

Highly Reversible Oxygen-Redox Chemistry at 4.1 V in $\text{Na}_{4/7-x}[\square_{1/7}\text{Mn}_{6/7}]\text{O}_2$ (\square : Mn vacancy)

Benoit Mortemard de Boisse¹, Shin-ichi Nishimura^{1,2}, Eriko Watanabe¹, Laura Lander¹, Akihisa Tsuchimoto¹, Jun Kikkawa³, Daisuke Asakura⁴, Masashi Okubo^{1,2} and Atsuo Yamada^{1,2}

¹The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

²ESICB, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

³National Institute of Materials Science, Tsukuba, Ibaraki 305-0044, Japan

⁴AIST, Tsukuba, Ibaraki 305-8568, Japan

E-mail: benoit.mortemard@battery.t.u-tokyo.ac.jp

The tremendous industrial demand resulting from the market penetration of electric vehicles has significantly raised the requirement for rechargeable batteries with higher energy density. One research focus is the development of higher energy positive electrode.

Quantitatively, in the conventional charge-compensation regime which relies on the redox capability of transition metals, the theoretical capacity is maximized for the chemical composition of AMO_2 (A : alkali metal; M : transition metal). However, recent studies have shown that A -excess transition-metal oxides, $\text{A}_{1+x}\text{M}_{1-x}\text{O}_2$, can deliver large extra capacities exceeding the theoretical limit of the M -redox reaction *via* additional redox of nonbonding oxygen $2p$ orbital. Therefore, exploiting additional oxygen redox would significantly contribute to surpassing the current energy-density limit of batteries.

In this work, we propose introducing transition metal vacancies (*e.g.*, $\text{A}_x[\square_y\text{M}_{1-y}]\text{O}_2$, \square : transition metal vacancy) as a possible approach for stable oxygen-redox reactions. The damaging M migration would be suppressed if the ionic radii of A and M differ largely. In this regard, sodium shows larger contrast in ionic radii with $3d$ transition metals and its compounds look promising. Therefore, we investigate the reversible oxygen-redox capacity of a layered sodium manganese oxide $\text{Na}_2\text{Mn}_3\text{O}_7$ ($\text{Na}_{4/7}[\square_{1/7}\text{Mn}_{6/7}]\text{O}_2$ in conventional Na_xMO_2 notation, **Figure 1a**). Considering the inherent manganese vacancies in the $[\square_{1/7}\text{Mn}_{6/7}]\text{O}_2$ layers, we expect the oxygens neighboring \square to have nonbonding $2p$ orbitals, leading to an oxygen-redox capacity upon Na^+ extraction. In this study, we show that $\text{Na}_{2-x}\text{Mn}_3\text{O}_7$ can operate as a highly reversible 4.1 V oxygen-redox cathode (**Figure 1b**).

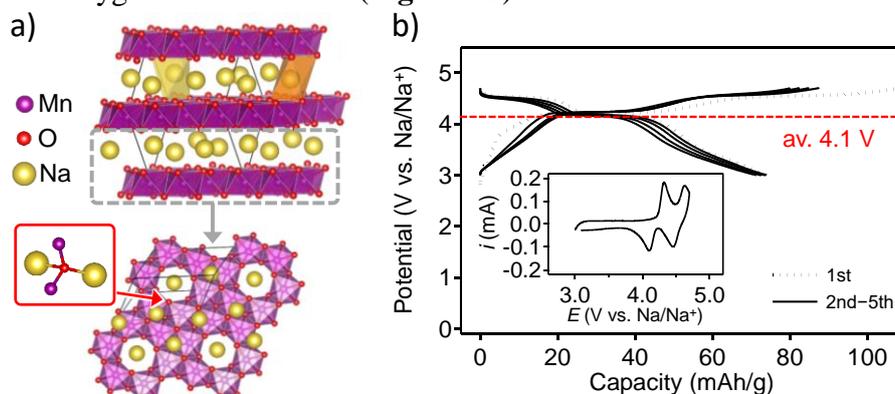


Figure 1. a) Structure of $\text{Na}_2\text{Mn}_3\text{O}_7$ showing the existence of Mn vacancies and b) galvanostatic charge/discharge curves of $\text{Na}_2\text{Mn}_3\text{O}_7$ recorded between 3.0 and 4.7 V vs. Na/Na^+ .

References:

- [1] D.-H. Seo et al., *Nat. Chem.* 8 (2016) 692-697. [2] M. Okubo and A. Yamada, *Applied Materials & Interfaces* 9 (2017) 36463-36472. [3] E. Adamczyk and V. Pralong, *Chem. Mater.* 29 (2017) 4645-4648.