Magnesium insertion batteries — an alternative to lithium?

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Abstract

Li^+, Na^+ and Mg^{2+} insertion in five hydrated, layered vanadium bronzes, LiV_3O_8, NaV_3O_8, KV_3O_8, $Mg(V_3O_8)_2$ and $Ca(V_3O_8)_2$, was studied with regard to their use as electroactive materials in ion-transfer batteries. The behaviour of all bronzes is similar: variation in the content of bound lattice water in the bronzes is responsible for a difference in the electrochemical properties of the same material dried at different temperatures. The presence of this water is essential; the amount of H_2O in the $NaV_3O_8 \cdot (H_2O)_y$ and $Mg(V_3O_8)_2 \cdot (H_2O)_y$ bronzes has been optimized to get the best electrochemical performance. The specific charges of both optimized bronzes calculated from the first discharge are about 330 and 150 mAh/g for Li^+ and Mg^{2+} insertion, respectively.

Keywords: Magnesium; Lithium; Sodium rechargeable batteries; Insertion

1. Introduction

High energy density rechargeable electrochemical cells with a lithium negative electrode, an aprotic electrolyte and a positive electrode exploiting insertion electrochemistry are currently under development in many laboratories. The merit of this concept is that the same number of cations generated at one of the electrodes is also consumed at the opposite electrode. Thus, in contrast to customary batteries, there is no need for comparatively large solvent volumes accommodating the stoichiometric amount of the salt involved in electrochemical reactions.

The majority of the relevant literature dealing with insertion reactions in battery development focuses on the use of lithium. However, due to the natural abundance of magnesium and its relatively low equivalent weight of 12 g/F — higher than lithium (7 g/F) but lower than sodium (23 g/F) — metallic magnesium might be an alternative to lithium in a future ion-transfer battery. Other advantages include a relatively low price of about US\$ 3000/ton [1] versus US\$ 21 000/ton for lithium [2] and an expected higher safety of batteries based on metallic magnesium compared with lithium or sodium. On the other hand, the electrochemistry of metallic magnesium at ambient temperatures is still far from being well understood, and the electrochemical insertion reactions of magnesium have been seldom investigated [3–6].

The aim of our present research activities is to characterize the electrochemistry of various potentially promising metal oxides, sulfides and other insertion compounds in organic solvents and low-temperature salt melts containing Mg^{2+}. Until now, only materials based on vanadium and molybdenum oxides [7] showed promising specific charge and reversibility. We have demonstrated reversible cycling of V_2O_5 in Mg^{2+}-containing electrolytes at room temperature for the first time [8]. In acetonitrile-based electrolytes, specific charges of up to 380 mAh/g have been reached using V_6O_{13} but the specific charge declined rapidly during cycling [9]. Further experiments showed that the group of vanadium bronzes of the NaV_3O_8-type, although having lower specific charges, are more promising for the magnesium battery [10,11]. In this paper, the insertion electrochemistry of Mg^{2+} in the vanadium bronzes is compared with the insertion of Li^+ and Na^+.
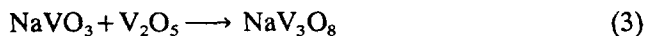
2. Experimental

2.1. Preparation of the bronzes

Five bronzes, LiV_3O_8, NaV_3O_8, KV_3O_8, $Mg(V_3O_8)_2$ and $Ca(V_3O_8)_2$ were prepared as follows. An aqueous solution of LiOH, NaOH or KOH or an aqueous suspension of MgO or CaO was stirred with a stoichiometric amount of V_2O_5 at ~50 °C overnight. The yellow colour of V_2O_5 turned gradually to red-brown

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under slow precipitation of the *hydrated* bronze. The latter was filtered, washed with H_2O, and vacuum-dried at room temperature for several days. After a mild grinding, the hydrated bronze was further dried under dynamic vacuum at 50, 100, or 200 °C overnight. The following steps have been proposed to occur [12]:

$$6NaOH + V_2O_5 \longrightarrow 2Na_3VO_4 + 3H_2O \tag{1}$$

$$Na_3VO_4 + V_2O_5 \longrightarrow 3NaVO_3 \tag{2}$$

$$NaVO_3 + V_2O_5 \longrightarrow NaV_3O_8 \tag{3}$$

In fact, the chemical formulae of our bronzes should be written as $NaV_3O_8 \cdot (H_2O)_y$, $Mg(V_3O_8)_2 \cdot (H_2O)_y$, etc., where $(H_2O)_y$ denotes an unknown, variable amount of bound water, including $y = 0$.

