JOURNAL OF APPLIED ELECTROCHEMISTRY 11 (1981) 247–251

Electrochemical behaviour of lithium iodide monohydrate

R. D. ARMSTRONG, K. LANDLES

Electrochemistry Research Laboratories, School of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne, UK

Received 22 July 1980

The electrochemical behaviour of lithium iodide monohydrate in contact with stainless steel and lithium electrodes has been studied. This electrolyte is shown to conduct lithium ions, suggesting possible applications in the battery field.

1. Introduction

Liang and his co-workers have found that the ionic conductivity of pure lithium iodide can be enhanced by the addition of dopants [1, 2] and have reported a solid-state battery system [3] in which the electrolyte is lithium iodide doped with alumina. Owens and Hanson have improved upon this system by adding alumina and controlled amounts of water [4]. Stoneham [5] has attempted to explain the enhancement by suggesting that a highly conducting layer forms around the inert particles and that lithium iodide monohydrate may be involved in this layer. Owens *et al.* later reported [6] that addition of pre-dried alumina did not enhance the conductivity of anhydrous lithium iodide and that the increase in conductivity noted by previous workers when alumina particles were added to lithium iodide was due to the presence of moisture resulting in the formation of a hydrate. We have investigated lithium iodide monohydrate as a solid electrolyte in its own right and our findings are reported in this paper.

2. Experimental

Two principal techniques were employed, namely a.c. impedance and d.c. polarization. The electrolyte was prepared for measurement in a dry-air glove-box ($\leqslant 10$ ppm water vapour) as follows: a quantity of lithium iodide monohydrate (BDH, 96% pure, confirmed by X-ray analysis) sufficient to give a pellet thickness of $\simeq 0.05$ cm was placed between two cylindrical stainless steel electrodes ($2.0\,\text{cm}^2$ area) which were a sliding fit in a perspex conductivity cell. Sealant was then placed around the electrodes to prevent access of external atmosphere to the electrolyte. The cell was removed from the dry box and placed in a hydraulic press which was equipped with insulated end-plates to allow conductivity measurements to be made *in situ*; the pressure versus conductivity measurements were recorded in this way. Pellets were also formed by this technique at a pressure of $1000\,\text{kg cm}^{-2}$, whereupon the cell was removed from the press and replaced in the dry box. This allowed the removal of the stainless steel electrodes (possibly blocking) in the dry atmosphere and the placing of discs of lithium metal between them and the electrolyte pellet so that exchange of lithium ions between electrodes (possibly non-blocking) and electrolyte was possible. Measurements were made in the dry box using a vice to apply a contact pressure of $25\,\text{kg cm}^{-2}$ measured on a statimeter. This arrangement was linked electrically to external measuring equipment, either a.c. or d.c.

The a.c. measurements were made using a Solartron 1174 frequency response analyser (FRA) sweeping from 1 MHz to 1 Hz in steps of ten points per decade. The total impedance Z was expressed in terms of its real and imaginary parts, Z' and Z'', which were plotted out on the X and Y axes, the data being processed by a microcomputer (North Star Horizon) in conjunction with a Hewlett Packard graph plotter. Details of the use of the Solartron FRA have been covered by Armstrong *et al.* previously [7].

D.c. measurements were made using a power supply in series with the cell and a current-measuring

0021–891X/81/020247–05$02.50/0

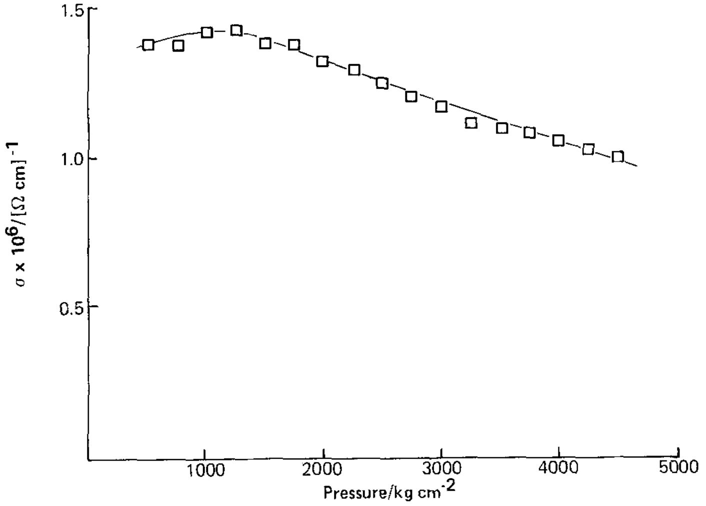

Fig. 1. Conductivity versus pressure for lithium iodide monohydrate from a.c. impedance measurements.

resistance. The potential drop across the current-measuring resistance was measured on a digital voltmeter and recorded on a chart recorder.

