

Insights on Structural Evolution and Charge Storage Mechanism of $\text{Na}_4\text{Mn}_9\text{O}_{18}$ as Active Material for Aqueous Rechargeable Sodium-Ion Storage Systems

Mehdi Soleimanzade^{a, b}, Mazdak Hashempour^a, Maksim Bogdanchik^a, Riccardo Romanenghi^a, Federico M. Cernuschi^b, Massimiliano Bestetti^a and Antonello Vincenzo^a

^a Dipartimento di Chimica, Materiali e Ingegneria Chimica Giulio Natta, Politecnico di Milano

^b Ricerca sul Sistema Energetico (RSE spa)

As a renewable and sustainable energy storage technology, aqueous rechargeable sodium-ion storage systems have raised great interest due to environmental friendliness, safety and low cost. Unlike conventional lithium-ion batteries, aqueous sodium-ion systems have some distinct advantages for large-scale stationary electric storage, such as the abundant natural resource of Na and the possibility to achieve long-term stability and reversibility. In addition, aqueous electrolytes are inherently safer and more eco-friendly than organic electrolytes [1]. On the other hand, the use of aqueous electrolytes poses significant challenges in the selection of electrode materials. First, their redox potentials should be within the electrochemical stability window of water. Second, the side reactions between electrode materials and H_2O or residual O_2 may tremendously affect their cyclic stability [2]. Among the different eligible materials, channeled structure $\text{Na}_4\text{Mn}_9\text{O}_{18}$ (NMO) is still one of the most promising candidate as cathodic material for aqueous Na-ion storage systems, because of its abundance, low price ($\$7.6 \text{ kg}^{-1}$ [3]), relatively high theoretical capacity (121 mAh g^{-1}), non-toxicity, and simple synthesis by different routes. However, this material has yet to be characterized in detail in terms of its storage mechanisms and stability performance in aqueous environment. In this study, we undertake an in depth characterization of the kinetics of NMO electrode processes in 1 M Na_2SO_4 electrolyte, within its safe potential window in this electrolyte, namely 0.25-1.1 V_{SHE} , as defined in the present work. We use cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) to deconvolve the complex behavior of this system and discriminate the different contributions of double-layer capacitance, pseudocapacitance and sodium ion insertion to charge/discharge at varying potential. First, by the power law analysis of voltammetry we identify kinetic processes and make an evaluation of their respective contribution; then, the analysis and modeling of EIS measurements, performed at varying potential after equilibration of the system, allow us to calculate the currents associated with the above processes at varying potential and as a function of the frequency. In particular, the EIS method proves that the diffusional or intercalation contribution is dominant over the entire safe potential window. The latter methodology holds great promise to be a powerful tool for an effective deconvolution of the complex behavior of the NMO / aqueous electrolyte system, enabling an in depth understanding of the role of different processes in its dynamic performance.

References

- [1] Y. You *et al.*, “Recent developments on aqueous sodium-ion batteries,” *Mater. Technol.*, 2016.
- [2] D. Bin *et al.*, “Progress in Aqueous Rechargeable Sodium-Ion Batteries,” *Adv. Energy Mater.*, vol. 8, no. 17, pp. 1–31, 2018.
- [3] C. Vaalma *et al.* “A cost and resource analysis of sodium-ion batteries,” *Nat. Rev. Mater.*, vol. 3, 2018.

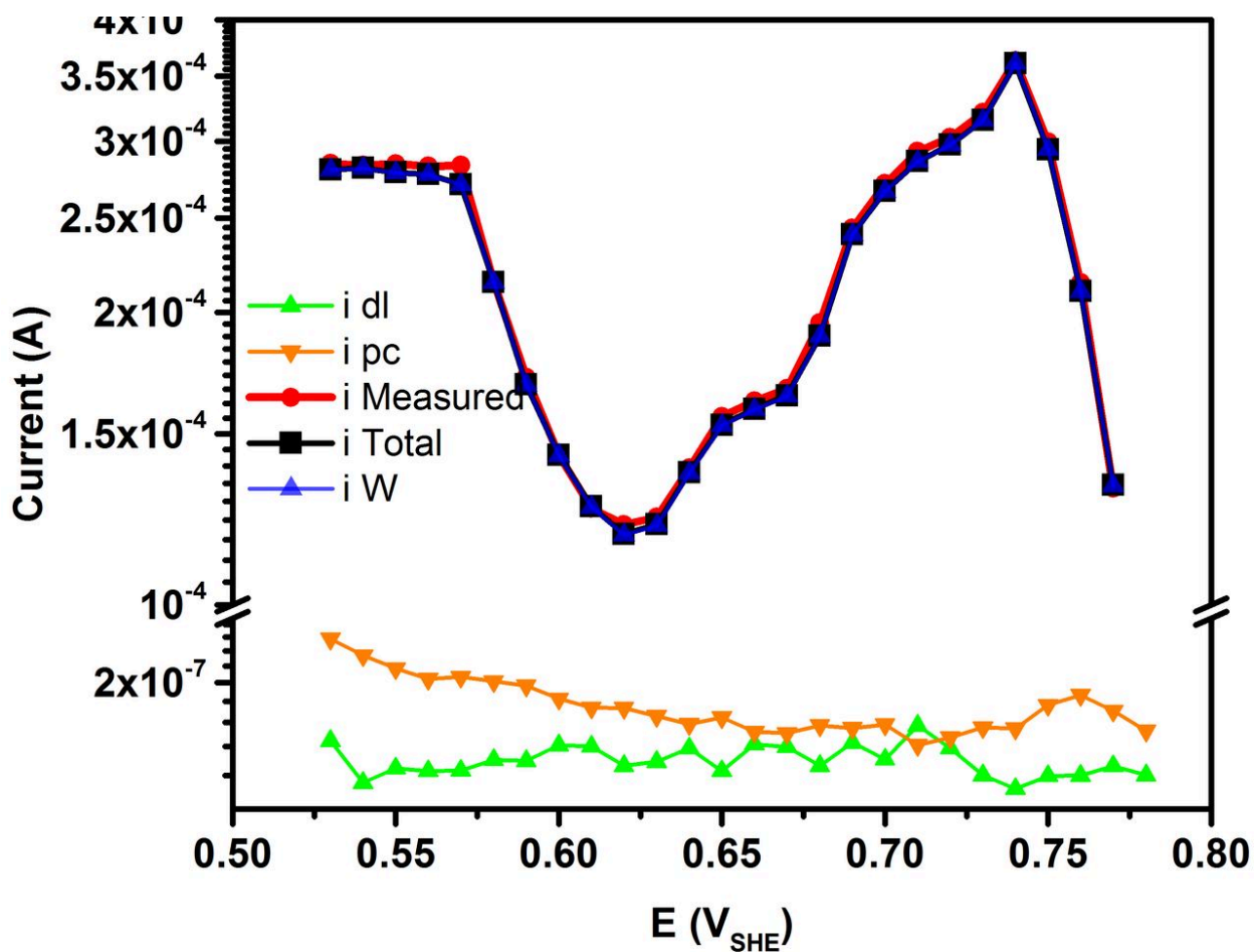


Figure 1. Contribution of i_{dl} , i_{pc} and i_w double layer, pseudocapacitance and diffusion currents respectively. i_{Total} and $i_{Measured}$ is also plotted to compared the sum of all currents with measured one. Inlet magnified currents of i_{dl} and i_{pc} .