

Development of New Electrode Materials for Next-Generation Na-Ion Batteries

Towards sustainable energy storage systems, Na-ion batteries have gained great interest. Aiming to high energy density positive electrode materials, the use of oxygen anion redox has been investigated in Mn-based layered oxides. Herein, the effect of substituent(s) for Mn in P2-type $\text{Na}_{0.67}[\text{Cu}_{0.1}\text{M}_{0.1}\text{Mn}_{0.8}]\text{O}_2$ ($\text{M} = \text{Cu}, \text{Mg}, \text{Zn}$) on charge compensation mechanism is studied using different spectroscopic techniques. Hard X-ray photoelectron spectroscopy confirms reversible participation of oxygen anion during extraction/insertion of Na^+ for all samples. More bulk sensitive X-ray absorption spectroscopy reveals reversibility of transition metal redox, which is absent beyond 4.2 V where $\text{O}^{2-/(2-\delta)-}$ redox occurs instead in P2-type $\text{Na}_{0.67}[\text{Cu}_{0.1}\text{Cu}_{0.1}\text{Mn}_{0.8}]\text{O}_2$.

Li-ion batteries (LIBs) are the most advanced electrochemical energy storage systems, playing an important role in the changeover from fossil fuels to renewable energy. However, the scarcity of lithium sources has driven alternative systems beyond LIBs. Among the potential beyond LIBs technologies, Na-ion batteries (NIBs) are on the verge of commercialization. Among positive electrode materials, P2-type [1] layered transition metal oxides (Na_xTMO_2), where Na^+ ions occupy trigonal prismatic sites and two TM oxide (MO_2) slabs in a hexagonal

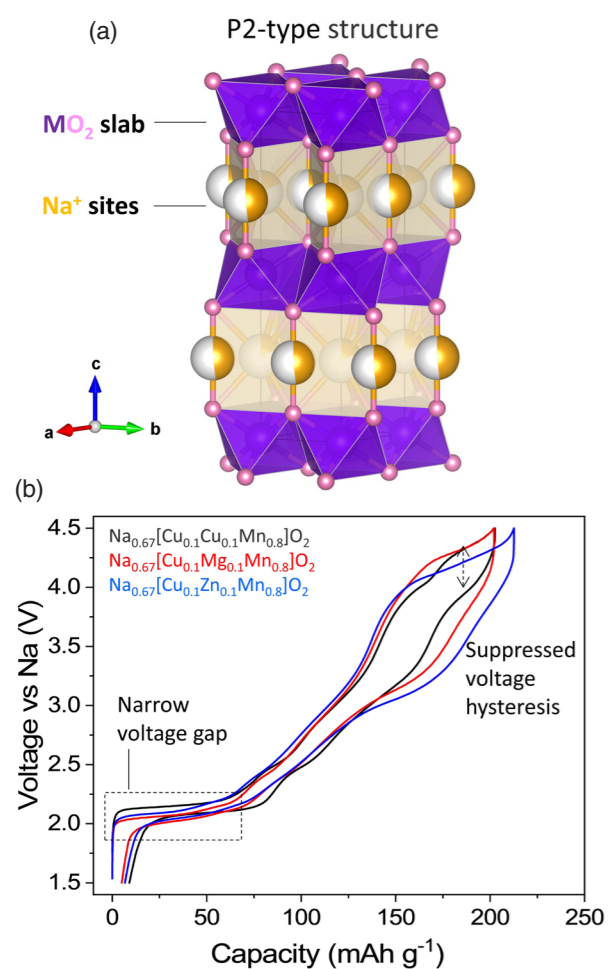


Figure 1: (a) A schematic illustration of P2-type Na_xTMO_2 . (b) Charge/discharge profiles for P2-type $\text{Na}_{0.67}[\text{Cu}_{0.1}\text{M}_{0.1}\text{Mn}_{0.8}]\text{O}_2$ ($\text{M} = \text{Cu}, \text{Mg}, \text{Zn}$) on the second cycle, cycled in the voltage range of 1.5 - 4.5 V at a rate of 10 mA g^{-1} . (b) is adopted with permission from ref [2]. Copyright 2022 American Chemical Society.

unit cell (Fig. 1(a)), are one of the most promising candidates. However, capacity originating from only TM is insufficient, therefore cumulative use of TM and oxygen anion redox has been suggested. As the mechanism and the activity of oxygen anion redox depend on the constituents in MO_2 slabs, it is of interest to study the effect of substituent(s) in Mn-based P2-type compounds, $\text{Na}_x[\text{Mn}_y\text{M}_{1-y}]\text{O}_2$, on the aforementioned matters.

