

SOLID-STATE SODIUM CELLS — AN ALTERNATIVE TO LITHIUM CELLS?

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Summary

The cycling properties of laboratory cells based on the insertion of sodium into vanadium oxides using polymer electrolyte at 80 °C are reported. In the best system: Na|PEO, NaClO₄|V₂O₅ (modified), C, high reversibility, and an energy density comparable with the Li/TiS₂ system have been obtained.

1. Introduction

The solid-state lithium battery with polymer electrolyte is by now a well established experimental concept, moving into the stage of technological development for commercial applications. We have become interested in extending this battery concept. One of the possibilities investigated was the use of sodium instead of lithium as negative electrode material. This takes advantage of the higher abundance and lower price of sodium and of the generally higher conductivity of sodium conductors compared with lithium conductors. The fact that sodium does not form alloys with aluminium is also important, allowing use of this lighter and cheaper metal, instead of nickel, as current collector in bipolar cells.

In a first series of experiments using amorphous molybdenum trisulphide, MoS₃, as positive electrode material [1], it was found that the sodium electrode in contact with an electrolyte based on poly(ethylene oxide) was practically reversible — a fact that is attributed to the formation of a passivating film on the sodium/polymer interface [2]. The experiments with MoS₃ also showed that positive electrode materials with higher reversibility were needed if the solid-state sodium battery was to be of any technological interest. A search for new sodium insertion materials was therefore initiated, starting with the family of vanadium oxides in which many candidates for lithium electrode materials are found [3]. The present paper reports the results of cell cycling using three of these materials. As sodium ions are larger than lithium ions, materials with relatively large cavities were initially

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chosen for investigation — a channel structure, $\beta\text{-Na}_x\text{V}_2\text{O}_5$, and two layered structures, $\text{Na}_{1+x}\text{V}_3\text{O}_8$ and $\alpha\text{-V}_2\text{O}_5$.

2. Experimental

The preparation of oxides, and the method used for making poly(ethylene oxide) sodium perchlorate electrolyte films has been reported previously [2, 4]. The concentration of salt in the electrolyte films used in this work corresponds to 12 monomer units per Na ($[\text{EO}]/[\text{Na}] = 12$). Composite electrode films containing, by weight, 64% vanadium oxide, 9% acetylene black (Shawinigan, 50% compressed), 19% PEO, and 8% NaClO_4 , were cast on aluminium or nickel foil from suspensions/solutions of the compounds in acetonitrile. The thickness of the electrode films used in this study was 60 - 70 μm .

Cells containing a sodium foil (100 - 200 μm) on metal support, a polymer electrolyte film (50 μm), and a composite electrode film were assembled inside an argon-filled glovebox and mounted, with spring loading to ensure good contact between cell components, in O-ring-sealed containers. All cells were operated at 80 °C.

The amount of oxide present in the cells was determined by weighing the composite electrode films prior to cell assembly. Due to the small mass of active material (≈ 1 mg) and to the inhomogeneity of the films, the amount could only be determined within $\pm 10\%$.

Cycling was performed with constant-current discharge to 1.0 V, followed by current-limited potentiostatic recharge to 3.5 V. The rate of discharge is given as the time it would take to charge the overall composition of the vanadium oxide with 1 Na per formula unit.

3. Results and discussion

The vanadium bronze $\beta\text{-Na}_x\text{V}_2\text{O}_5$ has a structure with wide channels where sodium ions can be accommodated at different sites. In thermodynamic equilibrium the sodium content can only be varied between 0.22 and 0.40 [5], but the corresponding lithium-compound, which has nearly the same small, thermodynamic stability interval, can reversibly accommodate as much as 1.33 Li per formula unit at room temperature [6]. In solid-state sodium cells the sodium stoichiometry can be varied between 0.25 and 1.6 in the voltage range from 3.5 to 1.0 V, giving a stoichiometric energy density of 245 W h kg^{-1} or 590 W h l^{-1} for this couple. The corresponding values for $\beta\text{-Li}_x\text{V}_2\text{O}_5$ are 590 W h kg^{-1} or 1680 W h l^{-1} . There are, however, strong indications that the original host structure breaks down during the first discharge as soon as the thermodynamic limit is exceeded, after which the material becomes amorphous. Figure 1 shows the capacity as a function of cycle number for cells using this material as positive electrode.