2.2. Characterization of the bronzes

The chemical composition of the bronzes was verified by flame atomic emission spectroscopic analysis. Differential scanning calorimetric (DSC) measurements were performed using a Perkin-Elmer DSC-7 equipment. Infrared (IR) spectra (1024 scans at 2 cm^{-1} resolution) of the bronzes were taken on a Perkin-Elmer system 2000 FT-IR spectrometer using a Graseby Specac diffuse reflectance accessory. About 4 wt.% of the bronze was thoroughly mixed with 96 wt.% of KBr immediately before the measurement. The spectra were converted to Kubelka-Munk units. X-ray diffraction (XRD) studies were performed on samples sealed in glass capillaries using a STOE automatic powder diffractometer; the data analysis was performed with the LATCON program.

2.3. Electrochemical measurements

The electrochemical properties of the bronzes were studied by very slow cyclic voltammetry and galvanostatic cycling; a standard electrochemical instrumentation was used. To give the electrodes electronic conductivity and mechanical stability, each of the bronzes to be tested was mixed with an equal part of Teflonized carbon black (25 wt.% polytetrafluoroethylene (PTFE) + 75 wt.% acetylene black, prepared according to Ref. [13]). The mixture was pressed on platinum current collector. The working electrodes had geometrical areas of 1.3 cm^2 and contained about 10 mg of electroactive material. For the sake of comparison, the currents were normalized by the mass of the electroactive material and are expressed in mA/g. Specific charges, expressed in mAh/g, were calculated from the integrated charge and the mass of the bronze in the PTFE-bonded electrode.

Hermetically sealed three-electrode cells were used in which working and counter electrodes were mechanically pressed (~ 2 kg/cm^2) together against a separator soaked with the electrolyte. The cells had an internal configuration like button cells. Metallic magnesium, sodium, or lithium served as counter electrodes. Ag/Ag^+ ($+3.57$ V versus Li/Li^+), Na/Na^+ ($+0.22$ V versus Li/Li^+), Li/Li^+, and Al/Al^{3+} ($+1.4$ V versus Li/Li^+) reference electrodes were used in electrolytes containing corresponding ions but all potentials were recalculated into the Li/Li^+ scale.

Electrochemical measurements in 'wet' (0.5–2 M H_2O), 0.5–1 M $Mg(ClO_4)_2$-containing acetonitrile (AN) solutions as well as in 'dry' (<50 ppm H_2O) propylene carbonate (PC) containing 0.5 M $Mg(ClO_4)_2$, 0.5 M $NaClO_4$ or 0.5 M $LiClO_4$, respectively, were performed at room temperature, whereas measurements in a salt melt containing 3 wt.% $MgCl_2$, 56 wt.% $AlCl_3$ and 41 wt.% 1-ethyl-3-methylimidazolium chloride (EMIC) were performed at 80 °C. The salt melt was made and purified as described in Ref. [10]. The $AlCl_3$/EMIC mixture (liquid at room temperature) was purified by electrolysis between aluminium and nickel electrodes for one week; water-free $MgCl_2$ was added afterwards. The preparation of the electrolytes, as well as the cell assembly, were performed in an argon-filled glove box in which the H_2O and O_2 levels were not allowed to exceed 5 ppm.

3. Results and discussion

Compounds with layered structures are promising candidates for insertion electrodes. According to our XRD investigations [11,14], each of the prepared vanadium bronzes is a poorly crystalline layered compound. Fig. 1, in which the first voltammetric cycles of $Mg(V_3O_8)_2$ are compared for three cations, shows that it is possible to insert Li^+, Na^+ and Mg^{2+} into
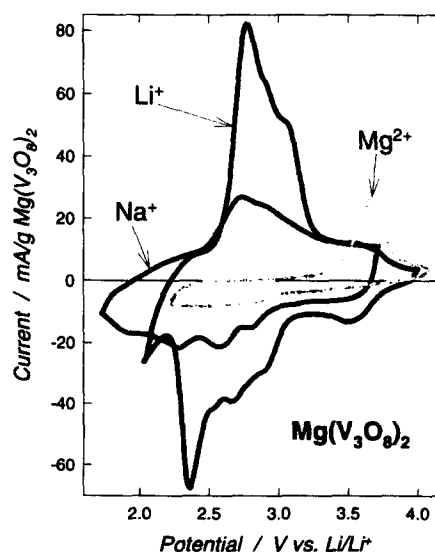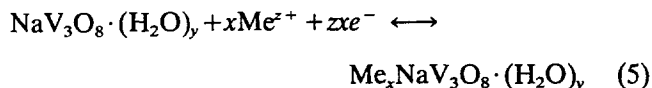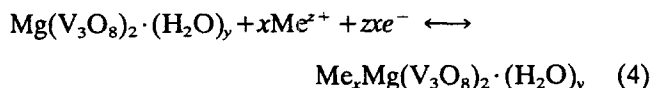

