

Short Communication

High Temperature Batteries with a Solid Sulphate Electrolyte

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Many sulphate mixtures are suitable as electrolytes for high temperature all-solid batteries, and it is possible to use easily available metals such as magnesium, calcium or zinc as the anode. We have previously shown that not only the theoretical energy density, but also the obtained power density, can be high for cells where divalent cations are added to cubic phases of Li_2SO_4 or LiNaSO_4 [1 - 5], which have a very high electrical conductivity. We have also reported on cells where divalent sulphates have been added to hexagonal Na_2SO_4 , a phase for which the conductivity can be strongly enhanced by introducing other cations [5 - 7]. We are now taking up a third possibility, namely, where a divalent sulphate, such as CaSO_4 , MgSO_4 or ZnSO_4 , is the main constituent. Li_2SO_4 was chosen as the dopant, since the phase diagrams $\text{Li}_2\text{SO}_4\text{-CaSO}_4$ and $\text{Li}_2\text{SO}_4\text{-MgSO}_4$ have been determined by Ljungmark [4, 8] and $\text{Li}_2\text{SO}_4\text{-ZnSO}_4$ by Schroeder [2 - 4, 9].

The cells were prepared and tested according to the procedure used for the two other types of cells [1 - 5]. In Table 1 the results for some cells with

TABLE 1

Experimental results for some cells with a solid sulphate electrolyte

Cells with a low content of monovalent cation, Nos. 9 - 13, are compared with two cells, Nos. 1 and 5, where the monovalent cation is abundant [1 - 5]. In all cases the cathode consisted of a mixture of manganese dioxide and carbon. The cell diameter was 20 mm and the electrolyte thickness was about 1 mm.

Cell no.	Anode material	Cathode material	Electrolyte composition	Temperature (°C)	E.m.f. (V)	Internal resistance (Ω)
9	Mg	MnO_2	$\text{Li}_{0.70}\text{Mg}_{0.65}\text{SO}_4$	610	2.3	30
10	Zn	MnO_2	$\text{Li}_{0.50}\text{Zn}_{0.75}\text{SO}_4$	485	1.2	10
11	Zn	MnO_2	$\text{Li}_{0.30}\text{Zn}_{0.85}\text{SO}_4$	483	1.2	20
12	Zn	MnO_2	$\text{Li}_{0.10}\text{Zn}_{0.95}\text{SO}_4$	481	1.2	45
13	Zn	MnO_2	$\text{Li}_{0.06}\text{Zn}_{0.97}\text{SO}_4$	484	1.2	105
1	Mg	MnO_2	$\text{Li}_{1.76}\text{Mg}_{0.12}\text{SO}_4$	745	2.3	1.4
5	Zn	MnO_2	$\text{Na}_{1.6}\text{Zn}_{0.2}\text{SO}_4$	380	1.2	50

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a high content of divalent sulphate are compared with two cells where either Li^+ or Na^+ is the abundant cation. For each of the cells 9 - 13, the electrolyte has a composition corresponding to a two-phase region in the phase diagram, and the concentration of the non-conducting compound ($\text{Li}_{0.66}\text{Mg}_{0.67}\text{SO}_4$ or ZnSO_4) is larger than that of the compound with a high conductivity. As expected, the internal resistance is much higher for the cells where a divalent cation is abundant than it is for the ones with a high concentration of lithium, while they are comparable with cells where sodium is the most common cation.

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- 1 B. Heed and A. Lundén, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, England, 1975, p. 573.
- 2 B. Heed, A. Lundén and K. Schroeder, *10th IECEC Conf., Newark, Delaware, 1975*, p. 613.
- 3 B. Heed, A. Lundén and K. Schroeder, in J. Wood, O. Lindqvist, C. Helgesson and N.-G. Vannerberg (eds.), *Reactivity of Solids*, Plenum Press, New York, 1977, p. 713.
- 4 B. Heed, A. Lundén and K. Schroeder, *Electrochim. Acta*, 22 (1977) 705.
- 5 B. Heed, *Thesis*, Chalmers University of Technology, 1975.
- 6 H. H. Höfer, W. Eysel and U. von Alpen, *J. Solid State Chem.*, 36 (1981) 365.
- 7 Y. Saito, K. Kobayashi and T. Maruyama, *Solid State Ionics*, 3/4 (1981) 393.
- 8 H. Ljungmark, *Thesis*, University of Gothenburg, 1974.
- 9 K. Schroeder, *Thesis*, University of Gothenburg, 1975.