used to make contact between the electrode and the electrode and the contact store storage therefore appears to be capacitive, unlike the present thermal cells such as Au|Li₄SiO₄|Au, in which electrochemical reactions occur.

EXPERIMENTAL

 Li_4SiO_4 and Li_2TiO_3 were synthesised and pressed into pellets, as described previously.³ Three methods of electrode preparation were used. (1) For most experiments, gold-foil electrodes were

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attached to the pellet faces using gold paste and the arrangement was fired at ca. 500 °C for 30 min to decompose the paste and harden the gold residue. (2) Gold foil was contacted directly with the pellet surface using a small vice; insulating glass discs were used to separate the cell from the metal vice. (3) Thin-film electrodes of Ag or Au were evaporated onto the pellet faces which was then placed in the above vice.

The cells, attached to Pt electrode wires via the gold foil, were placed inside a vertical tube furnace whose temperature was controlled and measured to ± 3 °C. The cells were charged at constant voltage, as described previously,³ and the charging current recorded on a chart recorder. The cells were discharged through loads of either 10 or 10010 Ω and the currents again recorded. In other experiments, the cell voltage on open circuit was measured with a Keithley multimeter which had an internal impedance of ca. 10⁸ Ω .

Two X-ray powder diffraction techniques were used to analyse pellet surfaces: a Philips, Hägg Guinier focusing camera and a Philips diffractometer. For the camera, small amounts of material (2-5 mg) were scraped from the pellet surface, crushed finely and placed in the sample holder. For the diffractometer, the whole of the pellet was placed in the instrument with the surface of interest angled towards the incident X-ray beam. The resulting films and traces were analysed by comparison with standard powder diffraction data reported in the powder diffraction file, Joint Committee for Powder Diffraction Standards, Swarthmore, U.S.A.

RESULTS

Previous experiments^{2, 3} had shown that cells such as Au|Li₂TiO₃|Au, with an electrolyte pellet of mass *ca.* 0.25 g, were capable of storing from 1 to 100 C of charge after charging at $\gtrsim 400$ °C with an applied voltage of *e.g.* 1.5 V. Experiments have now been carried out in order to analyse and identify the products formed on charging the cells.

ANALYSIS OF CELL REACTIONS

In the first experiment, the surfaces of a charged pellet which had been in contact with the electrodes were removed, dissolved in dilute acid and analysed by atomic absorption spectroscopy. This preliminary experiment showed that an excess concentration of lithium was present at the negative electrode after the cell had been charged. Details are as follows. A cell of the type Au|Li₂TiO₃|Au was constructed, using gold paste for the electrodes, and charged; integration of the current-time curve showed that 3.5 C of electricity passed on charging. The gold electrodes were then removed from the pellets; they did not come off cleanly but instead a layer of white electrolyte material adhered to the gold. The electrodes were immersed in 0.5 mol dm⁻³ HCl to dissolve any soluble Li⁺ compounds. The gold did not dissolve and a subsidiary experiment showed that Li_2TiO_3 is not soluble in 0.5 mol dm⁻³ HCl. Hence any Li₂TiO₃ adhering to the electrode surface did not interfere with the subsequent analyses. The resulting solutions were analysed by atomic absorption methods using standard procedures. The results showed a significant concentration of Li⁺ ions in the cathode (negative electrode) solution, but no detectable Li⁺ ion concentration in the anode (positive electrode) solution. Because only a portion of each pellet surface was effectively sampled, it was not possible to make an accurate estimate of the excess Li⁺ ion concentration at the negative electrode. However, the measured concentration was of the same order of magnitude as that calculated from the quantity of electricity passed on charging. This confirmed that Li⁺ ions were, in some way, deposited at the cathode during charging.

