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Supporting Information

Charge Storage Mechanism and Degradation of P2-Type Sodium Transition Metal Oxides in Aqueous Electrolytes

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Figure S1. High angle XRD fitting of the Rietveld refinements for: a) NaNMFe, b) NaNMCo, c) NaNMCu, and d) NaMCu and CuO. The tick marks at the bottom of each graph represent the P2 peak locations in each material, while the gray (bottom) tick marks in d) represent CuO.



Figure S2. Scanning electron micrographs of electrodes of each composition of the P2 oxides: a) NaNMFe, b) NaNMCo, c) NaNMCu, and d) NaMCu. The particle size and morphology does not vary with the transition metal composition.

NaNMFe		NaNMCo		NaNMCu		NaMCu	
Pristine (Å)	Water- exposed (Å)	Pristine (Å)	Water- exposed (Å)	Pristine (Å)	Water- exposed (Å)	Pristine (Å)	Water- exposed (Å)
5.265	5.818	6.038	6.036	5.793	5.419	5.717	5.642
5.617	5.75	5.849	5.676	5.855	5.306	5.826	5.664
5.821	6.626	5.996	7.1*	5.824	4.681	5.652	6.48*
5.861	5.412	5.978	6.087	5.93	4.956	5.823	5.719
5.759	5.97	5.889	6.58	5.797	4.788	6.076	5.866
5.563	6.367	5.623	6.19	5.93	5.753	5.9	5.625
6.071	6.211	5.647	5.322	5.625	5.599	6.015	5.63*
5.991	5.62	5.651	5.754	5.626	5.45	6.018	4.42*
2.644^{\square}	7.488	5.319	7.04*	5.562	5.3125	5.958	5.34
	6.34		4.52*	5.564	5.283	5.966	5.266
	5.63		6.78*		5.629		
	6.72		5.02*				
			6.195				

Table S1. Raw data for the interlayer spacing calculations from STEM images.

^O Data point taken on 5 interlayer spacings. *Data point taken on a single interlayer spacing

Unless otherwise noted, measurements were taken across 10 interlayer spacings (between 11 oxide layers) from HAADF-STEM images, using ImageJ.



Figure S3. TGA of the pristine powders immediately after removal from the glovebox and of the water-exposed powders after 16 days. The pristine powders (dashed lines) show a small mass loss due to adsorbed water. Both a) NaNMFe and b) NaNMCo show clear steps corresponding to the removal of interlayer water, while c) NaNMCu and d) NaMCu show small steps that can be attributed to water adsorbed onto the surface.

I. High pH Electrochemistry

In an aqueous electrolyte, there is the possibility of H^+ or H_3O^+ intercalation rather than Na^+ intercalation. To determine whether the intercalating species is Na^+ or H^+ , pristine NaNMCo electrodes were cycled at 1 mV s⁻¹ in aqueous Na_2SO_4 electrolytes of pH 6, 9, 11, and 13 followed by XRD characterization. According to the Nernst equation,¹ the potential at which intercalation or deintercalation occurs should shift with concentration of the intercalating species:

$$E = E^0 + \frac{RT}{nF} ln^{\text{ind}} \left(\frac{[A^+]a_{ox}}{a_{red}} \right)$$

where:

E°: formal potential $[A^+]$: concentration of Na⁺ or H⁺ $a_{ox} = a_{red}$: activity of the solid phases undergoing redox reaction R: gas constant T: temperature

n: e transferred (~ 0.3)

F: Faraday constant

Here, the oxidized (ox) phase is Na_{0.6-x} MO_2 , and the reduced (red) phase is Na_{0.6} MO_2 . The activity of both of these solid phases is 1. **Table S2** shows the calculated redox peak shifts from the formal potential for electrolytes of pH 6, 9, 11, and 13, with n = 0.3 and T = 25°C. A redox peak shift of ~ 1 V (due to an electrolyte pH change from 6 to 13) would indicate H⁺ intercalation, while invariant redox peaks with increasing pH would indicate Na⁺ intercalation.^{1,2}

Table S2. Calculated redox peak shifts (from E°) for Na⁺ or H⁺ intercalation as a function of increasing electrolyte pH.

pН	$\operatorname{Na}^{+}(V)$	$\mathrm{H}^{+}\left(\mathrm{V}\right)$
6	0.059	-1.2
9	0.059	-1.8
11	0.059	-2.2
13	0.064	-2.6

If H⁺ were the intercalating species, the redox peaks would shift negatively and out of the investigated potential range (0 - 0.8 V) with increasing pH. For Na⁺ as the intercalating species, the redox peak shift would only increase by a maximum of 5 mV.

