

Insertion of Li⁺, Na⁺ and Mg²⁺-ion into VO₂(B) from aqueous nitrate solutions

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The metastable VO₂(B) is known for its ability to reversibly intercalate different ions. The nanostructured VO₂(B) was suggested as cathode material for Na⁺-ion and Mg²⁺-ion batteries with organic electrolytes^{1,2}. The composite VO₂(B)-reduced graphene oxide was tested in organic electrolytes as a cathode for Li⁺-ion and Na⁺-ion batteries³. In our previous research VO₂(B) was tested as an anode in aqueous Li⁺-ion battery VO₂(B)/LiNO₃(sat.)/LiCr_{0.15}Mn_{1.85}O₄.⁴ The electrochemical performance of VO₂(B) for battery applications may be highly dependent on morphology and preferential growth of crystals. Herein, the insertion of Li⁺, Na⁺ and Mg²⁺ into solvothermally prepared VO₂(B) from aqueous nitrate solutions is presented in comparative electrochemical study, using cycling voltammetry (CV) and galvanostatic (GS) cycling.

CV conducted at 10-50 mV·s⁻¹ showed fast and stable insertion/deinsertion of Li⁺, Na⁺ and Mg²⁺-ions into/from VO₂(B).⁵ The insertion of each of three ions from nitrate solutions (LiNO₃, NaNO₃ and Mg(NO₃)₂), at scan rate 10 mV·s⁻¹, appeared as a strong cathodic peak at negative potentials (-0.677 V - Li⁺, -1.040 V - Na⁺ and -0.795 V - Mg²⁺) vs. SCE. The deinsertion of Li⁺-ions occurred also in the form of single peak, at -0.502 V, while the extraction of both Na⁺-ions and Mg²⁺-ions appeared as a multi-step, most likely as a two-step process, Figure 1. In the case of Na⁺-ion the first anodic peak, of relatively low intensity, appears at -0.860 V while the remaining two, much stronger and overlapped peaks, are significantly shifted in the positive direction at 0.0 V and +0.240 V vs. SCE. The extraction of Mg²⁺-ions is accompanied by a strong peak at -0.583 V and lower intensity overlapped peaks at 0.030 and 0.160 V. The interrelationship of all redox peaks, obtained for NaNO₃ and Mg(NO₃)₂ aqueous solutions, was further investigated by shifting upper scan limit to lower potentials which exclude anodic peaks at positive potentials and then by returning this scan limit to starting value. In this way it was found that main deinsertion peaks of Na⁺-ion are strong overlapped peaks at positive potentials, while all deinsertion peaks of Mg²⁺-ion should be taken as important. Galvanostatic (GS) experiments with VO₂(B) electrode in aqueous nitrate solutions were performed at current rates 200, 500, 1000 mA·g⁻¹, also in three electrode cell (Pt – counter and SCE reference electrode). The most stable discharge/charge process, with smallest capacity fade, was obtained for all three ions at highest current rate 1000 mA·g⁻¹. At the end of GS cycling at current rate 1000 mA·g⁻¹ the insertion/extraction capacities of VO₂(B) were 99.1/96.2 mAh·g⁻¹ for Li⁺, 92.3/77.8 mAh·g⁻¹ for Na⁺ and 136.0/118.8 mAh·g⁻¹ for Mg²⁺. The best GS performance of VO₂(B), with the highest Coulombic efficiency (97 % at 1000 mA·g⁻¹), was obtained for Li⁺-ion. Voltage profiles in charge indicate a two-step extraction of Mg²⁺ ions, while the extraction of Na⁺ ions manifest itself more as a one-step than a two-step process.

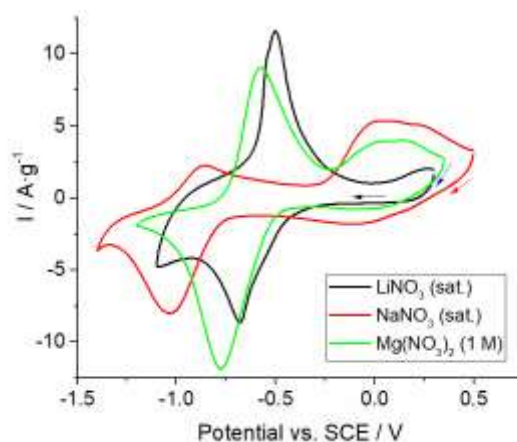


Figure 1. Cyclic voltammograms of VO₂(B) at 10 mV·s⁻¹ in different nitrate solutions

Acknowledgement: The Ministry of Science, Technological Development and Innovation of Republic of Serbia financially supported this project (contract number: 451-03-65/2024-03/200146).

References

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