

The electrochemical behavior of sodium vanadium oxides in sodium batteries

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Layered oxides with Na_xMO_2 formula (M: transition metal), were studied in the 80's for their intercalation properties, then for 20 years all the researches were focused on lithium batteries, that exhibit the high energy density required for portable devices. In the perspective of the development at very large scale of renewable energy systems that require stationary batteries, the prevailing parameters are the lifetime, the price and the material availability. From these points of view, sodium based batteries have to be investigated. In our lab we recently undertook a general investigation of the layered Na_xMO_2 system. This presentation is focused on the Na_xVO_2 system that exhibits a very rich and complicated behavior (1,2).

By classical high temperature chemistry only two phases can be synthesized: O3- NaVO_2 and P2- $\text{Na}_{0.72}\text{VO}_2$. These two materials were used as positive electrode materials in sodium batteries to characterize their electrochemical behavior. Due to the oxygen packing difference each of them is at the origin of a whole material family.

The electrochemical cycling curves obtain in both cases are given in Fig. 1 and 2.

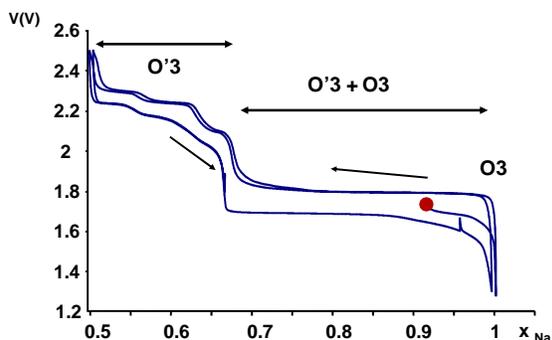


Fig. 1 Cycling curve from O3- NaVO_2 .

In both systems, the deintercalation is fully reversible in the $0.5 < x < 1$ domain; while the reversibility is lost if a too large amount of sodium is deintercalated ($x < 0.5$). Nevertheless, the shape of the cycling curves is completely different with many voltage plateaus characteristics of phase transitions. In situ XRD experiments were done to confirm the phase diagrams. Depending on the sodium amount, superstructures or modulated structures are observed. Several compositions were characterized by synchrotron experiments. They have allowed

determining the sodium vacancy ordering. In the case of the $\text{Na}_{1/2}\text{VO}_2$ composition formation of V-V pairs of V trimers are observed are observed for the O'3 and P2 phases respectively.

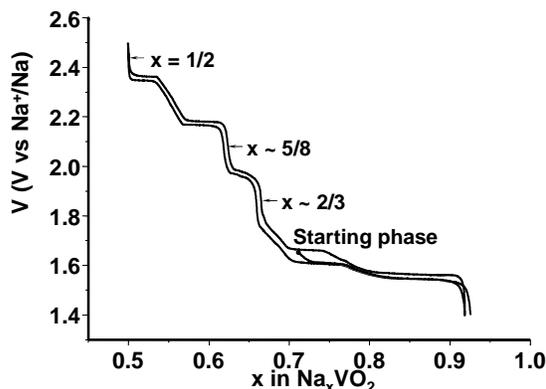


Fig. 2 Cycling curve from P2- $\text{Na}_{0.72}\text{VO}_2$.

In a previous study we shown that a thermal treatment at 200°C of the O'3- $\text{Na}_{0.60}\text{VO}_2$ phase led irreversibly to the P'3- $\text{Na}_{0.60}\text{VO}_2$ one (3). Our study was then extended to the study of the electrochemical of these materials.

As shown in Fig. 3 the cycling curve of the P'3 type phase is very similar to the O'3 one in the $0.5 < x < 0.66$ composition range. If more sodium is intercalated there is formation of O3- NaVO_2 and the electrochemical behavior return back the classical one reported in Fig. 1.

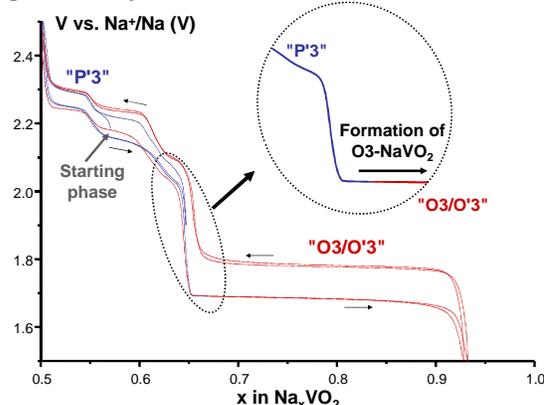


Fig. 3 Cycling curve from P'3- $\text{Na}_{0.56}\text{VO}_2$.

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References

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