3. Results and discussion

Fig. 1 shows the conductivity versus pressure curve for lithium iodide monohydrate from a.c. measurements using blocking electrodes. The a.c. spectrum recorded at 1750 kg cm^{-2} is shown in Fig. 2. The conductivity versus pressure curve shows a maximum at 1000 kg cm^{-2}, at which point the conductivity is $1.425 \times 10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. With increasing pressure on the sample, the amount of void is reduced as the sample approaches its crystallographic density [8] of 3.13 g cm^{-3} (Fig. 3). This would account for the increasing conductivity approaching the maximum; however, the conductivity begins to diminish beyond the maximum even though the sample has not reached its maximum density.

The decrease in conductivity with increasing pressure may occur because the lithium iodide monohydrate is partially converted to its α-phase structure, which is stable at atmospheric pressure at temperatures below $-5°$ C, and which has a lower conductivity than the β phase.

To establish the nature of the conductivity, a

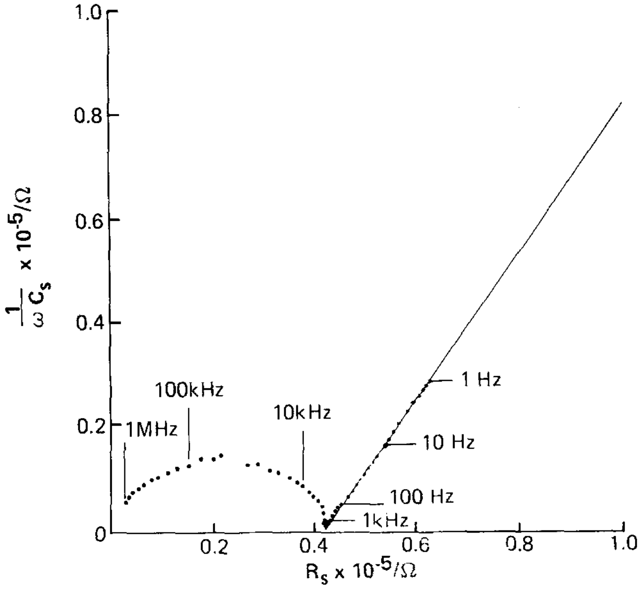

Fig. 2. Typical a.c. impedance spectrum for lithium iodide monohydrate using stainless steel blocking electrodes at 1750 kg cm^{-2} pressure.

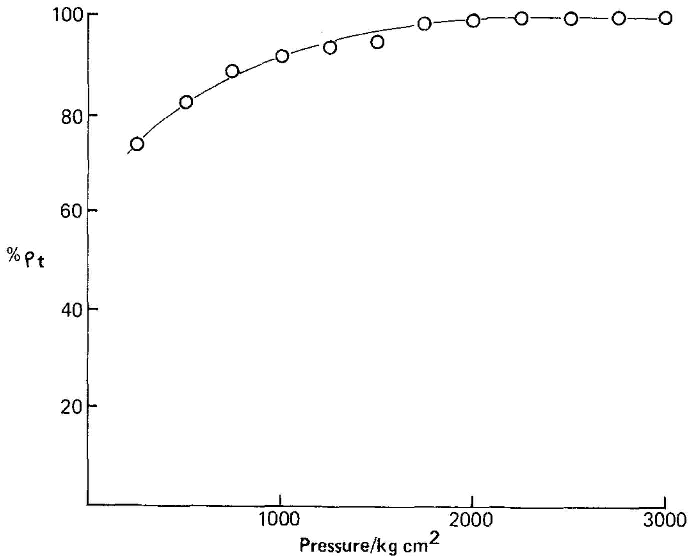

Fig. 3. Percentage of theoretical density versus pressure for lithium iodide monohydrate.

d.c. potential of 0.2 V was applied across the electrolyte using blocking and non-blocking electrodes. With blocking electrodes a current of 0.06 μA flowed, but this was of the same order as the background current or leakage current noted when an insulator was substituted for the electrolyte. This showed that the electrolyte had no significant electronic conductivity. With non-blocking electrodes, a steady current of 3.0 μA flowed, showing that the electrolyte was probably a lithium ion conductor.