In this work, P2-type $\text{Na}_{0.67}[\text{Cu}_{0.1}\text{M}_{0.1}\text{Mn}_{0.8}]\text{O}_2$ ($\text{M} = \text{Cu}, \text{Mg}, \text{Zn}$) are studied to understand charge compensation mechanism during electrochemical Na^+ extraction/insertion and structural integrity depending on the substituent(s). To examine electrochemical properties of those materials, coin cells, made with Na metal as reference/counter electrode and 1M NaPF_6 in propylene carbonate as electrolyte, were galvanostatically cycled between 1.5 - 4.5 V. On the second cycle, all samples exhibit a large voltage gap between charge and discharge curves in the high voltage region while the plateau region at around 2 V shows a narrow voltage gap (Fig. 1(b)). The former hints oxidation of oxygen anions since most of Na_xTMO_2 feature voltage hysteresis during the oxidation of oxygen anions. The latter implies reversible structural evolution. It is worth noting that the voltage hysteresis in P2-type $\text{Na}_{0.67}[\text{Cu}_{0.1}\text{Cu}_{0.1}\text{Mn}_{0.8}]\text{O}_2$ (also written as $\text{Na}_{0.67}[\text{Cu}_{0.2}\text{Mn}_{0.8}]\text{O}_2$) is suppressed due to the absence of detrimental structural changes, confirmed by in situ and ex situ X-ray diffraction measurements.

To verify the participation of oxygen anions in charge compensation, ex situ hard X-ray photoelectron spectroscopy (HAXPES) measurements were carried out at different states of charge for the three samples. In Mn $2p_{3/2}$ spectra (Fig. 2(a)), all samples show minor oxidation of Mn^{3+} upon charge to 4.2 V and no additional oxidation after further charge to 4.5 V. After discharge to 2.3 V, the shoulder in a lower binding energy reemerges. Concerning Cu $2p_{3/2}$ spectra (Fig. 2(b)), only P2-type $\text{Na}_{0.67}[\text{Cu}_{0.1}\text{Cu}_{0.1}\text{Mn}_{0.8}]\text{O}_2$ exhibits $\text{Cu}^{2+/3+}$ redox reaction which occurs below 4.2 V. Looking at the evolution of O 1s spectra (Fig. 2(c)), an oxidized lattice oxygen component appears upon charge in all samples, and the percentage of the oxidized lattice oxygen increases and decreases in a reversible way, validating reversible oxygen anion redox.

