

## SELF-DISCHARGE IN SOLID STATE CELLS

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### Summary

The contribution of self discharge processes to solid state battery behaviour is often assessed using the Wagner polarisation technique, which yields a value for electronic conductivity. The validity of this procedure, is, in principle, suspect because of the different natures of the Wagner cell and the working battery. Results are presented for room temperature silver and copper solid state batteries, for which it appears that, in fact, results for Wagner cells can yield useful data pertinent to self discharge.

### Introduction

Unlike aqueous electrolytes, solid electrolytes are quite likely to exhibit a non-negligible electronic contribution to conductivity. Solid state cells containing such electrolytes tend to self-discharge on standing, thus lowering shelf life. To ascertain the potential application of a given solid electrolyte to a battery system, it is desirable to have a knowledge of its electronic conductivity characteristics.

When the electronic conductivity of the electrolyte approaches that of the ionic contribution, a further problem arises; the measured open circuit voltage,  $V$ , differs from the emf,  $E$ , expected from the galvanic cell reaction, since

$$V = E \frac{R_e}{R_i + R_e} = E \frac{\sigma_i}{\sigma_i + \sigma_{el}} \quad (1)$$

The regime over which this discrepancy is significant is shown in Fig. 1.

The electronic conductivity may be due to electrons and/or positive holes, and during self-discharge these two species move in opposite directions, as shown in Fig. 2. The corresponding cell reactions are



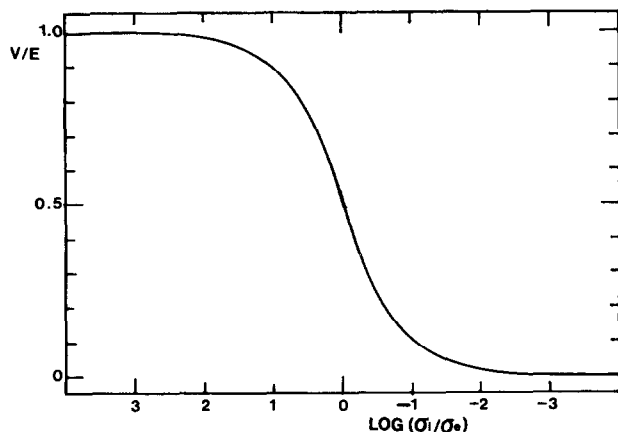


Fig. 1. Comparison of ionic and electronic conductivity with respect to the open circuit voltage.

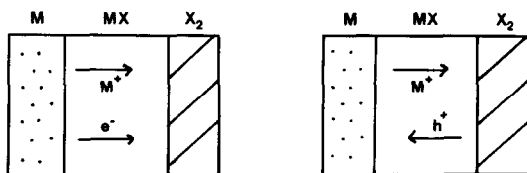


Fig. 2. Self-discharge by either (a) electron or (b) hole movement in the solid electrolyte.



Two simple methods for measuring electronic conductivity are:

- (i) The Wagner polarization approach [1, 2];
- (ii) direct measurements of the self-discharge characteristics of the test cells.

#### Wagner polarization technique

The Wagner polarization technique uses a blocking electrode to eliminate the ionic part of the current. The blocking electrode is irreversible to the conducting species, the other electrode being reversible. For a silver iodide electrolyte in which the conducting species is cationic, a possible cell is:

Ag metal|AgI electrolyte|C(graphite)

A potential, less than the decomposition potential of the electrolyte, is applied such that:

—Ag|AgI|C +

Ultimately a steady state is achieved where the migration of ions due to the external applied potential is balanced by a back migration of ions due to

a concentration gradient. The resultant current at steady state,  $I_{e1}$ , is measured as a function of the applied voltage  $V'$ , which must be below the decomposition potential of the electrolyte.

For the case of an electrolyte which is a mixed electron and hole conductor, an equation:

$$I_{e1} \{ \exp(V'F/RT) - 1 \}^{-1} = RTA \{ \sigma_e \exp(-V'F/RT) + \sigma_h \} / LF \quad (3)$$

has been derived [3, 4]. It is assumed that the chemical activities of all species present at the blocking electrode are only dependent on the externally applied potential. Contributions arising from the chemical nature and/or impurity content of the blocking electrode are neglected. This relates the current,  $I_{e1}$  ( $= I_e + I_h$ ), that flows as a consequence of electronic processes, to the applied voltage,  $V'$ , and the electron,  $\sigma_e$ , and hole  $\sigma_h$ , conductivities which would have been observed in a cell of the type M/MX/M, rather than the Wagner cell [5]. The electron contribution,  $\sigma_e$ , is obtained from the slope of a logarithmic graph of  $I_{e1} \{ \exp(V'F/RT) - 1 \}^{-1}$  against  $RTA \{ \exp(-V'F/RT) \} / LF$ . The hole contribution can be obtained from the ordinate value at the point where  $\exp(-V'F/RT)$  is equal to one, *i.e.*, when  $V' = 0$ .