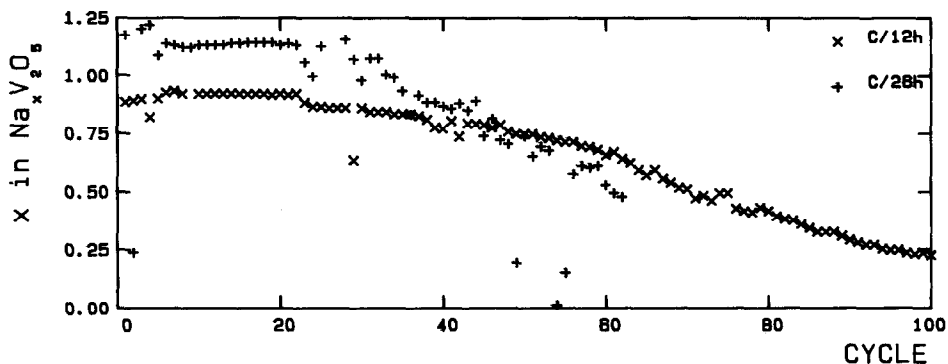


Fig. 1. Cell capacity as a function of cycle number for cells of the composition: $\text{Na}|\text{PEO}-\text{NaClO}_4([\text{EO-units}]/[\text{Na}] = 12)|\beta\text{-Na}_x\text{V}_2\text{O}_5$, C, PEO, NaClO_4 . The discharge rates are indicated on the Figure.

Despite the loss of crystallinity of the host material, these batteries can be cycled 50 - 100 times before half the initial capacity is lost. One of the cells represented in Fig. 1 shows the recovery from temporary internal short circuits ("soft dendrites"), a phenomenon also known from lithium cells.

Layered materials such as $\text{Na}_{1+x}\text{V}_3\text{O}_8$ offer another possibility of finding open structures. This structure consists of puckered layers of VO_6 octahedra stabilized by interlayer sodium ions. $\text{Na}_{1+x}\text{V}_3\text{O}_8$ can take up slightly more than 2 additional sodium ions in the potential range from 3.5 to 1.0 V *versus* sodium, giving a stoichiometric energy density of 340 W h kg^{-1} or 850 W h l^{-1} (the values for $\text{Li}_{1+x}\text{V}_3\text{O}_8$ are 650 W h kg^{-1} or 1650 W h l^{-1}). The structure of the host lattice is retained upon cycling, although a steady capacity decrease is observed — Fig. 2, lower curve. The cycling performance can, however, be improved if the amount of

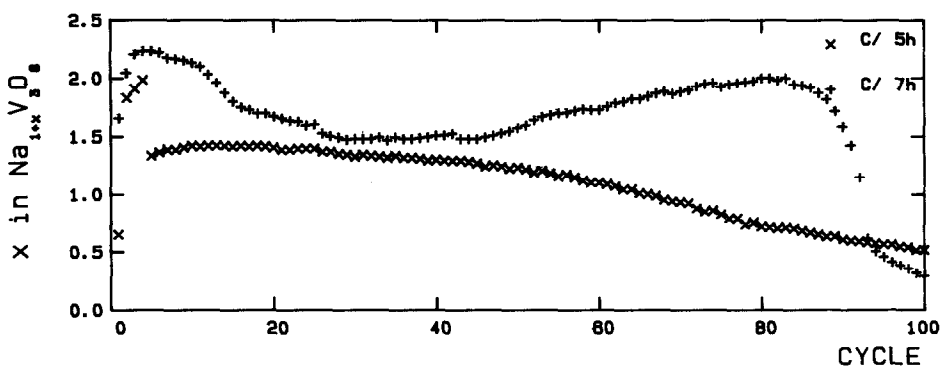


Fig. 2. Cell capacity as a function of cycle number for cells of the composition: $\text{Na}|\text{PEO}-\text{NaClO}_4([\text{EO-units}]/[\text{Na}] = 12)|\text{Na}_{1+x}\text{V}_3\text{O}_8$, C, PEO, NaClO_4 . The discharge rates are indicated on the Figure. The positive electrodes used had different compositions: x, standard composition (see text); +, 17% $\text{Na}_{1+x}\text{V}_3\text{O}_8$, 21% acetylene black (by weight).

active material in the positive electrode is reduced and the amount of conductive diluent correspondingly increased, as shown in Fig. 2, upper curve. The capacity increase observed here after ≈ 30 deep cycles can be ascribed to an improved particle-particle contact, and a decrease in the internal cell resistance induced by viscous creep of the polymeric electrode component. The sudden drop in cell capacity after 85 - 90 cycles is probably due to failure of the sodium electrode. Although the loading of active material in this cell is too low for practical purposes, the many cycles without capacity loss is evidence of the inherent reversibility of sodium insertion in this material.