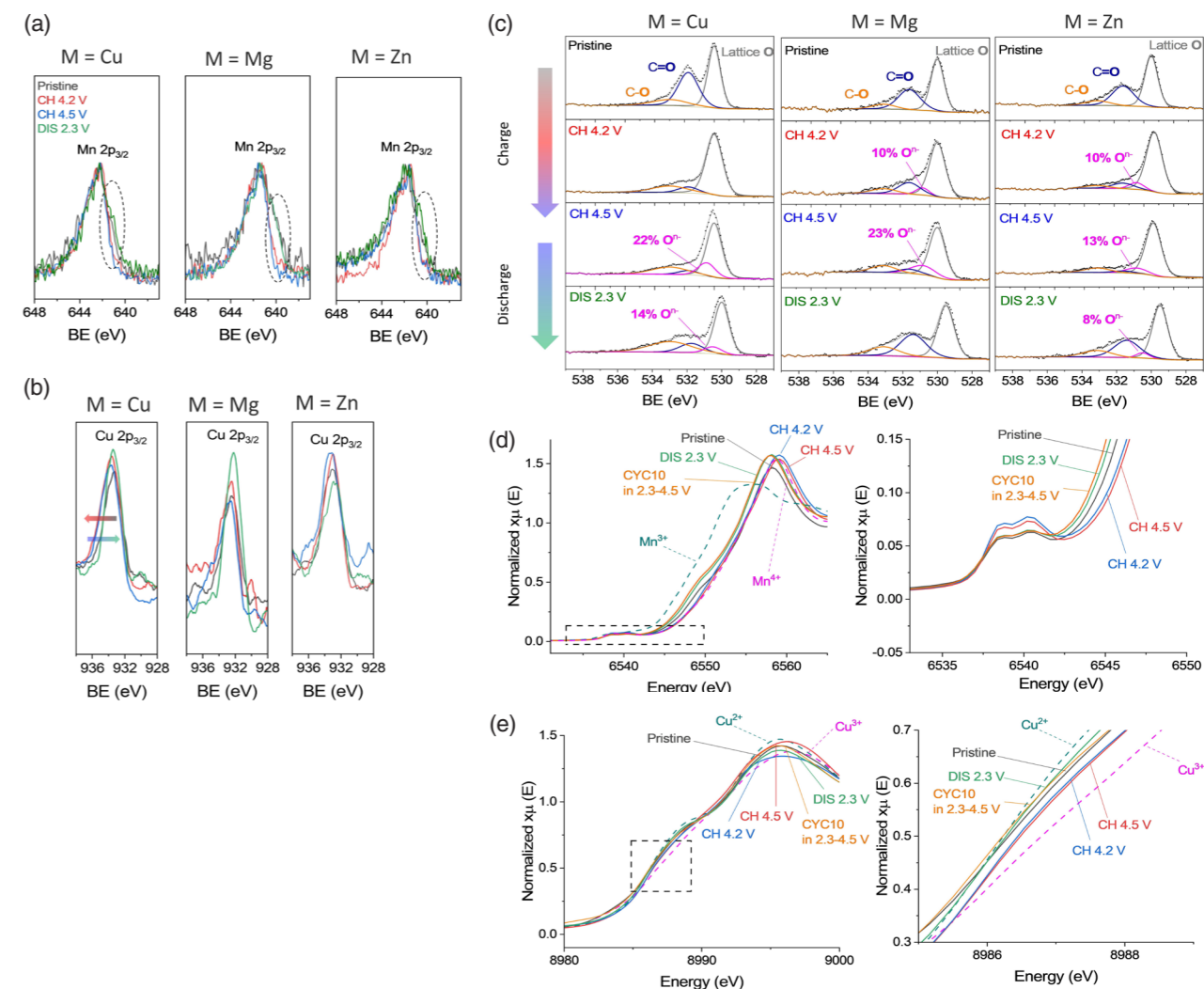


Figure 2: HAXPES spectra of (a) Mn $2p_{3/2}$, (b) Cu $2p_{3/2}$ and (c) O 1s for P2-type $\text{Na}_{0.67}[\text{Cu}_{0.1}\text{M}_{0.1}\text{Mn}_{0.8}]\text{O}_2$ ($\text{M} = \text{Cu}, \text{Mg}, \text{Zn}$), measured at pristine state (pristine), after charge to 4.2 V (CH 4.2 V), charge to 4.5 V (CH 4.5 V), and discharge to 2.3 V (DIS 2.3 V). The dashed circle highlights a shoulder in lower binding energy. The percentage of oxidized lattice oxygen of O^{2-} ($\text{O}^{2-} + \text{lattice O}$) is shown in magenta. (d) Mn K-edge spectra, highlighting pre-edge on the right side. (e) Cu K-edge spectra, highlighting half height of the normalized absorbance on the right side. (a-e) are adopted with permission from ref [2]. Copyright 2022 American Chemical Society.

Although HAXPES can provide relatively bulk information compared to standard X-ray photoelectron spectroscopy technique using an Al $K\alpha$ X-ray source, the depth of analysis is still limited than that of X-ray absorption near-edge structure (XANES). Given that P2-type $\text{Na}_{0.67}[\text{Cu}_{0.1}\text{Cu}_{0.1}\text{Mn}_{0.8}]\text{O}_2$ demonstrates reversible $\text{Mn}^{3+/4+}$, $\text{Cu}^{2+/3+}$, and $\text{O}^{2-/(2-\delta)-}$ as well as superior structural stability than the others, additional Mn and Cu K-edge XANES spectra (Fig. 2(d) and 2(e), respectively) were collected at beam line BL-12C to confirm the changes in the transition metal valence in bulk. Ex situ measurements were performed for the five samples. Qualitative comparison of the recorded spectra with those of standard samples reveals that Mn valence of pristine sample is close to tetravalent and Cu is divalent. After charge to 4.2 V, both Mn and Cu K-edge spectra shift to higher energy, indicating Mn oxidation to Mn^{4+} and Cu oxidation to Cu^{3+} . No additional shift in both K-edge spectra after charge to 4.5 V indirectly support oxygen anion oxidation. After discharge to 2.3 V, the Mn K-edge spectrum shifts to a

slightly lower energy than the pristine state, due to extra Na^+ insertion and the Cu K-edge one reverts to the pristine one. The spectra after 10 cycles in 2.3 - 4.5 V are identical to those after the first discharge to 2.3 V, indicating a stable electronic structure over 10 cycles.

In this study, we investigate the impacts of substituent(s) on crystal and electronic structures, highlighting the benefit of high Cu^{2+} concentration beyond 4.2 V. For more competitive NIBs with LIBs, the combination of cation permutation and development of spectroscopy techniques is necessary.

REFERENCES

- [1] C. Delmas, C. Fouassier and P. Hagenmuller, *Phys. B.* **99**, 81 (1980).
- [2] E. J. Kim, T. Hosaka, K. Kubota, R. Tatara, S. Kumakura and S. Komaba, *ACS Appl. Energy Mater.* **5**, 12999 (2022).

BEAMLIN

BL-12C

E. J. KIM and S. KOMABA (Tokyo Univ. of Sci.)