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Introduction

Aqueous Na-ion batteries (ASIB) are deemed to be promising candidates for future sustainable stationary energy storage systems. However, there is still a number of issues to be solved before their full potential can be utilized. In addition to finding suitable electrode materials there are also issues related to the stability of the aqueous electrolyte/electrode interface. We present some of the recent advances in understanding and enabling NASICON phosphate framework materials [1] for the use in ASIBs.

Na_{1+2x}Mn_xTi_{2-x}(PO₄)₃ potential cathode system

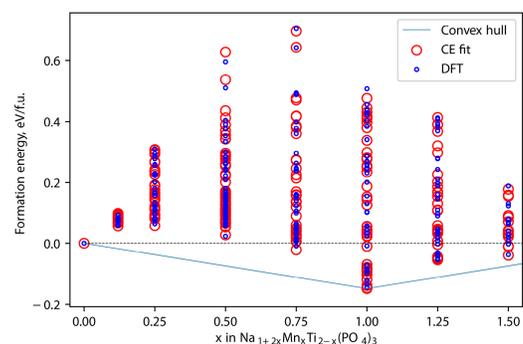


Fig. 1 PBE+U, hybrid B1WC and cluster expansion calculated convex hull for Na_{1+2x}Mn_xTi_{2-x}(PO₄)₃ system.

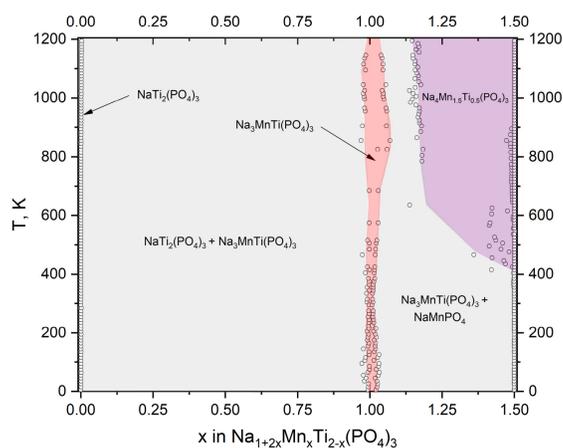


Fig. 2 Semi-grand canonical Monte-Carlo simulated finite temperature phase diagram for Na_{1+2x}Mn_xTi_{2-x}(PO₄)₃ system.

- Computational, XRD and Raman experiments show that Na_{1+2x}Mn_xTi_{2-x}(PO₄)₃ system phase separates into Na₃MnTi(PO₄)₃ and NaTi₂(PO₄)₃ (for x < 1.0) and NaMnPO₄ (x > 1.0) [2].
- α - Na₃MnTi(PO₄)₃ is a Na-ordered low symmetry (C2 (No. 5)) phase [2].
- Na/V_{Na} ordering in is the driving force for phase separation [2].
- Mn-O anti-bonding character is another driving force for Mn-rich lattice instability [2].
- Mn(II) phosphates very unstable in aqueous electrolytes.

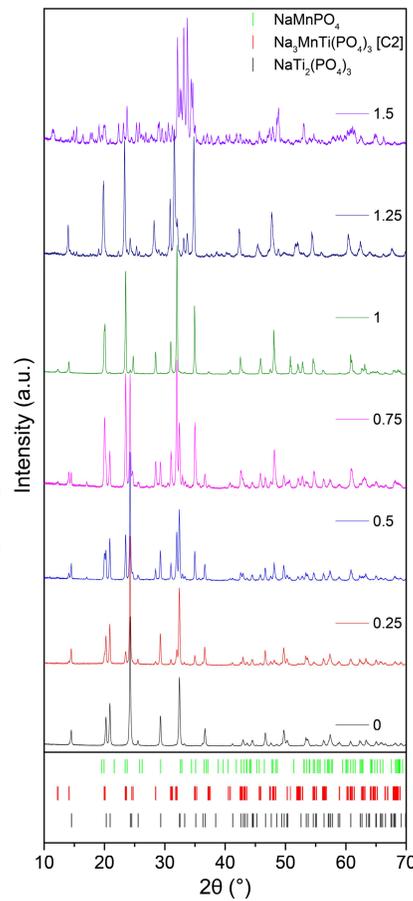


Fig. 3 Experimental XRD confirmation of phase separation in Na_{1+2x}Mn_xTi_{2-x}(PO₄)₃ system.