Fig. 1. Voltammograms in the 'dry' ClO_4^-/propylene carbonate electrolytes (1st cycles at 50 μV/s) of $Mg(V_3O_8)_2 \cdot (H_2O)_y$, dried at 50 °C.

this particular bronze. A comparison between the five synthesized bronzes has shown that the electrochemistry of the other bronzes is similar. During electrochemical reduction, cations (Me^{z+}) are inserted into, and during re-oxidation expulsed from the bronzes. An overall electrode reaction scheme can be written as:

$$Mg(V_3O_8)_2 \cdot (H_2O)_y + xMe^{z+} + zxe^- \longleftrightarrow$$

$$Me_xMg(V_3O_8)_2 \cdot (H_2O)_y \quad (4)$$

$$NaV_3O_8 \cdot (H_2O)_y + xMe^{z+} + zxe^- \longleftrightarrow$$

$$Me_xNaV_3O_8 \cdot (H_2O)_y \quad (5)$$

As typical examples, results achieved on NaV_3O_8 and $Mg(V_3O_8)_2$ are shown below.

It followed from the comparison of specific charges of the bronzes dried at different temperatures that the bronzes dried at 200 °C were electrochemically much less active than the bronzes dried at 50 or 100 °C [10]. Our recent detailed DSC as well as IR spectroscopic results evidence that variations of the water content in the bronzes are responsible for the observed difference in the electrochemical properties of the same material dried at different temperatures. The as-prepared bronzes, synthesized by a solution technique, contain a fairly high amount of water. Part of this water is loosely bound and easily removed at temperatures below 100 °C. This loosely bound water is undesirable in electrode materials intended for non-aqueous cells because it might contaminate the electrolyte. The rest of the H_2O molecules contained in the bronzes, identified by IR as lattice water, is lost in the temperature range from 100 to 200 °C. The presence of this lattice water is essential for good electrochemical performance of the bronzes. The amount of H_2O in the structure has been optimized to get the best electrochemical performance.

Lithium insertion in LiV_3O_8 and related bronzes has been recently investigated in several laboratories; in Ref. [15] the use of pure PC as well as of mixtures of PC and ethylene carbonate (EC) is claimed to give the best results. PC was therefore chosen also for our experiments. Fig. 2 compares the specific charges of an optimized bronze, $NaV_3O_8 \cdot (H_2O)_y$, ($y \sim 1.5$) measured in dry PC containing $LiClO_4$, $NaClO_4$ and $Mg(ClO_4)_2$, respectively. The data have been derived from cyclic voltammetry and galvanostatic cycling experiments; both methods gave matching specific charges. Results similar to those shown in Fig. 2 for the $NaV_3O_8 \cdot (H_2O)_y$ bronze have also been obtained with the best performing $Mg(V_3O_8)_2 \cdot (H_2O)_y$ bronze.

As expected, the highest specific charge of about 330 mAh/g is reached for the insertion of Li^+ ions. This charge corresponds to about $1.4e^-$ and $1.3e^-$ per one vanadium atom in the sodium and magnesium bronze, respectively. The specific charge slightly decreases dur-
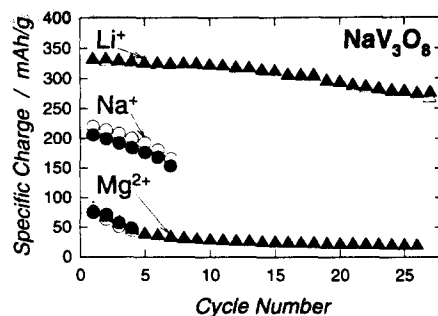

Fig. 2. Specific charge in the 'dry' ClO_4^-/propylene carbonate electrolytes of $NaV_3O_8 \cdot (H_2O)_y$ dried at 50 °C. Filled symbols: discharge, and open symbols: charge, (O) from voltammetric cycling as in Fig. 1; (△) from galvanostatic cycling ($Li^+ = 50$ mA/g, 1.0–4.0 V; $Mg^{2+} = 10$ mA/g, 2.1–4.1 V versus Li/Li^+).

ing cycling — after 25 deep cycles it is about 280 mAh/g. The coulombic efficiency of the Li^+ insertion is nearly 100%.

