

Oxygen redox activity through a reductive coupling mechanism in the P3-type nickel-doped sodium manganese oxide

Eun Jeong Kim^{Δ,§}, Le Anh Ma[¶], Laurent C. Duda[#], David M. Pickup[◦], Alan V. Chadwick[◦], Reza Younesi^{§,¶}, John T.S. Irvine^Δ, A. Robert Armstrong^{Δ,§,}*

^ΔSchool of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, United Kingdom

[§]ALISTORE-ERI, 80039, Amiens Cedex, France

[¶]Ångström Advanced Battery Centre, Department of Chemistry Ångström Laboratory, Uppsala University, Uppsala, SE-75121, Sweden

[#]Department of Physics and Astronomy, Division of Molecular and Condensed Matter Physics, Uppsala University, Uppsala, S-75120, Sweden

[◦]School of Physical Sciences, University of Kent, Canterbury, Kent CT2 7NH, United Kingdom

* ara@st-andrews.ac.uk

Table S1. Rietveld refinement results for as-synthesized $\text{Na}_{0.67}\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_2$

$R_{\text{exp}} : 3.55 \%$ $R_{\text{wp}} : 4.23 \%$ $R_{\text{p}} : 3.45 \%$ 98% P3 2% NiO						
Space group $R\bar{3}m$ $a = 2.8650(1)$ Å $c = 16.8159(16)$ Å						
atom	Wyckoff symbol	x/a	y/b	z/c	Occupancy	Biso
Mn1/Ni1	3a	0	0	0	0.825/0.175(3)	0.3(2)
Na1	3a	0	0	0.167(2)	0.51(5)	4.6(7)
O1	3a	0	0	0.4004(13)	1	0.86(12)
O2	3a	0	0	0.6141(13)	1	1.5(2)

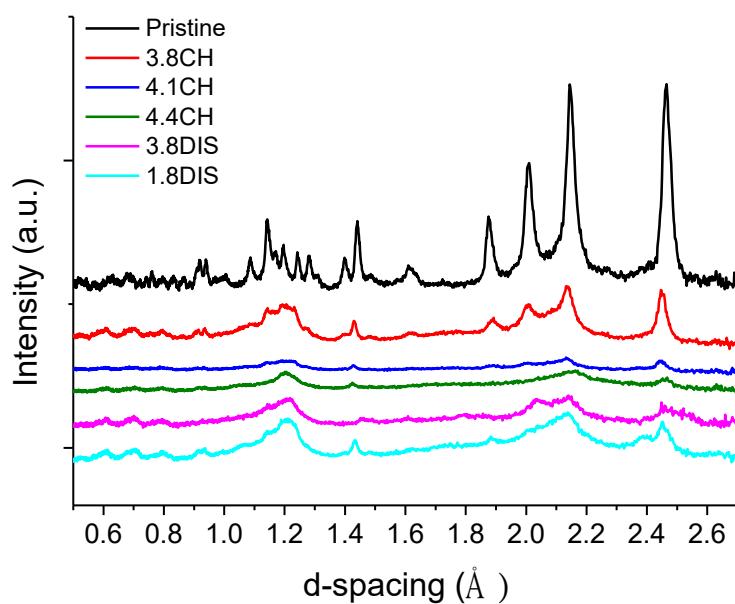


Figure S1. PND patterns for $\text{Na}_{0.67}\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_2$ extracted at different states of charge.

