

ROTATING RING-DISC ELECTRODE STUDY MANGANESE AND VANADIUM BASED MATERIAL OPERATION AND DEGRADATION AS AQUEOUS NA-ION BATTERY CATHODES



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Introduction

The demand on energy has been irreversibly increasing over time and the main energy sources up to date are fossil-based. In 2020, only 21% of electrical and 10% of overall energy was produced from renewable sources. The main advantage of these sources a price, however, due to significant contribution to greenhouse gasses, it faces strong social and political pressure. This coupled with the decreased price on solar and wind power technologies are making renewable energy more attractive, however, the absence of energy storage devices remains a bottleneck for fully utilizing produced energy.

Rechargeable Lithium-ion batteries are among the most common commercial energy storage devices, but when it comes to large-scale storage, their advantages, such as high power and energy density, are less important than price and safety of operation. Both of these problems can be resolved by using cheap sodium as a charge carrier and non-toxic aqueous electrolytes. Traditionally, such set-up was limited by a narrow potential window, but recently developed water-in-salt electrolytes are making aqueous batteries a viable option.

Another factor limiting the usage of aqueous Na-ion batteries is an absence of stable, high voltage cathode materials. Among viable alternatives, NASICON-structured $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$ (NMTP) reported by Goodenough et al. as well as $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) show high operating voltage, capacity and stability in organic media. However, material degradation in aqueous electrolytes remains a major issue. Here the operating process & degradation was studied in 1M Na_2SO_4 electrolyte using a rotating ring-disc electrode (RRDE).

Principle of RRDE operation

RRDE consists of 5mm diameter glassy carbon working disc electrode and a thin concentric platinum ring with a 375 μm insulating gap in between. Collection efficiency is dependent strictly on geometrical measurements and is estimated for this to be 24,9%, however, surfaces can wear off by usage, therefore, it's beneficial to calibrate it.

Calibration is done by a certain redox couple ($\text{K}_3[\text{Fe}(\text{CN})_6]$ in this case). Initially, both ring and disc are held on high potential, so no reaction takes place, then the disc is swept towards negative potentials, initiating reduction. The product of the reaction is oxidized back on the ring. The recorded current ratio is used as collection efficiency. This value should be independent of the rotation rate. The process was repeated on disc with carbon dried carbon paste, to take the surface change into account.

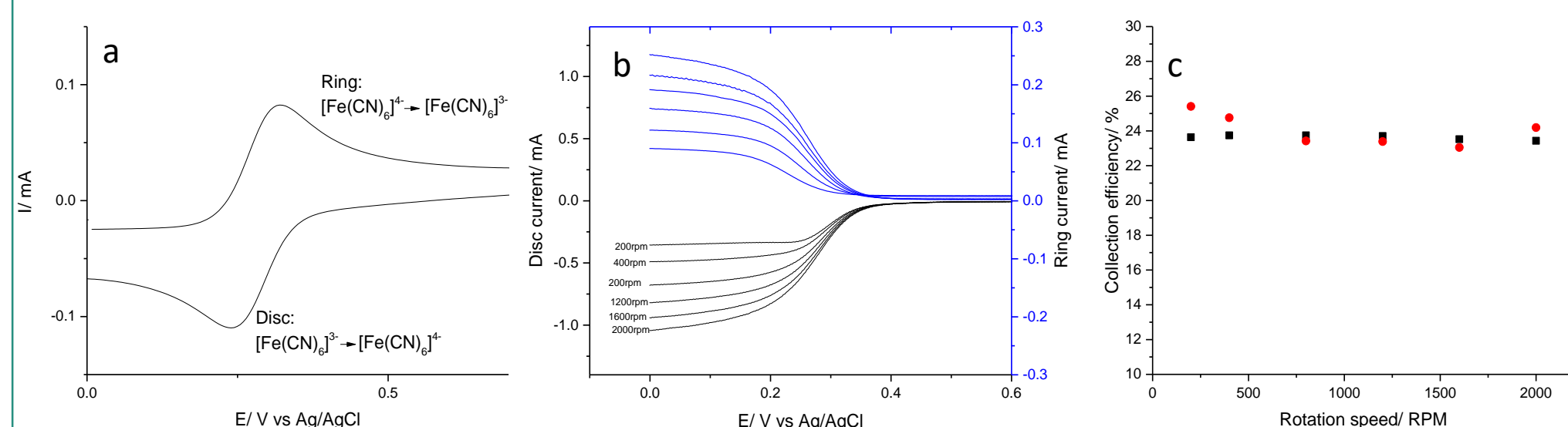


Fig 1. Calibration of RRDE collection efficiency: a) redox reactions on ring and disc, b) recorded currents on different rotation rates and c) collection efficiency for clean (black) and slurry-casted (red) discs