Figure S4a shows the CVs of electrodes cycled from 0 - 0.6 V in electrolytes of pH 6 to 13. During the first cycles, the redox peak potentials of the NaNMCo at each pH show little variation as H⁺ concentration decreases significantly from 10^{-6} M to 10^{-13} M. The as-prepared electrolyte had a pH of ~ 6, with 2 M Na⁺ to 10^{-6} M H⁺ and thus a significantly higher probability of Na⁺ intercalation than H⁺. The invariant redox peaks and similar current density as electrolyte pH varies strongly indicate that the majority intercalating species is Na⁺ rather than H⁺. *Ex situ* XRD (**Figure S4**b) was conducted to determine the structural effects of electrochemical cycling with varying pH. The results indicate that regardless of pH, NaNMCo transforms into two phases after cycling to 0.6 V. **Figure S5** shows the effect of cycling the NaNMCo to a higher anodic potential of 0.8 V as a function of electrolyte pH. The *ex situ* XRD (**Figure S5**b) results show that regardless of pH, when cycled to a higher anodic potential, NaNMCo almost completely transforms into the birnessite-like phase. This supports the hypothesis that the transformation to a hydrated birnessite-like phase is driven by the increased electrostatic repulsion between the oxygen anions across the interlayer as the amount of Na⁺ decreases during electrochemical cycling, which is determined by the maximum anodic potential.



Figure S4. Effect of the 1 M Na₂SO₄ electrolyte pH on the electrochemical behavior of NaNMCo: a) First cycle CVs of NaNMCo between 0 - 0.6 V show similar redox peak positions as a function of electrolyte pH, with slightly higher current response at pH 13 due to increased OER activity. b) *Ex situ* XRD of the electrodes cycled to 0.6 V show the formation of two phases after cycling regardless of pH. Due to the limited Na⁺ extraction at 0.6 V, the electrodes cycled at each pH only partially transform to the birnessite-like phase.



Figure S5. a) First cycle CVs of NaNMCo between 0 - 0.8 V at pH 6, 9, and 11, showing similar redox peak positions as a function of pH. b) *Ex situ* XRD of the electrodes cycled to 0.8 V shows that by cycling to a higher anodic potential, NaNMCo (regardless of electrolyte pH) almost completely transforms into a hydrated birnessite-like phase.



Figure S6. Electrochemical cycling at 0.5 mV s⁻¹ in 1 M Na₂O₄ of a) NaNMCo from 0 - 0.8 V, b) NaNMCo from 0 - 1.1 V, c) NaMCu from 0 - 0.8 V, and d) NaMCu from 0 - 1.1 V. Each has an acetylene black ("A.B.") background at 0.5 mV s⁻¹ for reference.



Figure S7. Scanning electron micrograph of a NaNMCo particle after water exposure.

II. Electrochemical Impedance Spectroscopy

The impedance results were modeled with the equivalent circuit shown in Figure S8, where:

- R_s represents the electrolyte solution resistance
- The first parallel circuit, consisting of CPE₁ and R₁, represents the high frequency capacitance and resistance, respectively. CPE is a frequency-dependent constant-phase element ($CPE = [B(j\omega)^n]^{-1}$); B and n (0 < n < 1) are frequency-independent constants.
- The second parallel circuit is a Randles-type circuit which represents the lower frequency impedance associated with bulk ion intercalation. It consists of a constant phase element (CPE₂), a charge-transfer resistance (R_{ct}), and a Warburg element (Z_w) that represents the

impedance associated with ion diffusion in the solid state
$$\left(\begin{array}{c} Z_w = \frac{c}{\sqrt{j\omega}} \\ \end{array} \right)$$

Figure S9a and b show the Nyquist plots of NaNMCo and NaMCu cycled to 0.8 V, where the markers indicate the measured data points and the lines represent the equivalent circuit model fit. The slopes of the lines in **Figure S9**c and d were used to calculate the Na⁺ diffusion coefficient:

$$D = \frac{R^2 T^2}{2A^2 n^2 F^4 C^2 \sigma^2}$$

where D is the diffusion coefficient (cm² s⁻¹), R is the gas constant, T is the temperature, A is the area of the electrode, n is the number of electrons transferred per ion intercalated, F is the Faraday constant, C is the ion concentration, and σ is the slope of the real component of the impedance [Re(z)] vs. $\omega^{-1/2}$.³



Figure S8. Equivalent circuit used for modeling the EIS results.



Table S3. Calculated values for R_s , R_{ct} , and D for NaNMCo and NaMCu before and after cycling to 0.8 V vs. Ag/AgCl.

Figure S9. EIS results of NaNMCo and NaMCu before and after cycling to 0.8 V for 10 cycles at 0.5 mV s⁻¹. a) Nyquist plot of NaNMCo and b) NaMCu showing a large increase in charge transfer resistance after cycling. Real impedance [Re(z)] vs. $\omega^{-1/2}$ for c) NaNMCo and d) NaMCu before and after cycling, where the slope of the linear region was used in the calculation of the diffusion coefficient.

References

- 1 A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, Inc., Hoboken, NJ, 2nd edn., 2001.
- 2 Y. Wang, J.-Y. Lou, W. Wu, C.-X. Wang and Y.-Y. Xia, *J. Electrochem. Soc.*, 2007, **154**, A228–A234.
- 3 C. Yuan, Y. Zhang, Y. Pan, X. Liu, G. Wang and D. Cao, *Electrochim. Acta*, 2014, **116**, 404–412.