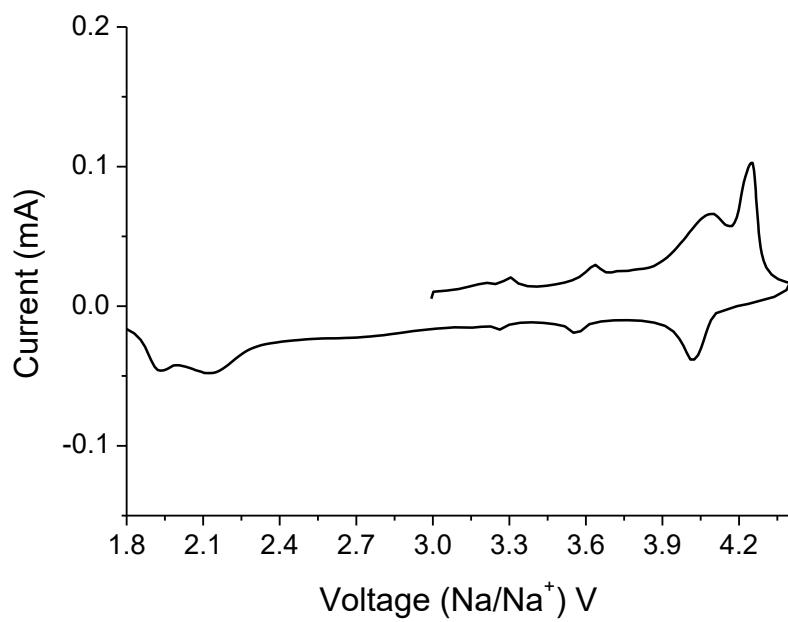


Figure S2. Voltammetric analysis of $\text{Na}_{0.67}\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_2$ at a scan rate of $30 \mu\text{V s}^{-1}$.

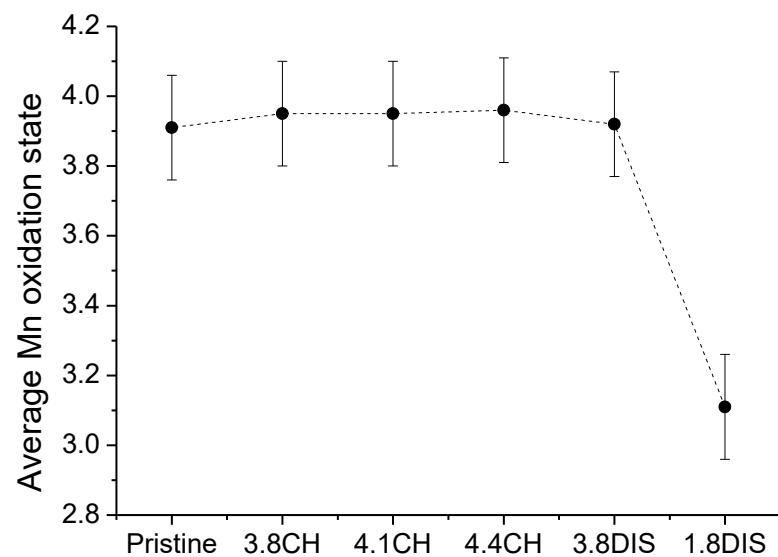


Figure S3. Variation of Mn oxidation state, calculated from the position of the centroid of the pre-edge for $\text{Na}_{0.67}\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_2$ extracted at different states of charge.

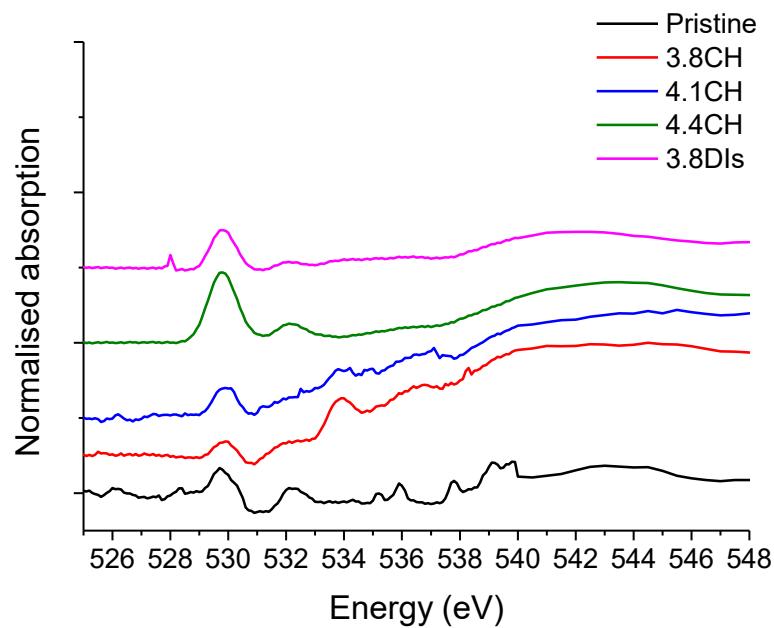


Figure S4. O K-edge SXAS spectra recorded in TEY mode for $\text{Na}_{0.67}\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_2$ extracted at different states of charge.