For the idealised cases where either the electron, or the hole, contribution can be neglected, if the applied voltage exceeds about 0.3 V, then eqn. (3) reduces to:

$$(a) I_h = RTA \sigma_h \{ \exp(V'F/RT) \} / LF \quad (4)$$

for hole conductors, or

$$(b) I_e = RTA \sigma_e / LF \quad (5)$$

for electron conductors

It should be noted that the current that results from the passage of electron holes is dependent on applied voltage, whereas that associated with electrons is not.

### Self-discharge testing

A typical working cell, in which the active material in one of the electrodes (anode or cathode) is deliberately limited, is allowed to self-discharge until the cell reaction has been completed. It is necessary to assume that the mass efficiency,  $K$ , of the limiting electrode is the same as that for an equivalent cell loaded in such a way that the electronic current passing through the self discharge pathway can be neglected. Additionally, the electronic conductivity is assumed to remain constant during the discharge, or self-discharge, period. The electronic conductivity,  $\sigma_{e1}$ , is then given by:

$$\sigma_{e1} = \frac{mKFl}{MA} \left[ \int_{t_0}^{t_1} V(t) dt \right]^{-1} \quad (6)$$

where the voltage-time integral is taken from the start of self-discharge to the end of the voltage plateau for the cell reaction.


TABLE 1

Summary of results from copper self discharge tests

|   | Cell number   |               |               |               |               |               |
|---|---------------|---------------|---------------|---------------|---------------|---------------|
|   | 1             | 2             | 3             | 4             | 5             | 6             |
| Mass of copper anode (g)  | 0.2067        | 0.2070        | 0.2070        | 0.2069        | 0.2073        | 0.2073        |
| Expected number of coulombs   | 314.1         | 314.6         | 314.6         | 314.4         | 315.1         | 315.1         |
| Number of coulombs used   | 66.0 ± 3.1    | 66.1 ± 3.2    | 66.1 ± 3.2    | 66.0 ± 3.2    | 66.2 ± 3.2    | 66.2 ± 3.2    |
| Time for self-discharge (h)   | 1560 ± 1      | 1486 ± 1      | 1500 ± 1      | 1528 ± 1      | 1474 ± 1      | 1482 ± 1      |
| Current (μA)  | 11.8 ± 0.6    | 12.5 ± 0.6    | 12.2 ± 0.6    | 12.0 ± 0.6    | 12.5 ± 0.6    | 12.4 ± 0.6    |
| OCV (V)   | 0.320 ± 0.004 | 0.320 ± 0.004 | 0.320 ± 0.006 | 0.320 ± 0.007 | 0.320 ± 0.005 | 0.320 ± 0.006 |
| Mass of Cumoti (g)  | 1.039         | 1.045         | 1.049         | 1.036         | 1.032         | 1.030         |
| Thickness of Cumoti (mm)  | 2.3 ± 0.2     | 2.3 ± 0.2     | 2.3 ± 0.2     | 2.3 ± 0.2     | 2.3 ± 0.2     | 2.3 ± 0.2     |
| Electronic conductivity<br>(S cm <sup>-1</sup> × 10 <sup>-6</sup> ) | 6.5 ± 0.6     | 6.9 ± 0.6     | 6.8 ± 0.6     | 6.6 ± 0.6     | 6.9 ± 0.6     | 6.7 ± 0.6     |

## Experimental

The self-discharge tests were carried out at  $25 \pm 1$  °C on cells of the form:

anode limited copper|6CuI:O SCH<sub>3</sub><sup>+</sup>Γ|I<sub>2</sub><sup>-</sup>-perylene

or

silver|13AgI:(CH<sub>3</sub>)<sub>2</sub>S(CH<sub>2</sub>)<sub>3</sub>S(CH<sub>3</sub>)<sub>2</sub><sup>2+</sup>2I<sup>-</sup>|(CH<sub>3</sub>)<sub>2</sub>S(CH<sub>2</sub>)<sub>3</sub>S(CH<sub>3</sub>)<sub>2</sub><sup>2+</sup>2I<sub>3</sub><sup>-</sup>,  
cathode limited

where the electrolytes are called Cumoti and Agbisi, respectively. Practical details have been reported elsewhere [6, 7].

## Results

### Copper cells

The results of a series of six self-discharge cells are presented in Table 1. The average mass efficiency from 12 loaded cells was  $21 \pm 2\%$  and the mean value of the electronic conductivity ( $\sigma_{e1}$ ) from self-discharge measurements is, therefore,  $6.7 \pm 0.8 \times 10^{-6}$  S cm<sup>-1</sup>.

