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A Rechargeable All-Solid-State Sodium Cell with Polymer Electrolyte

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INTRODUCTION
Secondary lithium cells with intercalation or insertion materials as positive electrodes are now an extensively studied subject. However, only few papers covering the corresponding sodium systems have yet appeared. Ostensibly this is due to the lack of reversible sodium/electrolyte half-cells functioning below 200°C. At higher temperatures most electrode materials will react via displacement reactions, which generally have lower electrode potentials and do not possess the inherent reversibility of intercalation reactions.

Liquid organic electrolytes consisting of NaI dissolved in propylene carbonate have been used for electrochemical preparation of sodium intercalated TiS₂ (1,2). The Exxon group has cycled both Na/TiS₂ and Na/MoS₃ using sodium triethyl (N-pyrrol) borate dissolved in 1,3-dioxolane as electrolyte (3,4). Most other groups have chosen to use two-electrolyte systems with an ionic conducting ceramic membrane. This membrane separates molten sodium from the liquid electrolyte forming contact to the active material in the positive electrode (5).

In this communication cycling of a cell with solid sodium in contact with a polymer electrolyte and with amorphous MoS₃ as positive electrode is reported.

EXPERIMENTAL
Amorphous MoS₃ was prepared by thermal decomposition of (NH₄)₂MoS₄ as described by Jacobson et al (3).

Sodium electrodes were made by pressing a layer of sodium onto a Ni foil, using polyethylene sheets to aid the spreading. In this way smooth layers of sodium with thicknesses between 50 μm and 100 μm were obtained.

Polymer electrolyte sheets (~30 μm) were prepared by evaporation of acetonitrile solutions of poly-(ethylene oxide) (PEO) and the proper amount of NaI, recrystallized from acetonitrile and vacuumdried at 180°C. The PEO (WSR 301 Polyox, MW = 4×10⁶, BDH) was used as received. The films were prepared and handled in an argon filled dry box. The NaI concentration in the films used corresponded to a Na/O ratio of 1:10. With this electrolyte, the operating temperature of the cell is confined to the interval between 98°C (melting of sodium) and 65°C, as the electrolyte conductivity decreases rapidly below this temperature.

Composite MoS₃ electrode films (~50 μm) with the overall composition: 72 w/o MoS₃, 20 w/o PEO, and 8 w/o NaI were prepared by evaporating acetonitrile suspensions/solutions of the ingredients onto nickel foils. In some cases graphite was added as conductive diluent, but no improvement of cell performance at these very low current densities was achieved.

The cell was mounted with spring load in a Ni-plated brass container sealed with a viton O-ring. This container was heated in air to 90 °C in a Buchi TO-50 oven.

RESULTS
The first two cycles of the cell

Na / PEO-NaI (10:1) / MoS₃

are shown in fig. 1. The current density used for discharge and charge was 15 μA/cm² in these cycles, corresponding to a stoichiometric discharge time of 45 h. The cell was discharged to 1.5 V.
Fig. 1. Initial cycles of the cell Na/NaI-PEO (10:1)/MoS$_3$ at 15 $\mu$A/cm$^2$. Charge recalculated as $X = \text{Na/Mo}$ based on total Mo-analysis of cell.

and recharged to 2.6 V vs Na. It is seen that the coulombic cycling efficiency (the ratio between discharge and charge capacity) is considerably less than unity, possibly due to disproportionation of the electrolyte. An advantage of using iodide-containing electrolytes in alkali metal batteries might be that the iodine liberated during overcharge recombines with the alkali metal and thereby scavenges the negative electrode of developing dendrites.

The discharge curve is smooth as expected for an amorphous electrode material, and 1.4 Na/Mo is inserted during the first discharge. Previously discharge capacities of up to 3 Na/Mo have been achieved (4), but the capacity has been shown to be sensitive to the details of the MoS$_3$ synthesis (6). The stoichiometric capacity calculated from the first discharge is 290 Wh/kg.

The development of the discharge capacity upon cycling is shown on Fig. 2. The charge and discharge current used was 150 $\mu$A/cm$^2$ in cycle 3 to 9, and 15 $\mu$A/cm$^2$ in the other cycles. Despite the rapid decrease in cell capacity, a total number of 10 Na/Mo have been cycled during the lifetime of this cell, and the available amount of sodium has been cycled 1.5 times. This shows that, even close to its melting point, sodium forms a sufficiently stable interface with a PEO-electrolyte to allow reversible operation of this electrode. Possibly the formation of a passive sodium ion conducting film on the interface is responsible for this stability.

It is thus concluded that solid state sodium batteries might be feasible by extension of lithium battery technology, especially when electrolytes with better conductivity and more reversible electrode materials are developed.

REFERENCES


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