Letter

Mobility of Protons and Oxygen Ions in Lithium Sulfate and Other Oxyacid Salts

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Some high-temperature sulfate phases can equally well be considered as plastic crystals (rotator phases) or as solid electrolytes (superionic conductors).[1,2] The strongly coupled rotational motion of the anions enhances the mobilities of all kinds of cations that are present. This has been called the "paddle-wheel mechanism" for cation mobility. At our laboratory, Heed demonstrated in 1971–2 that a fuel cell could be operated with a solid sulfate electrolyte.[3,4] However, the discovery was not followed up at that time. We have recently taken up a broader program concerning proton and oxygen ion mobility in different types of salts. It has been established in the meantime that protons can be mobile at high temperatures in some oxide materials.[5,6]

Experimental

$Li_2SO_4 \cdot H_2O$ of *p.a.* quality (Merck, Germany) was dried in air before use, first at 150 °C for two days and then at 500 °C for two days. Three types of electrodes were used: platinum, nickel sponge (Grade 2, Johnson Matthey & Co, London) and perovskite-type oxides ($La_{0.6}Sr_{0.4}MnO_3$ and $La_{0.5}Sr_{0.5}Mn_{0.7}Co_{0.3}O_{3-\delta}$, obtained from Kyushu University, Fukuoka, Japan and Siemens AG, München, Germany, respectively). Platinum electrodes are preferred when fundamental properties are studied and the highest possible accuracy is desired, while the other two types can be used also for large-scale applications e.g. in utility systems. The preparation technique used in the platinum case is described here, while that for the other alternatives is given elsewhere.[4] Electrolyte pellets with a diameter of 13 mm and a thickness of 1 to 2 mm were made in a cylindrical die using 300 MPa pressure. The two plane sides were then painted with platinum paste (Leitplatin 308A, Demetron, Hanau), and the cells were heated in air at 500 °C for at least six hours before operation.

The area of the cell that was exposed to gas at the electrodes had a diameter of 9 mm. The gas handling system available at present is primitive, and we have had to rely on information from the manufacturer concerning the composition of the gases. When working with cell B (see

below), it was essential to let the gases pass over CuO at 600 °C and then over P_2O_5 in order to remove traces of hydrogen and water.

Galvanic cells used. Transport numbers and ion mobilities were studied using the concentration cells:

H_2/electrode/sulfate/electrode/5 % H_2 in Ar   (A)

and

O_2/electrode/sulfate/electrode/2 % O_2 in Ar   (B)

Fuel cell performance was studied for:

H_2/electrode/sulfate/electrode/O_2 (C)

and

Town gas/electrode/sulfate/electrode/air   (D)

The composition of the available town gas varied; the hydrogen content lay between 54 and 64 %.

Results and discussion

It has been demonstrated by electromigration experiments with cubic lithium sulfate that the electronic conductivity is negligible in comparison with the ionic conductivity.[7] The same result has been obtained by means of conductivity measurements with blocking electrodes.[8]

For conventional solid oxide fuel cells, where O^{2-} is the mobile species, it is common to have an oxide, e.g. a perovskite, as oxygen electrode (cathode) while the hydrogen electrode (the anode) contains a metal[9] (Ni, Pt, etc.). However, in our experiments reported here we always prepared both electrodes from the same material.

In high-temperature oxide electrolytes either O^{2-} ions or protons are responsible for the ionic conductivity, while metal ions are the most mobile species in at least some phases of the studied oxyacid salts. For the concentration cells A and B above this means that the electrodes are blocking for metal ions (e.g. Li^+) and for either O^{2-} (cell A) or H^+ (cell B), while they are non-blocking for H^+ or O^{2-}, respectively.