Degradation & operation mechanisms of electrodes in aqueous media

Both electrode materials undergo degradation during operation in aqueous media, however, mechanism seems to be vastly different. For NMTP, degradation occurs during discharge phase, probably due to high solubility of produced Mn^{2+} , while for NVPF, charging phase is more damaging. Also, for NVPF, during measurement, two peaks are observed on a ring, suggesting that degradation occurs for both, $\text{V}^{3+} \rightarrow \text{V}^{4+}$ and $\text{V}^{4+} \rightarrow \text{V}^{5+}$ transitions. Integrating the charges on the ring and comparing it to the disc charge loss, also suggests that NMTP operation is 1 electron process.

References

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Electrode measurements

NASICON-type NMTP & NVPF electrodes were made by mixing active material with carbon black (20%) and PVDF (10%) binder prior to casting on the GC electrode. Electrode with 3mm diameter and 0.3mg of active material loading was obtained.

To study the degradation, cyclic voltammogram at 10mv/s was employed. Galvanostatic measurements were done at either 10C or 5C for NMTP and NVPF respectively. During operation, it's expected that soluble degradation products (either Mn^{2+} or V^{5+}) will be swept toward the ring, held at 1.2V or -0.7V vs Ag/AgCl, leading to oxidation to MnO_2 or reduction to V^{3+} respectively.

The results show that degradation occurs during discharging phase (cathodic sweep during CV) for NMTP and charge phase of NVPF (anodic sweep) with peak ring current recorded around 0.5V or 0.9V respectively (fig 1 & 2). A previous study for NMTP in organic media showed that degradation occurs as a result of overcharge/over-discharge.