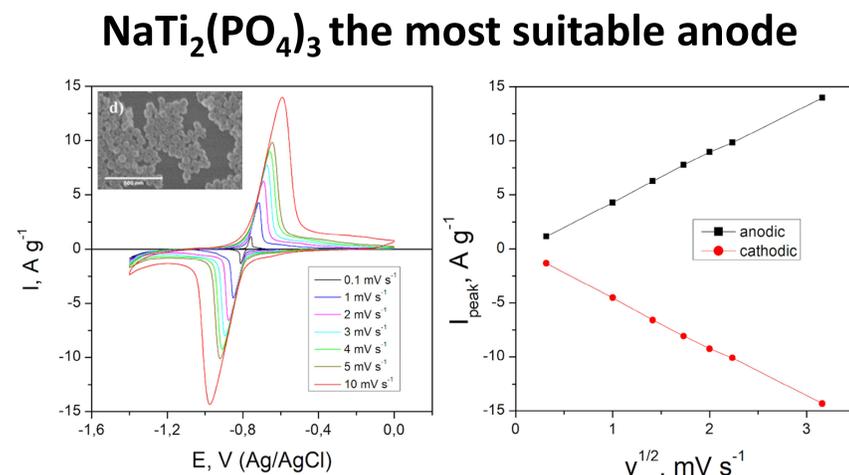


Fig. 4 Cyclic voltammograms of solvothermally prepared NaTi₂(PO₄)₃ nanoparticles in 1M Na₂SO₄ (aq.).

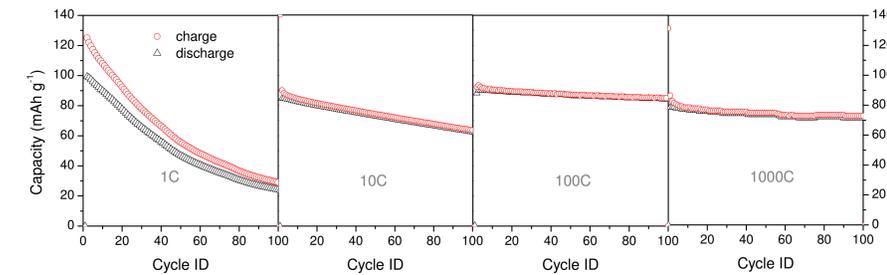


Fig. 5 Galvanostatic charge/discharge cycling of solvothermally prepared NaTi₂(PO₄)₃ nanoparticles at different C-rates in 1M Na₂SO₄ (aq.).

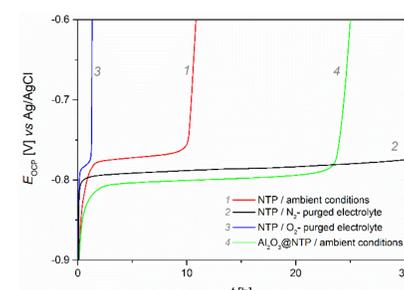


Fig. 6 Self-discharge study of NaTi₂(PO₄)₃

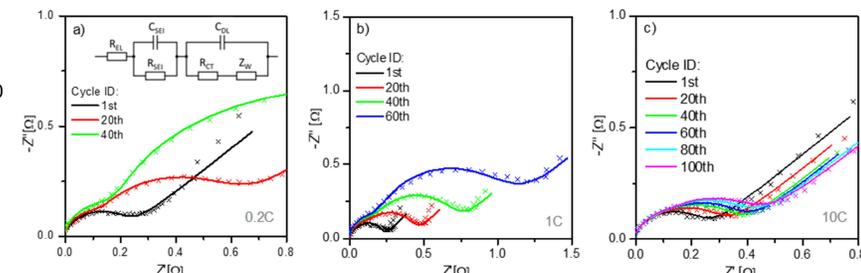


Fig. 7 Capacity retention of ALD coated electrodes

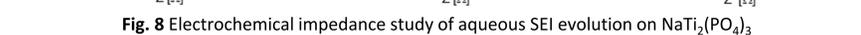


Fig. 8 Electrochemical impedance study of aqueous SEI evolution on NaTi₂(PO₄)₃

- ORR is the origin of the self-discharge and local pH increase leading to material dissolution, SEI formation and capacity fade [3,4].
- ALD electrode coatings one of the ways to mitigate degradation [3].

