

# ROTATING RING-DISC ELECTRODE STUDY OF MN-BASED MATERIAL OPERATION AND DEGRADATION AS AQUEOUS NA-ION BATTERY CATHODE



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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 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. shows one of the highest voltage plateaus (4.1V and 3.6V vs  $\text{Na}^+/\text{Na}$ ), with theoretical capacity of 117 mAh/g.. However, material degradation, especially in aqueous electrolytes remains a major issue. Here material degradation was studied in 1M  $\text{Na}_2\text{SO}_4$  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  $\mu\text{m}$  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.

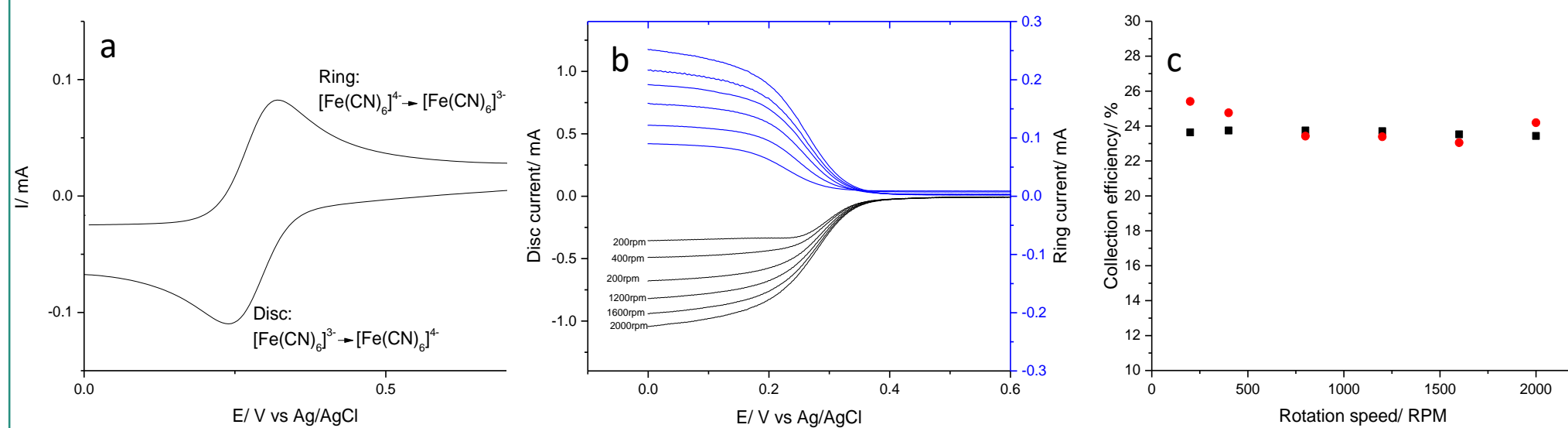


Fig 1. Calibration of RRDE collection efficiency: a) redox reactions on ring and disc, b) recorded currents on different rotation rates and c) collection efficiency for clean (black) and slurry-casted (red) discs

## Electrode measurements

NASICON-type NMTP electrodes were mixed 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, either galvanostatic cycling at a 10C rate (580mA/g) or cyclic voltammogram at 10mv/s was used. During operation, it's expected that soluble degradation product,  $\text{Mn}^{2+}$ , will be swept outwards due to forced convection and will be detected on a ring (oxidized to  $\text{MnO}_2$ ), held at 1.2V vs Ag/AgCl.

The results show that degradation occurs during discharging phase (cathodic sweep during CV), with peak ring current recorded around 0.5V (fig 2 c). A previous study in organic media showed that degradation in organic media occurs as a result of overcharge/over-discharge.