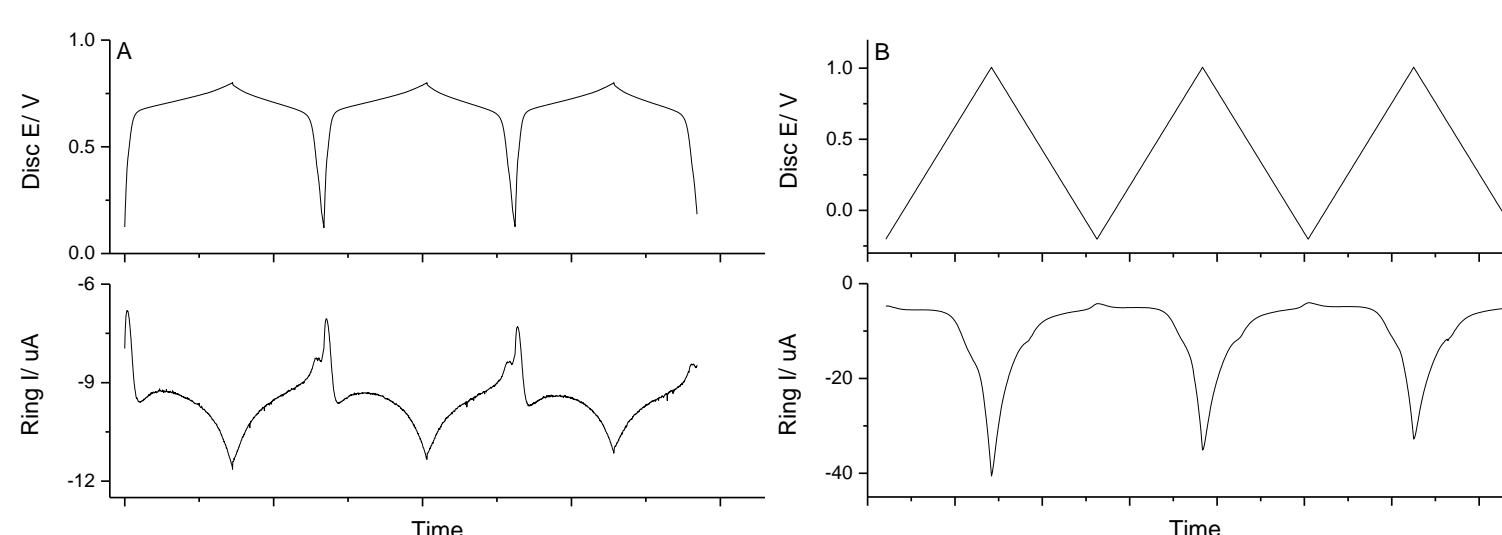


Fig 1. Galvanostatic (A) and cyclic voltammetry (B) measurements for NVPF on RRDE with ring polarized at -0.7V

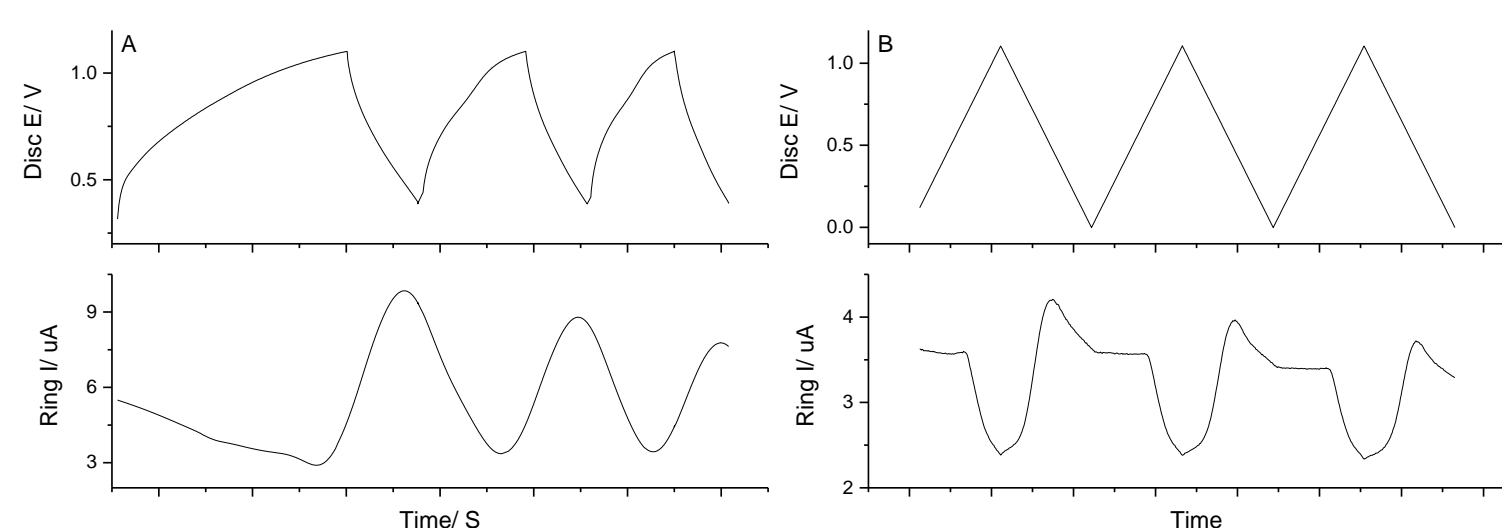


Fig 2. Galvanostatic (A) and cyclic voltammetry (B) measurements for NMTP on RRDE with ring polarized at 1.2V

Conclusions

- ✓ RRDE can be an effective and fast tool to study electrode material degradation in any media.
- ✓ Unlike previously reported Mn-based cathode materials, for NMTP in aqueous media, degradation occurs only during the discharge process, while NVPF degradation seems to be 2 step process, both occurring at charging.
- ✓ Results suggest that in aqueous electrolytes, only 1 sodium intercalation occurs for NMTP, therefore, the theoretical capacity is only 58.6 mAh/g vs 117 mAh/g reported for organic electrolytes

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