The next stage was to identify the nature of the product(s) at the electrode/electrolyte interface(s). In order to obtain sufficient amounts of products to be detected by X-ray powder diffraction, the cells were charged for 2-3 days. The surfaces of uncharged

cell	negative electrode	positive electrode
Li ₄ SiO ₄ , charged	Li ₄ SiO ₄ + Li ₂ CO ₃	$Li_4SiO_4 + Li_2SiO_3$
Li,SiO, uncharged	LisiO	Lisio
$Li_{2}TiO_{3}$, charged at 500 °C, 1.5 V	$Li_2TiO_3 + Li_2CO_3$	$Li_2TiO_3 + TiO_2$ (anatase)
Li ₂ TiO ₃ , charged at 700 °C. 0.5 V	$Li_2TiO_3 + unidentified$	$Li_2TiO_3 + unidentified$
Li_2TiO_3 , charged at 700 °C, 1.5 V	$Li_2TiO_3 + Li_4TiO_4$	$Li_2TiO_3 + TiO_2$ (rutile)
Li_2TiO_3 , charged at 900 °C, 1.5 V	$Li_2TiO_3 + Li_4TiO_4$	$Li_2TiO_3 + TiO_2$ (rutile)

TABLE 1.—RESULTS OF X-RAY DIFFRACTION ANALYSES

pellets were also analysed to serve as a reference. The results for Li_4SiO_4 and Li_2TiO_3 are summarised in table 1.

For the cell containing Li₄SiO₄, the overall charging reaction may be written as

$$Li_4SiO_4 + CO_2 \rightarrow Li_2CO_3 + Li_2SiO_3$$

and the individual electrode reactions are probably as shown schematically in fig. 1. Under the action of the applied field, Li^+ ions migrate preferentially towards the negative electrode where they react with CO_2 and O_2 from the air to form Li_2CO_3 . At the positive electrode, a Li^+ depleted layer forms which achieves electroneutrality by condensation of the isolated, orthosilicate tetrahedra to form metasilicate chains, together with liberation of oxygen gas. This scheme is consistent with the phase diagram of the system Li_2O -SiO₂,⁶ although it does seem, in principle, that further decomposition of the Li_2SiO_3 product at the anode could occur to yield, ultimately, SiO₂.



negative electrode :

2Li⁺+2e+¹/₂0₂+C0₂ -- Li₂C0₃

positive electrode :

$$\text{Si0}_4^{4-} \longrightarrow \text{Si0}_3^{2-} + 2e + \frac{1}{2}0_2$$

FIG. 1.—Schematic mechanism for charging the cell Au|Li₄SiO₄|Au in air at e.g. 500 °C.

For the cell containing Li_2TiO_3 , several reactions were identified and all appear to fit the same pattern: lithium ions migrate towards the cathode on charging where they form a lithium-rich phase, *e.g.*

at ca. 500 °C
$$2Li^+ + 2e + \frac{1}{2}O_2 + CO_2 \rightarrow Li_2CO_3$$

at $\gtrsim 700$ °C $2Li^+ + 2e + \frac{1}{2}O_2 + Li_2TiO_3 \rightarrow Li_4TiO_4$

The latter reaction occurs because Li_2CO_3 is too reactive to form as a stable product above *ca*. 700 °C. A lithium-poor phase, often one of the polymorphs of TiO₂, forms at the anode together with liberation of oxygen gas

$$TiO_3^{2-} \rightarrow TiO_2 + \frac{1}{2}O_2 + 2e$$

Thus the overall reactions may be written

$$\begin{split} \text{Li}_2\text{TiO}_3 + \text{CO}_2 &\rightarrow \text{Li}_2\text{CO}_3 + \text{TiO}_2 \\ 2\text{Li}_2\text{TiO}_3 &\rightarrow \text{Li}_4\text{TiO}_4 + \text{TiO}_2. \end{split}$$

or

and

At low charging voltage and high temperature (0.5 V, 700 °C) the products of charging could not be identified: the phase diagram of the system $\text{Li}_2\text{O}-\text{TiO}_2$ is known⁷ and the products of charging did not correspond to any of the equilibrium phases on the diagram, *i.e.* Li_4TiO_4 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or $\text{Li}_2\text{Ti}_3\text{O}_7$. Instead, the products appear to be new, probably metastable, lithium titanate phases.