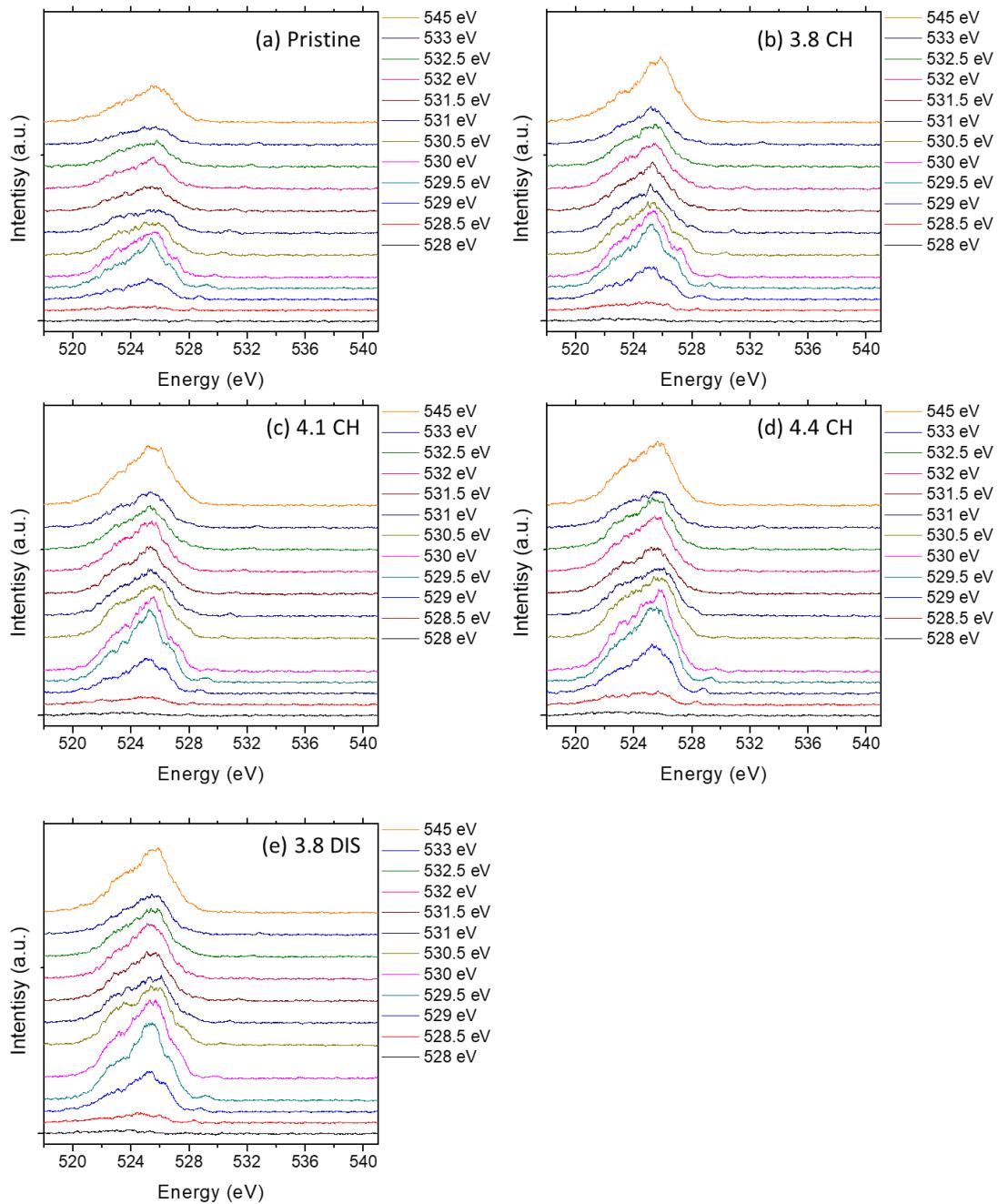


Figure S5. Complete overview of O K-edge RIXS spectra of $\text{Na}_{0.67}\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_2$ extracted at different states of charge.