The decomposition potential of the electrolyte in contact with lithium metal was investigated by placing a pellet of the electrolyte in contact with one non-blocking electrode and one blocking electrode. A d.c. potential was applied stepwise across the cell, the non-blocking electrode being negative. The system was allowed 15 minutes to reach a steady current between steps and this current was plotted against applied potential (Fig. 4). Between 1.0 V and 3.0 V, essentially no current flowed. At potentials greater than 3.0 V the current rose progressively and this was assumed to be due to the decomposition of the electrolyte. After a long period at 4.2 V, a yellowish brown discolouration was apparent around the positive electrode, indicating that the lithium iodide monohydrate had decomposed to iodine and lithium. Below 1.0 V, a cathodic current flowed which diminished as the applied potential was increased. This was assumed to be due to lithium dissolving anodically into the electrolyte and oxygen being reduced at the stain-

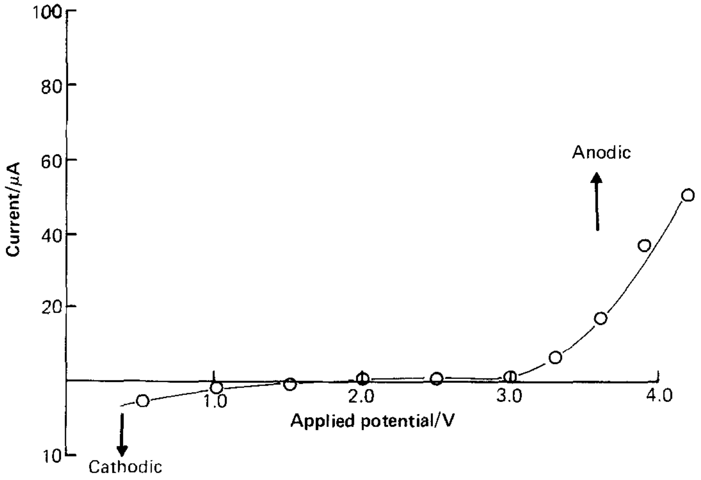

Fig. 4. Decomposition current at a stainless steel electrode versus applied potential for lithium iodide monohydrate.

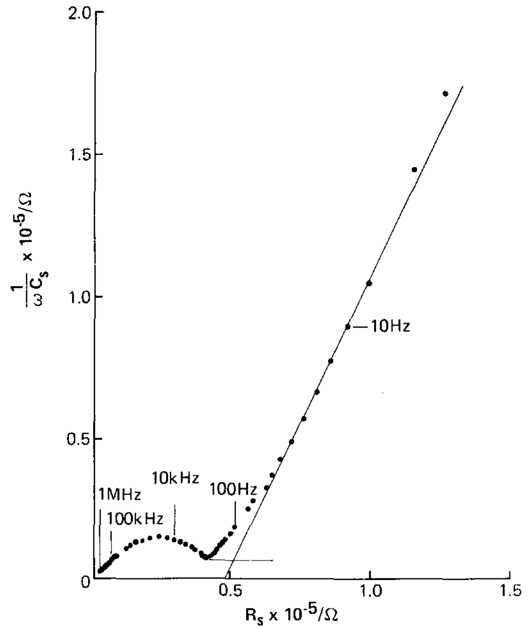

Fig. 5. A.c. impedance spectrum of lithium iodide monohydrate at a contact pressure of 25 kg cm^{-2} using stainless steel blocking electrodes.

less steel electrode, but on repeating the experiment in an argon atmosphere the same observations were made, suggesting that oxygen reduction was not responsible for the current, and that it was more likely to be due to the reduction of one or more of the impurities present in the lithium iodide monohydrate.

The nature of the interface between the electrolyte and the lithium electrodes was investigated as follows: an electrolyte pellet was formed in a cell, then its a.c. impedance was measured using blocking stainless steel electrodes at a contact pressure of 25 kg cm^{-2} (Fig. 5). The blocking electrodes were then replaced by non-blocking lithium electrodes, and the a.c. impedance was measured again at the same contact pressure (Fig. 6). The resistance of the pellet using blocking electrodes was found to be 50 kΩ, and using non-blocking electrodes, 12.5 kΩ. The difference was attributed to the more intimate contact between the soft lithium metal than with the hard stainless steel. With the lithium electrodes *in situ* under contact pressure, a potential was applied in increments of 10 mV, and time was allowed between increments for the system to steady.

Upon the application of 10 mV, a current flowed immediately and increased linearly with applied potential (Fig. 7) at the rate of 0.077 μA mV^{-1}, indicating that there was minimal interfacial resistance. The resistance of the pellet calculated from this d.c. current versus potential plot was 13 kΩ, which compares with 12.5 kΩ measured by a.c. impedance, giving an interfacial resistance of 0.25 kΩ/interface.

Had there been a significant charge transfer resistance, the a.c. impedance measured using non-blocking electrodes (Fig. 6) would have shown an additional semicircle adjacent to the first; there was no sign of this. At the maximum applied potential in this experiment, i.e. 0.2 V, a steady current of 15 μA was sustained. This is significantly higher than the 3 μA measured during an earlier experiment. The pellet thickness in both cases was 0.06 cm, so the difference is likely to be due to the longer period of exposure of the first pellet to the glove-box atmosphere, which would allow the small amount of moisture present in the dry box to react with the surface of the pellet and form some lithium iodide dihydrate, which has a lower conductivity of $\simeq 10^{-7}\,\Omega^{-1}\,\mathrm{cm}^{-1}$.