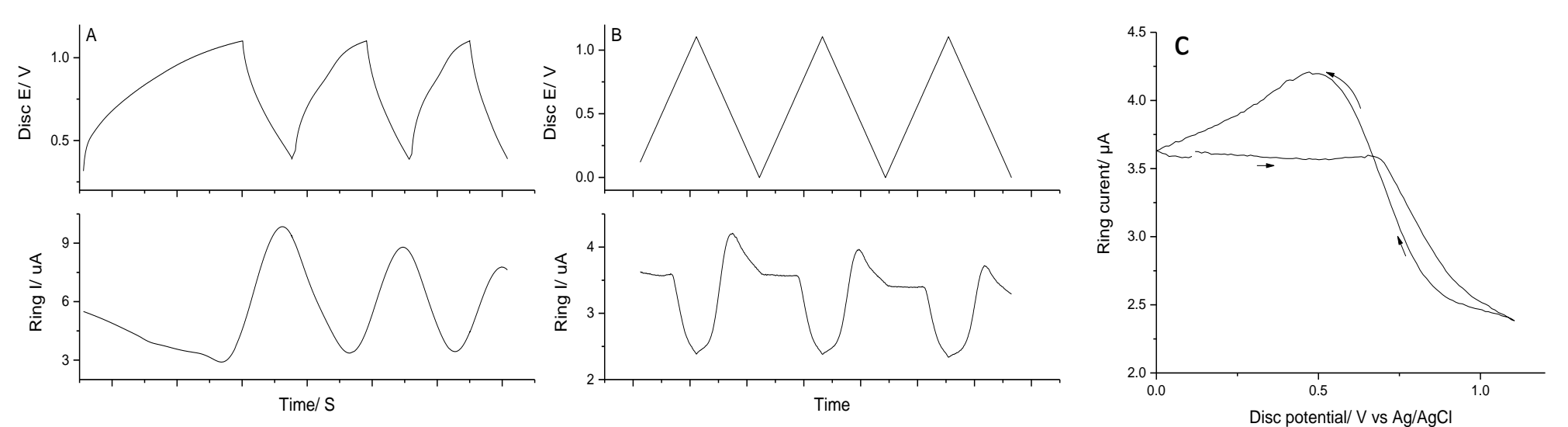


Fig 2. Degradation of NMTP: a) galvanostatic cycling at 10C, b) CV measurement at 10mv/s and c) ring current/disc potential relationship during CV measurements

## Degradation & operation mechanism of NMTP in aqueous media

The suggested mechanism of NMTP operation as cathode material is based on two redox couples ( $\text{Mn}^{2+}/\text{Mn}^{3+}$  and  $\text{Mn}^{3+}/\text{Mn}^{4+}$ ) and two sodium intercalation, yielding a theoretical capacity of 117 mAh/g in organic electrolytes. In that case, charge loss on a disc, as a result of degradation and dissolution of Mn species, should be equal to one recorded on a ring. However, in our study, the charge detected on a ring, after adjusting for collection efficiency, is higher than the loss on a disc during cycling (assessed with a difference in anodic peak area change). In fact, the ratio is close to 2, suggesting 2-electron process on a ring ( $\text{Mn}^{2+} \rightarrow \text{MnO}_2$ ) and 1 electron process on the disc. Degradation occurs when during discharging when water-soluble  $\text{Mn}^{2+}$  is formed.

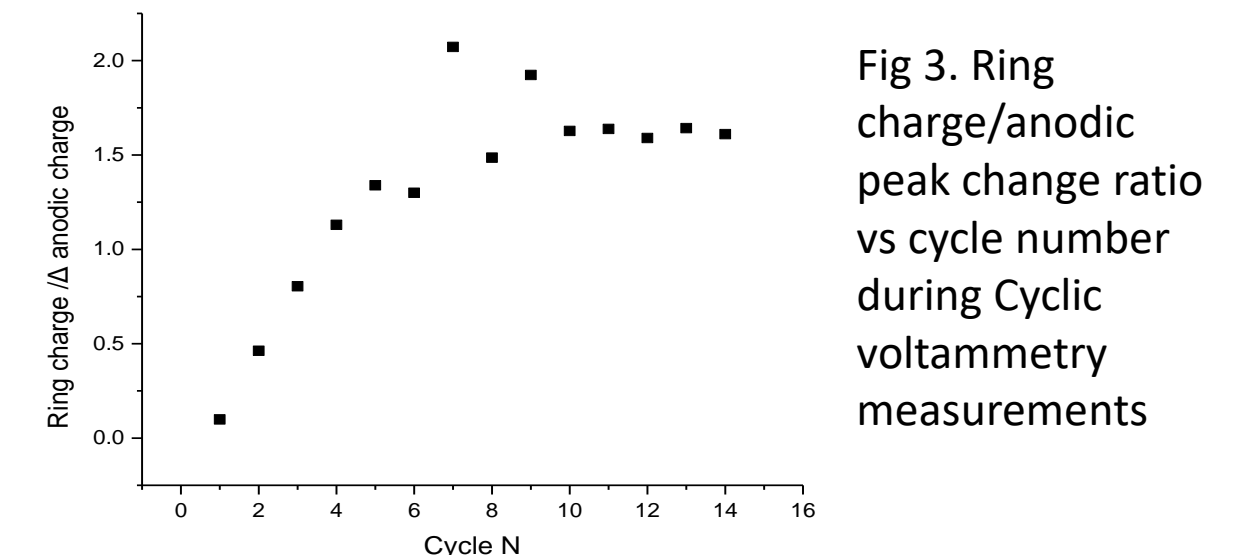


Fig 3. Ring charge/anodic peak change ratio vs cycle number during Cyclic voltammetry measurements

## References

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## Conclusions

- ✓ RRDE can be an effective and fast tool to study electrode material degradation provided that degradation products are soluble in a media.
- ✓ Unlike previously reported Mn-based cathode materials, for NMTP in aqueous electrolyte, degradation occurs only during the discharge phase.
- ✓ Results suggest that in aqueous 1M  $\text{Na}_2\text{SO}_4$  electrolyte, only 1 sodium intercalation occurs, therefore, the theoretical capacity of NMTP is only 58.6 mAh/g vs 117 mAh/g reported for organic electrolytes

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