Short Communication

A Lithium Solid-State Cell Based on the Li_{3.75}S_{0.75}P_{0.25}O₄ Electrolyte

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Lithium solid electrolytes are of great technological interest since they are compatible with high energy density electrode couples. So far, however, few materials which exhibit good lithium ionic conductivity at low temperature have been characterized. Very recently, Shannon and coworkers [1] have reported the general properties of new compounds, based on solid solutions of lithium silicate with various salts, which may be regarded as lithium conductors. Among these, $Li_{3.75}Si_{0.75}P_{0.25}O_4$ shows relevant properties, such as a good stability and a total conductivity of about 10^{-3} (ohm cm)⁻¹ at 200 °C.

Therefore, it seemed to us of interest to test this conductor for possible application in solid-state lithium power sources capable of operating at moderately high temperatures. In this connection, the cell

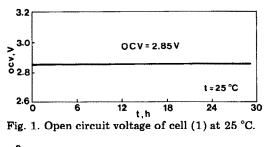
Li/Li_{3.75}Si_{0.75}P_{0.25}O₄/I₂-Ph

where I_2 -Ph is the iodine-phenothiazine charge transfer complex [2], was considered. The cell was assembled in a dry box by placing into contact a lithium disc, a sintered electrolyte disc and a pellet of I_2 -Ph. The cell was then housed in a plastic container having stainless-steel terminals. The iodinephenothiazine charge transfer complex acts as an iodine electrode with excellent properties in solid-state cells, as clearly shown in the case of those based on silver [2].

The open circuit voltage (OCV) of cell (1) was 2.85 V at 25 °C. This value compares well with the thermodynamic one (2.90 V) related to the LiI formation at 25 °C [3]. The 50 mV difference may in fact be attributed to the free energy of dissociation of the iodine complex [2]. This result shows that the conductivity of $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}O_4$ is essentially ionic and therefore this compound may be regarded as a real lithium solid electrolyte. The negligible electronic contribution to the conductivity of the electrolyte is further demonstrated in Fig. 1 which shows how the OCV of cell (1) remains constant with time.

In Fig. 2 is shown the polarization of cell (1), obtained at 80 °C by submitting the cell to square current pulses of 1 min period. The linear behaviour and the fast recovery of the OCV show that the polarization is mainly ohmic due to the internal resistance of the cell. From the data of Fig.

(1)



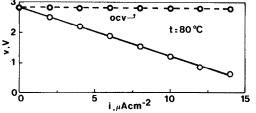


Fig. 2. Short time polarization of cell (1) at 80 °C. Electrolyte thickness: 1 mm.

2, this resistance is calculated to be 1.4×10^5 ohm, while the resistance of the electrolyte alone (1 mm thick) would be about 4×10^3 ohm at 80 °C [1]. The excess is undoubtedly to be attributed to electrode/electrolyte contact resistance. Improvements in these contacts would then produce sensible improvements in cell performance.

In the case of cell (1), its performance has been tested further by examining its discharge characteristics. Typical curves are reported in Fig. 3. The flatness of the curves shows the potential capabilities of the cell and together with the other results reported above indicate that the $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}$ -O₄ electrolyte may be considered for the development of lithium solid-state power sources.

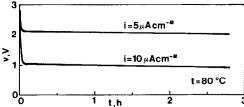


Fig. 3. Initial discharge curves of cell (1) at 80 °C. Electrolyte thickness: 1 mm.

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- 1 R. D. Shannon, B. E. Taylor, P. D. English and T. Berzins, Int. Symp. Solid Ionic and Ionic-Electronic Conductors, Rome, Sept. 1976.
- 2 M. Pampallona, A. Ricci, B. Scrosati and C. A. Vincent, J. Appl. Electrochem., 6 (1976) 269.
- 3 J. G. Gibson and J. L. Sudworth, Specific Energies of Galvanic Reactions and Related Thermodynamic Data, Chapman and Hall, London, 1977.