New $(A,Li)_xV_3O_8$ cathode materials (A=divalent cation) : synthesis, characterization and Li insertion properties

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The lithium trivanadate $Li_{1+\alpha}V_3O_8$ (α= 0.1-0.2) [1].is a promising electrode material for rechargeable lithium batteries. Modification of the inter-layer spacing has been realized in order to improve the battery performance. It has been achieved by insertion of small molecules, such as H_2O [2, 3], CO_2 [2] and NH_3 [2], or by exchanging Li^+ ions with other monovalent cations with larger sizes such as Na^+ [4, 5] and K^+ [6]. The improvement was proposed to come from both the expansion of the inter-layer distance, which causes an increase in Li^+ ion mobility, and an increase in specific surface area.

This is the first report of Li^+ ion exchange by a divalent cation in the inter-layer space of the $Li_{1.1}V_3O_8$ structure. The idea was that such cations should be less mobile than monovalent ones and that they should act as pillars which better pin the layers together, thus maybe preventing the two-phase transformation which penalizes the cyclability of the materials.

1) The compounds $Li_{1.1-2y}A_yH_zV_3O_8$ ($A^{2+}=Mg^{2+}$, Ca^{2+} or Ba^{2+}; y=0.05-0.27 ; z=0.04-0.14)

The new partially substituted materials with the formulation $Li_{1.1-2y}A_yH_zV_3O_8$ have been prepared by Li^+ to A^{2+} ion exchange in ethanol, from two different $Li_{1.1}V_3O_8$ of different morphologies, synthesized by heating a freeze-dried gel [7] at 350 (called SG350) or 650°C (called SG650). They are called “350 (or 650)-Ay”).

The ion-exchange reaction is accompanied by a very slight reduction with proton insertion. It also leads to a fragmentation of the grains (the surface area is larger) while keeping the morphology of the $Li_{1.1}V_3O_8$ precursor. The initial structure is maintained, but a slight contraction of the inter-layer spacing occurs, independent of the size of the divalent cation, due to an electrostatic effect.

The Li insertion behavior of the substituted materials shows two main kinds of behavior, depending on the precursor used for the synthesis. The 350°C derivatives exhibit both enhanced cycling capacity and decreased relative capacity loss on cycling. The diminution of relative capacity loss on cycling (see figure 1A) is believed to come from a structural stabilization by the divalent cation pillars, which better pin the layers together. The 650°C derivatives keep the excellent cyclability of the precursor (see figure 1B), as a consequence of the preservation of the initial morphology [8] and exhibit an enhanced cycling capacity due to the increase in surface area.

2) The compounds $A_{0.5}V_3O_8$ ($A^{2+}=Mg^{2+}$, Ca^{2+} or Ba^{2+})

A new Ca vanadate has been synthesized in aqueous solution by complete substitution of Li by Ca. The obtained compound is structurally related to the mineral hewettite $CaV_6O_{16}.9H_2O$ [9]. The completely dehydrated compound has been characterized. It has a different morphology, a formulation $Ca_{0.5}V_3O_8$ and a structure made of the same layers "V_3O_8" as in $Li_{1.1}V_3O_8$ but with different packing.

The electrochemical behavior vs. lithium insertion is very different from that of $Li_{1.1}V_3O_8$. It reveals in particular good performance in terms of stability during cycling at high rate (figure 2). The cycling performance of the Ba substituted compound obtained using the same synthesis principle is presented also and compared to that of $Ca_{0.5}V_3O_8$ in figure 2.

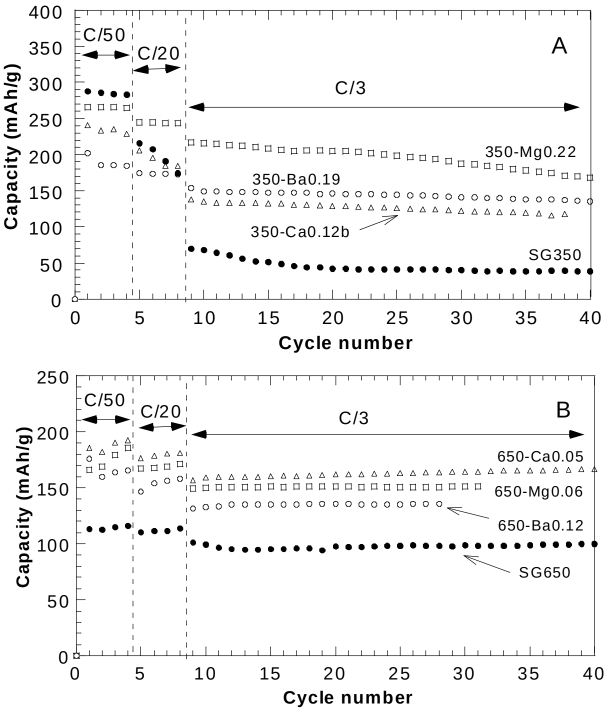

Fig.1 : Cycling behavior of several partially exchanged compounds from SG350 (A) and from SG650 (B).

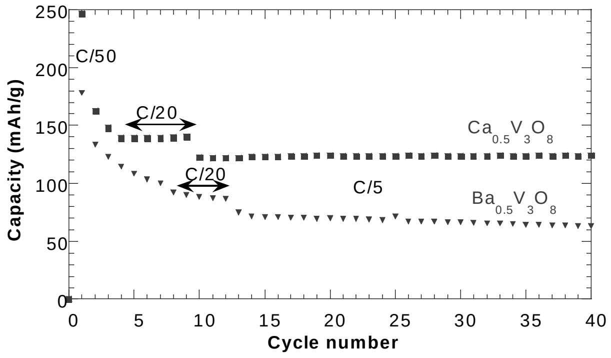

Fig.2 : Cycling behavior of two completely substituted compounds.

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