Na_{3-x}V_{2-x}Ti_x(PO₄)₃ suitable cathode

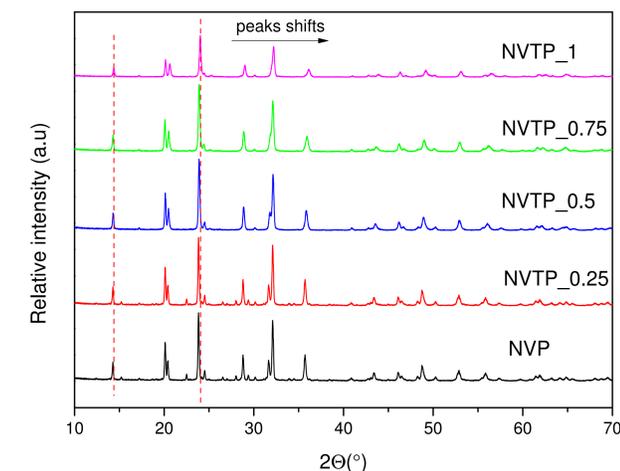


Fig. 9 XRD shows the formation of solid-solution in Na_{3-x}V_{2-x}Ti_x(PO₄)₃ over entire x range (0.0 to 2.0).

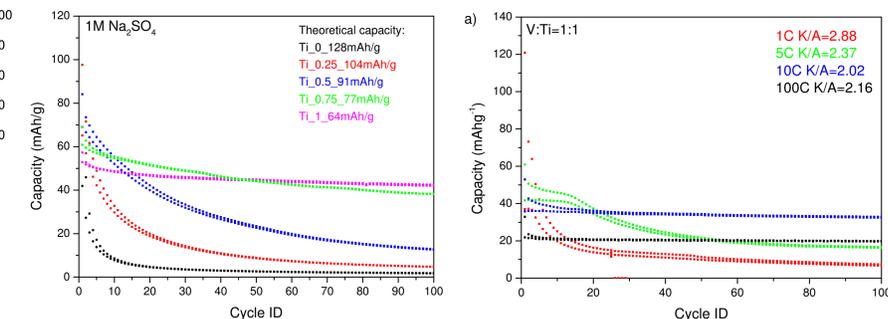


Fig. 10 Aqueous stability is directly proportional to Ti content (half-cells).

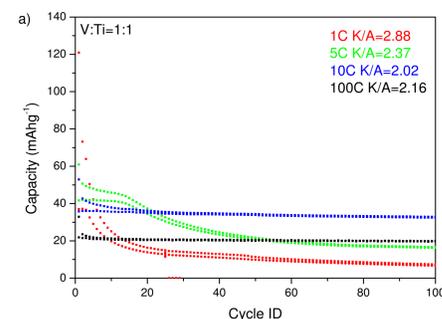


Fig. 11 Capacity fade vs. C-rate in full-cells.

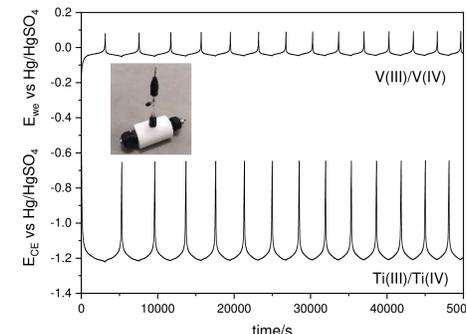


Fig. 11 Symmetric full cell cycling to discover parasitic reactions and study capacity balancing.

References:

- [1] J. B. Goodenough *et al.* Mater. Res. Bull. **11**, 203-220 (1976).
- [2] G. Snarskis *et al.* Chem. Mater. (under review).
- [3] G. Plečkaitytė *et al.*, J. Mater. Chem. A, **9**, 12670-12683 (2021).
- [4] S. Tutlienė *et al.*, J. Electrochem Soc. **168**, 060545 (2021).

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