In order to confirm that cell reactions were indeed responsible for the chargingdischarging processes, primary cells were constructed and their discharge monitored. These primary cells were:

> Au, $Li_2CO_3|Li_4SiO_4|Li_2SiO_3, Au$ Au, $Li_2CO_3|Li_2TiO_3|TiO_2, Au$.

The cells were constructed and studied in the same way as the cells Au|solid electrolyte|Au with one exception: the electrode reagents, *e.g.* Li_2CO_3 , were introduced into the cell by mixing them with gold paste and the mixtures smeared onto the pellet faces in the same way that gold-paste electrodes are normally prepared.

The discharge current obtained from one Li_2TiO_3 -containing primary cell is shown in fig. 2; after 18 h discharge, 0.21 C of electricity had passed. Qualitatively, this is similar to the behaviour of the secondary cell Au|Li_2TiO_3|Au shown in fig. 6 and 7 of ref. (3), although the actual magnitude of Q for the primary cell is several times lower than the values given in ref. (3) for the secondary cell. A more quantitative comparison of the discharge characteristics of the two types of cell has not been made because the two cells were prepared, in the charged condition, by entirely different routes.

The results given in fig. 2 show clearly that chemical reactions are responsible for the operation of the cells. The cells are therefore quite distinct from the large capacitors which have been prepared⁵ by using Ag⁺-containing solid electrolytes and a very large area of electrode/electrolyte contact. For the latter, it cannot be possible to construct capacitors in the charged condition such that they give a discharge current without having first been charged, whereas this has been demonstrated with our thermal cells.

Once the processes involved in the operation of the cells had been determined, it seemed likely that the presence of gold may be incidental to the cell reactions: the gold may function merely as an inert electrode. Two series of experiments were then conducted that showed this to be true.

In the first series, a variety of electrode materials was used to construct cells, all



FIG. 2.—Discharge of the primary cell Au, Li₂CO₃|Li₂TiO₃|TiO₂, Au at 467 °C.

TABLE 2.—CHARGE-DISCHARGE OF Li2TiO3-CONTAINING CELLS WITH DIFFERENT ELECTRODES

electrodes	T/°C	Q (charging)/C	time of charging/h	Q (discharging)/C	time of discharging/h
Au paste	555	5.43	25	1.08	14
Pt paste	554	2.52	22	0.03	0.5
Au foil	487	0.78	26	0.09	4.5
Au evaporated ^a	463	0.53	44	0.27	44
Ag evaporated	463	0.26	22	0.09	11

^a Cell operated in vacuum; all other cells operated in air.

of which contained a similar Li_2TiO_3 pellet as the solid electrolyte. Results of charging/discharging experiments on these are shown in table 2. With electrodes made from Pt paste, only a small discharge was obtained, but this was because the Li⁺ ions, which accumulated at the cathode on charging, reacted irreversibly with the Pt electrode

$$2Li^+ + Pt + \frac{3}{2}O_2 + 2e \rightarrow Li_2PtO_3$$
.

The Li_2PtO_3 , together with some Li_8PtO_6 , was identified by X-ray powder diffraction and formed a greenish-brown deposit on the surface of the Pt electrode. Once formed, this deposit did not disappear on subsequently allowing the cell to discharge.

