Puckered V₂O₅ polymorph as cathode material for Rechargeable Aqueous Hybrid-ion Batteries

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The ideal battery could be one combining the stability and energy density of LIBs with the advantages of zinc aqueous batteries, which could remarkably reduce the cost of the energy storage. Therefore, the development of high energy density and ecologically friendly aqueous hybrid-ion battery technology is crucial. More recently, Rechargeable Aqueous hybrid ion batteries (RAHBs) design attracted great interest due to the high operating voltage, low cost and high-power density compared to traditional Li and Zn aqueous batteries [1], [2]. The main difference from typical "rocking-chair" type, RAHBs operate based on two electrochemical redox processes separately on anode and cathode.

In previous works, hybrid system Zn/a-V2O5 in 4M ZnSO₄ + 3M Li₂SO₄ (pH=4) was reported with investigation of structural mechanisms upon discharge/charge process. At 1C, a capacity of 80 mAh $\mathrm{g}^{\text{-1}}$ is outstandingly stable over more than 300 cycles with a capacity retention of 100 %. Strong similarities with the well-known structural changes reported in nonaqueous lithiated electrolytes are highlighted, although the emergence of the usual distorted δ -LiV₂O₅ phase is not detected upon discharge to 0.8 V. The pristine host structure is restored and maintained along cycling with mitigated structural changes leading to the high capacity retention. The present electrochemical and structural findings reveal a reaction mechanism mainly based on Li+ intercalation, however co-intercalation of a few Zn²⁺ ions cannot be completely dismissed. The presence of zinc cations between the oxide layers may act as pillars to stabilize the structure upon the cycling [3].

Besides stable α -V₂O₅ phase another metastable γ' -V₂O₅ polymorph exists [4], [5]. The puckered layers of γ' -V₂O₅ allow reversible Li insertion in higher voltage window (3.6/3.5 V vs. Li+/Li) than α -V₂O₅ (3.4/3.2 V vs. Li+/Li). The layered structure of γ' -V₂O₅ consists of infinite ribbons made of VO₅ edge-sharing distorted pyramids leading larger interlayer spacing enables to accommodate large amount of guest cations (5.02 Å in γ' -V₂O₅ against 4.37 Å). Therefore, it attracts the current attention as cathode material for Li, Na-ion batteries in organic electrolyte.

However, in spite of attractive structural features, γ' -V₂O₅ phase has been never studied in aqueous batteries with hybrid electrolyte. In this work, for the first time the electrochemical and structural investigations will be provided in Zn /2.5M Li₂SO₄ + 3.4M ZnSO₄/ γ' -V₂O₅ system (Figure 1).

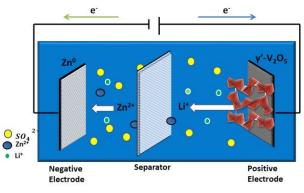


Figure 1. Schematic mechanism of Zn/2.5 M Li_2SO_4 + 3.4 M $ZnSO_4/\gamma^{*}\text{-}V_2O_5$ system

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References

[1] Liu, J., Xu, C., Chen, Z., Ni, S. & Shen, Z. X. Progress in aqueous rechargeable batteries. Green Energy Environ. 3, 20–41 (2018).

[2] Zeng, X., Hao, J., Wang, Z., Mao, J. & Guo, Z. Recent progress and perspectives on aqueous Zn-based rechargeable batteries with mild aqueous electrolytes. Energy Storage Mater. 20, 410– 437 (2019).

[3] Batyrbekuly, D. et al. Mechanistic Investigation of a Hybrid Zn/V 2 O 5 Rechargeable Battery with a Binary Li + /Zn 2+ Aqueous Electrolyte. ChemSusChem 13, 724–731 (2020).

[4] Baddour-Hadjean, R., Smirnov, M. B., Kazimirov, V. Y., Smirnov, K. S. & Pereira-Ramos, J. P. The Raman spectrum of the γ -V2O5 polymorph: A combined experimental and DFT study. J. Raman Spectrosc. 46, 406–412 (2015).

[5] Emery, N. et al. γ -Na 0.96 V 2 O 5 : A New Competitive Cathode Material for Sodium-Ion Batteries Synthesized by a Soft Chemistry Route. Chem. Mater. 30, 5305–5314 (2018).



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