

Rotating ring-disc electrode study of Manganese and Vanadium based material operation and degradation as aqueous Na-ion battery cathodes

Davit Tediashvili,^{1,2} Linas Vilčiauskas²

¹ Institute of Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Lithuania

² Center for Physical Sciences and Technology, Sauletekio al. 3, LT-10257 Vilnius, Lithuania

Davit.Tediashvili@fmc.lt

Rechargeable Li-ion batteries, offering high power and energy densities, are widely used as energy storage devices, especially for mobile applications. However, for large-scale stationary storage where the energy and power densities are of less concern, aqueous Na-ion batteries are deemed as a potential alternative. They offer attractive properties, such as safety (aqueous vs organic electrolytes) and price (Na vs Li as a charge carrier). [1] However, stable, high voltage electrode materials remain a bottleneck to fully utilizing and deploying this technology.

With a general formula of $\text{Na}_3\text{M}_2(\text{PO}_4)_3$, NASICON-structured materials are exceptional due to their unique framework structure providing fast Na-ion transport. They also offer high theoretical capacity and operating voltage, however, might suffer from poor cycling performance especially in aqueous electrolytes. [2] $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$ (NMTP) reported by Goodenough et al. [3] and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) offer high operating voltage, capacity, and stability in organic and water-in-salt electrolytes respectively. However, capacity fade is rapid in standard aqueous electrolytes.

Here we present a rotating ring-disc electrode (RRDE) study of NMTP & NVPF operation and degradation in an aqueous electrolyte solution. A similar study was performed on LiMn_2O_4 spinel electrodes in organic media, showing that degradation occurs either in fully charged or fully discharged states. [4] Our results indicate that in an aqueous media only one (Mn(III)/Mn(II)) redox pair is active, effectively halving the capacity and that dissolution occurs during a discharge only (~ 0.7 V vs Ag/AgCl). While for NVPF, degradation starts at the oxidation of V³⁺ and reaches peak during the full charge of the material

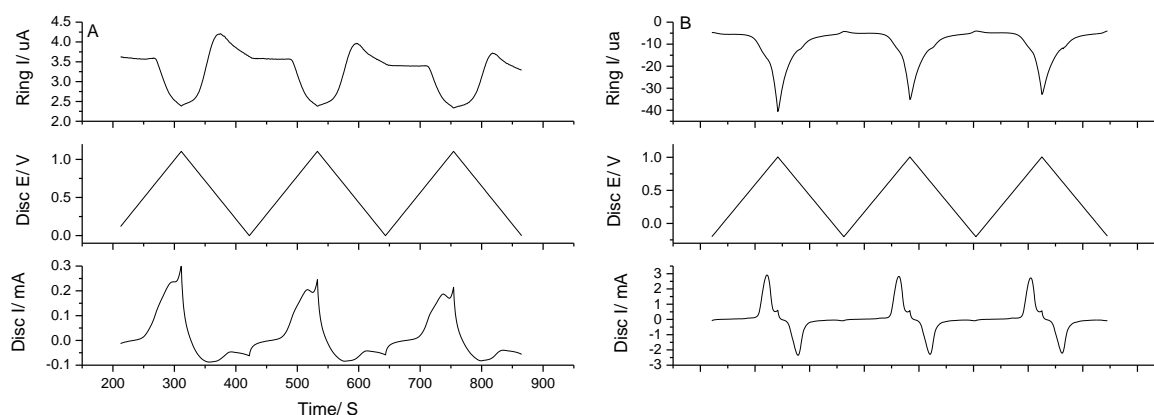


Figure 1. Applied potential on the disc and resulted current on the disc and ring for NMTP (A) and NVPF (B) during RRDE experiment

Acknowledgments:

This project has received funding from the European Regional Development Fund (Project No. 01.2.2-LMT-K-718-02-0005) under a grant agreement with the Research Council of Lithuania (LMTLT)

- [1] L. Suo et al., "Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries, *Science* **350**, 938-943 (2015).
- [2] D. Bin et al., Progress in Aqueous Rechargeable Sodium-Ion Batteries, *Advanced Energy Materials* **8** (17), 1-31 (2018).
- [3] H. Gao et al., Sodium extraction from NASICON-structured $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$ through Mn(III)/Mn(II) and Mn(IV)/Mn(III) redox couples. *Chemistry of Materials* **28** (18), 6553-6559 (2016)
- [3] L Wang et al., Study of Mn Dissolution from LiMn_2O_4 Spinel Electrodes Using Rotating Ring-Disk Collection Experiments, *Journal of Electrochemical Society*, **150** (7), 905-911 (2003).