With evaporated-metal electrodes or with gold-foil electrodes in pressure contact with the pellet, significant charging and discharging currents were also obtained. The currents were smaller than in the first cell but this may have been because these cells were operated at lower temperatures (see later). It was not possible to confirm this since the evaporated-film electrodes deteriorated at higher temperatures, *e.g.* at 550 °C. In addition, the cell containing evaporated-gold electrodes did not function satisfactorily in air: the gold film separated into isolated clusters which turned a pink colour and the cell could not be charged and discharged satisfactorily. A similar cell did operate satisfactorily in vacuum, however.

replaceable electrode	T∕°C	charging voltage/V	Q charging/C	Q discharging/C	time of charging and discharging/h
gold-foil cathode	455	1.5	3.6	1.46	72
gold-foil anode	463	1.5	0.25	0.04	50

TABLE 3.—EFFECT OF REPLACING AN ELECTRODE BY A FRESH ONE AFTER CHARGING

In the second series of experiments, gold-foil electrodes were used which were replaced by fresh electrodes after charging. Details are as follows. Two identical Li_2TiO_3 -containing cells were constructed. In each, one electrode was made from gold paste and the other was a piece of gold foil in pressure contact with a pellet surface. The cells were placed in a vice and charged: in one cell the gold-foil electrode was the cathode (negative electrode) and in the other it was the anode. After charging, the gold-foil electrodes were replaced by fresh pieces of gold foil and the cells allowed to discharge. Results are given in table 3. In the cell with the gold-foil cathode, the cells operated well, giving large values of Q, and the effect of replacing the gold-foil cathode after charging also did not appear to affect the subsequent discharge of the cell. However, the overall values of Q of this cell were an order of magnitude less than for the first cell.

The results of both series of experiments taken together indicate that the gold electrodes take no part in the chemical reactions of charging and discharging. The possibility exists, however, that the gold may catalyse the reactions, and the nature of the anode, in particular, may be important. This is shown by the results for the second cell in table 3: use of gold foil as the anode instead of gold paste appears to give much reduced cell performance.

TEMPERATURE DEPENDENCE OF CELL PERFORMANCE

Most of the preliminary studies on the cells Au|solid electrolyte|Au were made in the temperature range ca. 450-600 °C,^{2,3} since at these temperatures most of the cells gave large charging and discharging currents. No appreciable discharge has been obtained for any cell below ca. 350 °C.

The behaviour of $\text{Li}_{2}\text{TiO}_{3}$ -containing cells has now been studied over a wider range of temperatures, 350-900 °C. Separate cells were prepared for each temperature. All the cells were prepared in a similar way and had electrodes made from gold paste. All were charged and discharged for the same length of time, 24 h. Since the cells were not fully discharged after 24 h, this means that the values of Q obtained on discharge were underestimates of the actual amount of charge that was originally stored in the cells. Results are given in table 4. Over the range 350-810 °C, the values of Q on both charging and discharging increase by approximately four orders of magnitude. The amount of recoverable charge that is stored appears to pass through a maximum around 810 °C: the ratio Q (discharge): Q (charge) has values in the range 0.17-0.52 for temperatures in the range 350-810 °C, but at 900 °C the value drops to 0.007. This is probably because most of the excess lithium which appears at the cathode on charging is lost to the system at 900 °C either by volatilisation or by reaction with the Pt electrode wires.

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Q (discharging) $T/^{\circ}C$ Q (charging)/C O (discharging) Q (charging) 350 0.01 0.002 0.20 414 0.40 0.07 0.17 465 1.94 0.36 0.19 530 2.16 0.65 0.30 587 6.26 1.51 0.24 640 16.24 6.69 0.41 728 48.00 25.00 0.52 810 82.00 41.00 0.50 900 450.00 3.00 0.007

TAB	le 4.—E	FFECT OF	F TEMPERATU	re on	CHARGE	-DISCHARGE	OF	Au Li ₂ TiO ₃ Au	CELLS
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The results given in table 4 are values for the cells under operating conditions; they give no information as to the origin of the large temperature dependence that is observed. A large part of the temperature dependence is probably due to kinetic effects, *i.e.* the cells were charged for a constant time and not until they had reached the fully charged state (if, indeed, such a state can be defined). With increasing temperature the various cell reactions occur more quickly and hence more charge can be stored and subsequently released on discharge.