The results of the measurements on the Wagner cell are shown in Fig. 3, from which:

$$\sigma_e = 4.5 \pm 1.3 \times 10^{-6} \text{ S cm}^{-1}$$

$$\sigma_h = 6.0 \pm 0.9 \times 10^{-8} \text{ S cm}^{-1}$$

giving a total electronic conductivity of

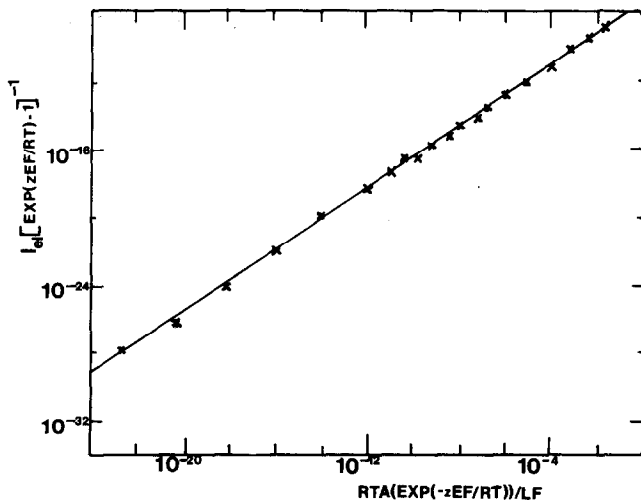


Fig. 3. Experimental Wagner plot for a copper/Cumoti/graphite sample.

$$\sigma_{el} = \sigma_e + \sigma_h = 4.6 \pm 1.3 \times 10^{-6} \text{ S cm}^{-1}$$

This compares with the value [8] of  $\sigma_e = 3.0 \times 10^{-6} \text{ S cm}^{-1}$  obtained using the simplified eqn. (5) applied to the results of measurements on another Wagner cell.

### *Silver cells*

A series of six cells was set up for self-discharge testing, but in each case failure after about one year occurred due to rupture of the cell assembly. Each of the cells was still on its voltage plateau, showing that the self-discharge process was not complete. The electronic conductivity,  $\sigma_{el}$ , can therefore only be estimated as having a value below  $10^{-8} \text{ S cm}^{-1}$ .

The results of the measurements on the Wagner cell are:

$$\sigma_e = 2.8 \pm 1.2 \times 10^{-10} \text{ S cm}^{-1}$$

$$\sigma_h = 1.6 \pm 0.9 \times 10^{-10} \text{ S cm}^{-1}$$

so that:

$$\sigma_{el} = 4.5 \pm 1.4 \times 10^{-10} \text{ S cm}^{-1}$$

### **Discussion**

It might initially be expected that Wagner cell results for electronic conductivity could not be representative of the situation in a working cell because:

(i) One of the working cell electrodes is replaced by carbon. Consequently, one of the electrode-electrolyte interfaces is different and, since electronic transfer depends on the character of the interfaces, the polarised cell behaviour must differ from the working cell.

(ii) The polarised Wagner cell is driven by an applied voltage; therefore the anode of the working battery becomes cathodically polarised in these measurements. This means that in the working cell, the movement of both electrons and holes appears to be against the field gradient. Wagner cell measurements would be expected to produce higher values of  $\sigma_e$  and  $\sigma_h$  than pertain to the working cell.

(iii) The Wagner cell is totally ionically polarised, and the ionic concentration gradient may affect the electronic transport.

(iv) Kennedy [5] has presented a detailed argument which suggests that Wagner measurements will predict the highest  $\sigma_e$  value and, conversely, the lowest  $\sigma_h$  value to be expected in the working cell.

Despite the above reservations, it can be seen that, for the copper solid state cell system under present study, satisfactory agreement is, in fact, obtained between Wagner and self-discharge tests. The electronic conductivity in this system is large enough to cause practical problems with respect

to shelf life. For the silver system, comparison could not be made between the two methods, but this is of little practical consequence because the electronic conductivity is negligible.

## Conclusions

Both the simple methods of estimating the electronic conductivity contribution to self-discharge processes in solid state batteries appear, unexpectedly, to give similar results. The Wagner method is to be preferred to self-discharge tests because it is substantially more rapid.

## Acknowledgements

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## List of symbols

|               |   |
|---------------|---|
| $V$           | Measured voltage of a cell  |
| $E$           | Galvanic voltage of a cell  |
| $R_e$         | Electronic resistance   |
| $R_i$         | Ionic resistance  |
| $\sigma_i$    | Ionic conductivity  |
| $\sigma_{el}$ | Total electronic conductivity   |
| $I_{el}$      | Total electronic current  |
| $V'$          | Applied voltage   |
| $F$           | Faraday's constant  |
| $R$           | Gas constant  |
| $T$           | Absolute temperature  |
| $A$           | Area of cell  |
| $\sigma_e$    | Electron conductivity   |
| $\sigma_h$    | Hole conductivity   |
| $L$           | Length of Wagner cell   |
| $I_h$         | Hole current  |
| $I_e$         | Electron current  |
| $K$           | Electrode mass efficiency   |
| $m$           | Mass of electrode active material                                       |
| $l$           | Length of electrolyte   |
| $'M$          | Relative molecular mass of electrode active material                    |
| $M$           | A metal from which the anode of a primary solid state cell can be made. |
| $MX_n$        | A halide of M.  |

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