The electrochemical insertion of Na^+ in the bronzes proceeds in the same potential range as the insertion of Li^+. The similarities in the fine structure of the voltammograms (Fig. 1) suggest that the insertion sites in the bronze are similar for both cations. However, the kinetics of the Na^+ insertion is obviously slower. The initial specific charge for the Na^+ insertion is about 200 mAh/g, and the available charge decreases more rapidly with the cycle number (Fig. 2). A similar gradual degradation during sodium insertion/extraction cycles in NaV_3O_8 (synthesized at high temperatures) has been observed by West et al. [16] in sodium cells with solid polymer electrolytes.

The lowest specific charge in 'dry' PC, about 80 mAh/g, was reached for the Mg^{2+} insertion. But, due to strong solvation effects [8], the specific charge of Mg^{2+} insertion significantly increases with the increasing number of H_2O molecules in the electrolyte, and it is also solvent dependent. For example, in 1 M $Mg(ClO_4)_2 +$ 2 M H_2O in AN, a specific charge of 210 mAh/g was measured. However, to avoid the reaction of metallic magnesium with water, fairly dry electrolytes are preferred in a secondary magnesium battery.

A rigorously dry environment can be reached in room temperature molten salts based on $AlCl_3$. Our experiments demonstrated that it is possible to insert Mg^{2+} from the salt melt in all bronzes. Fig. 3 shows an example of reversible Mg^{2+} insertion in $Mg(V_3O_8)_2 \cdot (H_2O)_y$. The specific charge can reach up to about 150 mAh/g during the first discharge which corresponds to about $0.6e^-$ per one vanadium atom, but it decreases during cycling; after 60 deep cycles, it stabilizes between 60 and 85 mAh/g depending on the particular experiment. IR spectroscopic investigations have shown that the lattice water bonded between the layers of the bronzes is removed during the cycling in Mg^{2+} containing electrolytes (Fig. 4). Attempts to replace the
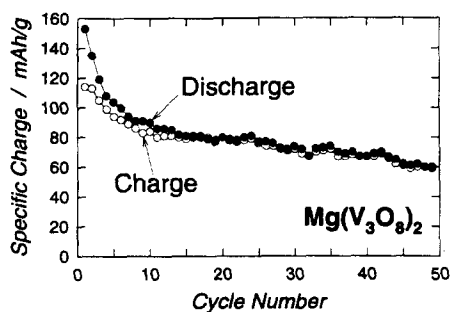
Fig. 3. Specific charge in the $MgCl_2/AlCl_3/1$-ethyl-3-methylimida-zolium chloride salt melt of $Mg(V_3O_8)_2 \cdot (H_2O)_y$ dried at 100 °C (from voltammetric cycling at 50 $\mu V/s$ from 1.9 to 3.1 V vs. Li/Li^+).
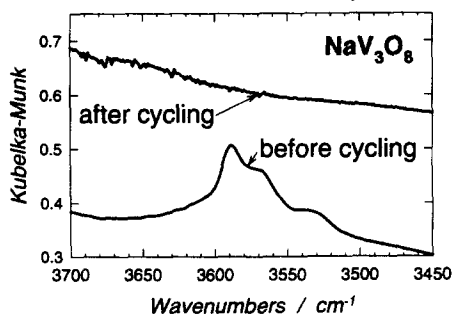

Fig. 4. Infrared spectra of $NaV_3O_8 \cdot (H_2O)_y$ dried at 100 °C showing the loss of lattice water during cycling in the 'wet' 1 M $Mg(ClO_4)_2 +$ 1 M H_2O/acetonitrile electrolyte.

bonded lattice water by molecules compatible with the non-aqueous electrolytes such as dimethylsulfoxide (DMSO) are in progress; specific charges of up to 210 mAh/g have already been reached in the salt melt for a $Mg(V_3O_8)_2$ bronze synthesized in DMSO instead of water.

4. Conclusions

As a first step to a novel rechargeable magnesium battery we have demonstrated reversible cycling of vanadium bronzes in dry, Mg^{2+}-containing electrolytes.

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