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Fuel cell performance. For the cells C and D, the open cell voltage is in the range 1.0–1.1 V independent of which type of electrode is used. A short-circuit current density of more than 300 mA cm^{-2} (with reference to the area exposed to gas) was achieved for the cubic phase of lithium sulfate, but it was much less for the other phases that have been tested so far.[4]

Transport numbers. We made independent estimates of the transport numbers of H$^+$ and O^{2-} by means of the concentration cells (A) and (B), respectively:

$$t(\text{H}^+) = E_{\text{obs}}/(RT/2F)\ln\ (p_1'/p_1'')$$ (1)

$$t(\text{O}^{2-}) = E_{\text{obs}}/(RT/4F)\ln\ (p_2'/p_2'')$$ (2)

where E_{obs} is the open cell voltage (OCV), R is the gas constant, F is the Faraday constant and p' and p'' ar the partial pressures of the gas in question at the electrodes. When introducing eqns. (1) and (2) we have assumed that other concentration gradients that might affect the OCV are negligible. Cases where more that one concentration gradient contribute to the OCV have been studied by Norby.[6,10]

The results obtained for lithium sulfate using cell A with platinum electrodes are shown in Fig. 1. For the high-temperature cubic phase the proton transport number is close to 0.9 without any evident temperature dependence, while it is of the order of 0.5 for the monoclinic phase at 500 °C.

When cell B was used, the results were of a qualitative nature only. We concluded that the upper limit for $t(\text{O}^{2-})$ is below 0.1 for both phases of lithium sulfate. It is difficult to visualize any mechanism for bulk migration of O^{2-} in oxyacid salts, while grain boundary effects seem plausible.

Proton conductivity. The proton conductivity as estimated by discharging cell A through a resistance which usually was of the order of 1 kΩ in the cubic phase and 10 kΩ in the monoclinic phase. A proton conductivity of 1.8×10^{-2} S
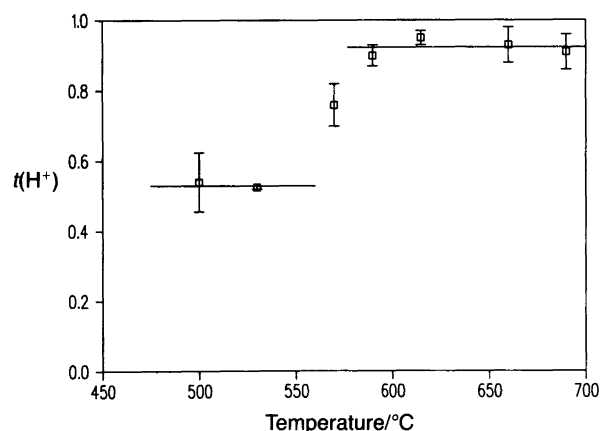

Fig. 1. Transport number for protons in lithium sulfate calculated according to eqn. (1). The error bars correspond to the standard deviation of the mean.

cm^{-1} was obtained at 610 °C, which is about 1.5 % of the lithium ion conductivity. At 500 °C the proton conductivity is of the order of 7×10^{-4} S cm^{-1}, while the results of five different studies of the ion conductivity[11] range from 0.9×10^{-4} to 8×10^{-4} S cm^{-1} (in this range impurities can affect the ion conductivity considerably). The results in the range 500 °C to 690 °C are summarized in Fig. 2, where we have tentatively drawn straight lines in order to estimate activation energies: 0.46 eV for the cubic and 1.04 eV for the monoclinic phase. These agree within experimental error with the corresponding activation energies for lithium ion conduction: 0.43 eV for the cubic phase[2] and 1.2 eV for the monoclinic phase.[8]
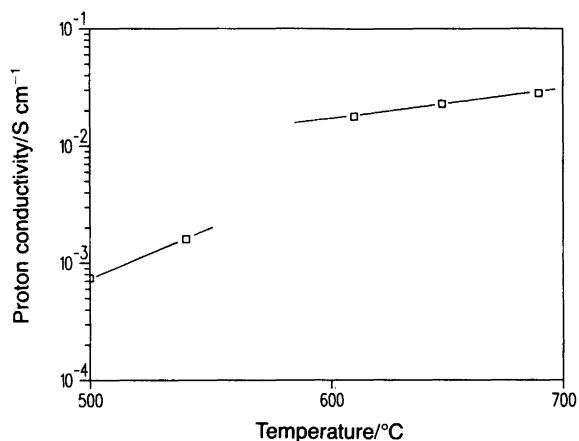

Fig. 2. Proton conductivity in pure lithium sulfate as determined by measurements on concentration cells with platinum electrodes.

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