

ELECTROCHEMICAL LITHIUM INSERTION IN THE SOL-GEL MIXED OXIDE $\text{Cr}_{0.11}\text{V}_2\text{O}_{5.16}$

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Vanadium pentoxide V_2O_5 is still the objective of many works, owing to its layered structure which allows the insertion of a large amount of lithium. Many efforts have been made to change and/or improve the electrochemical properties of this cathodic material for secondary lithium batteries. For instance, amorphous compounds, mixed oxides [1], and bronzes [2] have been proposed. A few years ago, we developed the sol-gel synthesis of new mixed oxides with the following chemical composition $\text{M}_{0.16}\text{V}_2\text{O}_{5.16}$ and $\text{M}_{0.11}\text{V}_2\text{O}_{5.16}$ where M is a divalent and a trivalent metallic cation respectively [3]. Among these materials, we briefly outlined the attractive performance exhibited by $\text{Cr}_{0.11}\text{V}_2\text{O}_{5.16}$ in comparison with the parent oxide [4].

In the present work, we report a detailed investigation of its electrochemical and structural features as Li insertion-extraction proceeds in the wide composition range $0 < x < 2$ in $\text{Li}_x\text{Cr}_{0.11}\text{V}_2\text{O}_{5.16}$. This oxide exhibits an orthorhombic symmetry with cell parameters very close to that of the sol-gel parent oxide. A Rietveld refinement of XRD and neutron diffraction data allows to localize Cr^{3+} ions in an octahedral oxygen environment within V_2O_5 layers and additional O^{2-} ions between these layers (Figure 1). The shape of voltammetric curves and discharge profile has been explained by limited structural changes due to the presence of short O-Cr-O-Cr-O chains in the c direction. The additional oxidation step at 3.65V for V_2O_5 and corresponding to Li extraction from the γ phase does not appear for the mixed oxide (Figure 2). We demonstrate that only the α and ϵ phases, mainly the ϵ phase are involved in the redox process for $0 < x \leq 2$ while the α , ϵ , δ , γ phases successively appear in $\text{Li}_x\text{V}_2\text{O}_5$. As Li insertion takes place in the mixed oxide, the interlayer parameter c increases from 4.38 to 4.76 Å for $x = 2$ while the a parameter slightly contracts from 11.48 to 11.35 Å without the emergence of the important puckering of the γ phase.

A kinetic study of Li transport in the oxide is performed using ac impedance spectroscopy and other transient methods. Li diffusion is at least one order of magnitude slower in the composition range $1 < x < 2$ than for $x < 1$. Moreover, ac impedance data indicate a significant change in the length of the diffusion pathway for high Li contents $x > 1$. This result is discussed in relation with the fatigue of the cathode during galvanostatic cycling. As a main consequence of the strengthening of the structure, from an initial capacity of 280 Ah/kg, 260 Ah/kg are still recovered after 20 cycles at C/10 rate.

References

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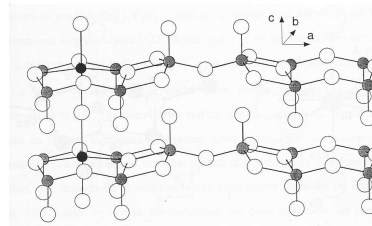


Figure 1 : Perspective view of the $\text{Cr}_{0.11}\text{V}_2\text{O}_{5.16}$ structure ; grey circles : V^{5+} ions ; white circles O^{2-} ions ; black circles Cr^{3+} ions

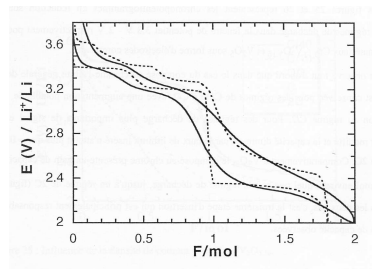


Figure 2 : Discharge-charge profiles for V_2O_5 (-----) and $\text{Cr}_{0.11}\text{V}_2\text{O}_{5.16}$ (—); (C/10)