ATMOSPHERE DEPENDENCE OF CELL PERFORMANCE

Since the reactions that occur in the operation of the cells involve the liberation and absorption of gas at the electrodes, it was anticipated that the cell performance would be atmosphere dependent. Experiments were carried out which qualitatively showed this to be so. Four Li_2TiO_3 -containing cells were prepared under similar conditions, using gold-paste electrodes. They were charged and discharged at 463 °C for the same length of time but in four different atmospheres. Results are given in table 5. The largest values of Q were obtained in oxygen and the smallest in nitrogen and *in vacuo*. The values of Q therefore decrease with decreasing partial pressure of oxygen. This is consistent with the reaction schemes proposed earlier since, on charging, oxygen gas must be present at the cathode in order for Li_2CO_3 to be formed. The small values of Q obtained in nitrogen and *in vacuo* may have been due to a small amount of residual oxygen present in the system.

atmosphere	Q (charging) /C	Q (discharging) /C	
 oxygen	2.74	0.90	
air	0.80	0.25	
nitrogen	0.22	0.04	
vacuum ^a	0.13	0.03	

TABLE 5.—EFFECT OF ATMOSPHERE ON CHARGE-DISCHARGE OF Au|Li₂TiO₃|Au cells

^a Estimated pressure 0.1 mmHg (\approx 13.33 Pa).

<i>T/</i> °C	charging voltage/V	Q (charging)/C	Q (discharging)/C
467	0.02	0.005	0.001
467	0.05	0.03	0.012
468	0.20	0.33	0.10
467	0.50	0.60	0.25
469	1.50	0.80	0.26

Table 6.—Effect of charging voltage on the charge–discharge of $Au|Li_2TiO_3|Au$ cells

EFFECT OF CHARGING VOLTAGE ON CELL PERFORMANCE

Most of the previous experiments were carried out at a standard applied voltage of 1.5 V. Since chemical reactions are responsible for the charging of the cells it seemed reasonable that a minimum cut-off voltage (but < 1.5 V) would exist below which no charging occurred. However, experiments conducted at different charging voltages showed that this was not strictly true. A series of Li_2TiO_3 -containing cells was prepared in the usual way and charged at voltages in the range 0.02-1.50 V. Results are given in table 6. The values of Q are very voltage dependent over the range 0.02-0.20 V but are approximately constant at higher voltages. It appears, therefore, that there is a minimum charging voltage for the cell to function normally which is in the range 0.2-0.5 V. At lower voltages, however, even as low as 0.02 V, the cell still functions but at a reduced level.

OPEN-CIRCUIT VOLTAGE MEASUREMENTS ON PARTIALLY CHARGED CELLS

It was shown earlier³ that in its charged state the cell Au|Li₂TiO₃|Au had an opencircuit voltage (o.c.v.) which was time dependent, but which after leaving for 24 h at 563 °C had reduced to an approximately time independent value of 0.47 V. This experiment has now been extended to include o.c.v. measurements at various levels of discharge of the cell. A Au|Li₂TiO₃|Au cell was prepared, charged in the normal way and then allowed to equilibrate on open circuit at 521 °C for 24 h. Results are shown in fig. 3. The initial o.c.v. value was *ca*. 1.5 V; with time, the o.c.v. decreased in an approximately exponential fashion to achieve a value of 0.425 after 6 h, after which the o.c.v. remained constant.

After 24 h on open circuit, the cell was allowed to discharge through a load resistance of $10^4 \Omega$ for 3 h and for which Q = 0.12 C. The cell was then again switched to open circuit and its o.c.v. monitored. After *ca*. 2 h on open circuit the cell had regained its original o.c.v. value of 0.425 V, after which it stayed constant for a further 19 h. This procedure of partially discharging the cell and then returning it to open circuit was repeated three more times. For the first two of these, an o.c.v. of 0.425 V was regained but after the final cycle the o.c.v. value was only 0.400 V. The cell was therefore probably close to complete discharge. The sum of the four discharging steps gave Q = 0.50 C, which was *ca*. 10% of the value on charging the cell initially.