$\alpha\text{-V}_2\text{O}_5$ can also be considered a layered material, with only weak inter-layer V-O bonds. The $\alpha\text{-Na}_x\text{V}_2\text{O}_5$ is only thermodynamically stable within a narrow composition interval ($0 \leq x < 0.02$), but a closely related α' -phase with decreased symmetry is stable at higher sodium concentrations ($0.7 \leq x \leq 1$) [5]. When sodium is electrochemically intercalated in $\alpha\text{-V}_2\text{O}_5$ at 80°C , the host lattice is continuously and irreversibly transformed into the α' -phase, from which sodium cannot be extracted electrochemically. Upon further sodium insertion the host undergoes a further irreversible transformation to a phase with 2 sodiums per formula unit. The new phase formed contains ≈ 0.3 Na strongly bound to the lattice, but the remaining part of the sodium content can be reversibly cycled. The stoichiometric capacity calculated from the second discharge is 430 W h kg^{-1} or 1040 W h l^{-1} , showing that this system has an energy storage capacity comparable with the celebrated Li/TiS₂ system, although below that of $\alpha\text{-Li}_x\text{V}_2\text{O}_5$ (750 W h kg^{-1} or 1840 W h l^{-1} at 120°C). Figure 3 shows the capacity as a function of cycle number for cells using this material in the positive electrode. The rate capability of these cells is very good, and only small differences are seen between the capacity curves at the 6 h and the 15 h load. The average capacity retention per cycle during the first 100 cycles is 99.1%, which is as good as most results reported for lithium-vanadium oxides.

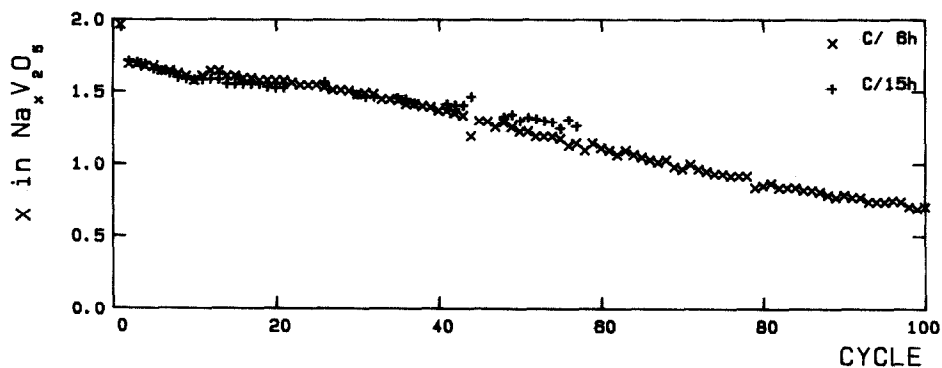


Fig. 3. Cell capacity as a function of cycle number for cells of the composition: Na|PEO-NaClO₄([EO-units]/[Na] = 12)| $\alpha\text{-Na}_x\text{V}_2\text{O}_5$, C, PEO, NaClO₄. The discharge rates are indicated on the Figure.

4. Conclusion

In terms of cycling capacity and rate capability, solid-state sodium cells with poly(ethylene oxide) based electrolyte have been demonstrated to be comparable with solid-state lithium cells. The stoichiometric energy densities are, typically, only about half of the corresponding lithium systems, but this disadvantage may be offset by the lower price and, perhaps, also by the fact that the higher electrolyte conductivity of the sodium systems may make thicker electrodes feasible. This should result in both cheaper manufacturing costs and higher packing efficiency, giving practical energy densities closer to the theoretical values. The modified α - V_2O_5 material appears to be the best choice at present, but all materials investigated deserve further development in terms of electrode formulation and preparation technique.

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