To confirm that lithium iodide monohydrate is

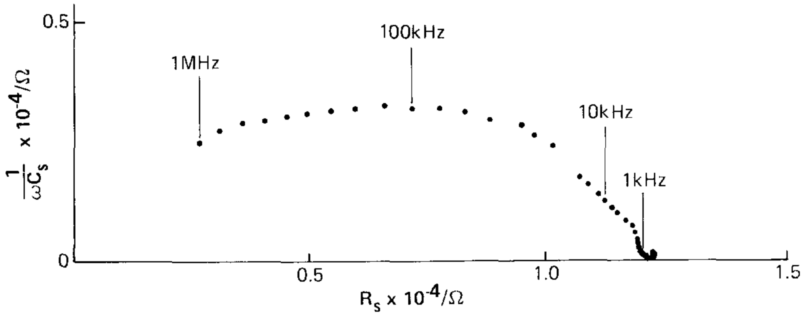

Fig. 6. A.c. impedance spectrum of lithium iodide monohydrate using lithium non-blocking electrodes.

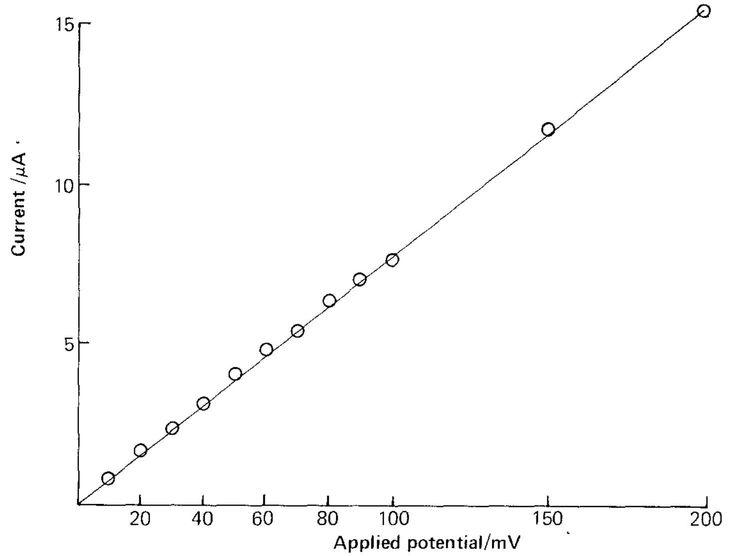

Fig. 7. Current versus applied potential for the system Li|LiI·H_2O|Li.

definitely a lithium ion conductor, a cell was assembled using one lithium electrode and one stainless steel electrode. 0.2 V was applied to the cell to deposit lithium metal on the stainless steel electrode, and a steady current of 5.0 μA was allowed to flow for 100 h. The cell was then dismantled and it was observed that lithium metal had deposited in the surface layer of the electrolyte between electrolyte crystals adjacent to the surface of the stainless steel. This gave a 'speckled' effect to the surface of the electrolyte.

4. Conclusions

Lithium iodide monohydrate has been established as a lithium ion conductor, with conductivity $\simeq 1.4 \times 10^{-6} \Omega^{-1} cm^{-1}$ at 23° C. The electrolyte is stable in contact with lithium metal at room temperature. At potentials greater than 3.0 V, at a stainless steel electrode, decomposition takes place with some iodine being formed. There is minimal interfacial resistance between the electrolyte and lithium metal.

Acknowledgement

We would like to acknowledge the Berec group for their financial support and Dr J. Lee, Dr G. Dudley and Dr W. Weppner for helpful discussions.

References

[1] C. R. Schlaiker and C. C. Liang, *J. Electrochem. Soc.: Solid State Sci.* **118** (1971) 1447.
[2] C. C. Liang, *J. Elecrochem. Soc.* **120** (1973) 1289.
[3] C. C. Liang and L. H. Barnette, *J. Electrochem. Soc.: Electrochem. Sci. Technol.* **123** (1976) 453.
[4] B. B. Owens and H. J. Hanson, US Patent 4007 122 (1977).
[5] A. M. Stoneham, E. Wade and J. A. Kilner, *Mater. Res. Bull.* **14** (1979) 661.
[6] B. B. Owens, S. Pack and J. B. Wagner, *Boston ECS Meeting, Abstract No. 368* (1979).
[7] R. D. Armstrong, M. F. Bell and A. A. Metcalfe, *J. Electroanal. Chem.* **77** (1977) 287.
[8] Von E. Weiss, *Z. Anorg. Allgem. Chem.* **341** (1965) 203.