These results, in which a partially discharged cell recovered its original o.c.v. value prior to discharge, are further proof that the origin of the behaviour of the cells is electrochemical rather than capacitive.



FIG. 3.—Open-circuit voltage measurements on a cell at various levels of discharge.

DISCUSSION

The results presented above have various implications and applications. It has been shown clearly that the cells are not very large capacitors but are true electrochemical cells. There is, therefore, little similarity between them and capacitors such as $Ag|RbAg_4I_5|C$.

Two cells have been studied in detail, those containing Li_4SiO_4 and Li_2TiO_3 . These were chosen for study because they were the cells that gave the highest values of Q on charging and discharging. However, similar effects, but of reduced magnitude, occur with a variety of electrolyte materials, including β -alumina.^{2, 3} It is interesting to speculate as to the likely products of charging the cell Au| β -alumina|Au in air at *e.g.* 500 °C. Probably, they are NaAlO₂ or Na₂CO₃ at the cathode and one of the polymorphs of Al₂O₃ at the anode, but experiments are needed to confirm this.

The mechanisms of operation of the cells are complex and several processes are likely to occur simultaneously, as shown, for instance, by the temperature dependence of the values of Q and the o.c.v. results. The results for Li_2TiO_3 indicate that different processes occur at different temperatures and/or at different applied voltages. The results presented here are therefore rather crude and describe an overall effect, not lending themselves to quantitative interpretation and analysis. Free-energy data are not available for many of the phases involved and hence calculations of cell voltages cannot be made.

The mechanism of operation of the cells has what is believed to be a novel characteristic in that the charging process, to give the electrode reagents, involves decomposition of the electrolyte. In normal cells and batteries charging occurs by transfer of material from one electrode compartment to the other and the electrolyte stays intact. For the present cells there is no distinction, in the discharged condition, between electrode and solid electrolyte. For example, Li₂TiO₃ is both the electrolyte and the product of discharge at the anode. The electrode reagents, in this case Li₂CO₃ (or Li₄TiO₄) and TiO₂, are therefore generated *in situ* on charging the cell.

As has been pointed out earlier,³ the cells have possible applications in a novel type of thermal cell or battery. In the charged condition the cells may be stored indefinitely at low temperatures since the discharge reactions cannot occur to any extent below

ca. 300 °C. The o.c.v. measurements also indicate that charged cells have a considerable life at high temperatures, e.g. 520 °C, since a cell maintained its original o.c.v., with intermittent spells of discharge, over a period of several days: on continuous open circuit the cell life is probably much longer.

The gold electrodes, which were used in the majority of the cells studied, appear to take no part in the cell reactions, apart from possibly acting as catalyst or active surface. It should be possible, therefore, to charge cells using other electrodes, such as silver.

The cells may also have possible applications as novel temperature or gas sensors: preliminary results show that the o.c.v. of a charged cell is dependent on both temperature and atmosphere.

It is reported that the cell Au $|\beta$ -alumina|Au behaves, at 25 °C, as an ideal double-layer capacitor,¹ provided care is taken over the preparation of the electrode/electrolyte contact. The present results are not in conflict with this room-temperature behaviour. The gold is still behaving as an essentially inert electrode at high temperatures but now electrochemical reactions occur at the electrolyte surface even at applied voltages as low as 20 mV.

The results obtained here confirm the belief that materials such as Li_4SiO_4 and Li_2TiO_3 are predominantly Li⁺ ion conductors. In order to explain the results that on charging (a) lithium-rich compounds form at the cathode, (b) lithium-poor compounds form at the anode and (c) the discharge efficiencies are relatively high, Li^+ ions must be the predominant current carrier through the pellet.

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