The Effect of Initial Structure on Performance of High-Entropy Oxide Anodes for Li-ion Batteries

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Supporting Information

1. Calculation of Theoretical Capacity for HEOR and HEOS Samples

HEOR:

Assuming that Mg^{+2} remains inactive, there is a total of 1.6 e^- per formula unit of $(Mg_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2})O$ with molecular weight 68.635 g/mol, thus

$$C_{HEOR} = 1.6 \cdot F / 68.635 = 624.8 \text{ mAh/g}$$

HEOS:

Assuming that titanium is inactive and present as Ti^{+4}, the other four metals must contribute a total of 5.6 e^- per formula unit of $(Ti_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2})_3O_4$ with molecular weight 236.052 g/mol, thus

$$C_{HEOS} = 5.6 \cdot F / 236.052 = 635.8 \text{ mAh/g}$$

Assuming that titanium is inactive and present as Ti^{+3}, the other four metals must contribute a total of 6.2 e^- per formula unit of $(Ti_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2})_3O_4$ with molecular weight 236.052 g/mol, thus

$$C_{HEOS} = 6.2 \cdot F / 236.052 = 703.9 \text{ mAh/g}$$

2. Details of Powder X-Ray Diffraction Data Fitting

Table S1: Pawley refinement parameters for HEOR [Fm-3m] and HEOS [Fd-3m].

	Refinement Residuals			Cell Parameters			Particle Size [nm]
Sample	**W_R [%]**	**R χ^2**	**GOF**	**a [Å]**	**V [Å^3]**	**d [g/cm^3]**	
HEOR	8.58	2.07	1.44	4.23 ± 0.01	76.07 ± 0.01	6.54	-
HEOR nano	4.89	2.45	1.56	4.23 ± 0.01	75.81 ± 0.01	6.56	158
HEOS	8.62	1.78	1.34	8.41 ± 0.01	596.06 ± 0.01	5.30	-
HEOS nano	5.61	2.59	1.61	8.41 ± 0.01	595.07 ± 0.01	5.31	149

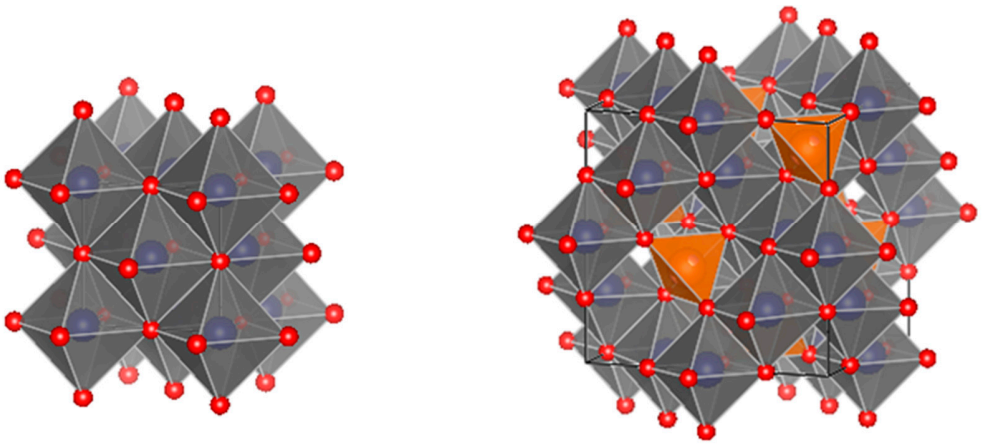

Figure S1: LEFT: Rock salt [Fm-3m] and RIGHT: spinel [Fd-3m] structures. The atoms in blue represent the octahedral positions on both structures, while the atoms in orange represent the tetrahedral position on the spinel.

Table S2: Comparison of various rock salt and spinel lattice parameters with HEOR and HEOS arranged in order of increasing lattice parameter.

Material	Rock Salt Lattice Parameter (Å)	Spinel Lattice Parameter (Å)	Reference
NiO	4.178		[32]
MgO	4.217		[32]
HEOR	4.23		This work
CoO	4.263		[32]
ZnO	4.270		[33]
FeO	4.326		[34]
Co_3O_4		8.085	[35]
Fe_3O_4		8.394	[36]
HEOS		8.41	This work
Fe_2ZnO_4		8.442	[37]
Co_2TiO_4		8.444	[38]
Zn_2TiO_4		8.470	[39]

3. Comparison of cyclic voltammetry curves

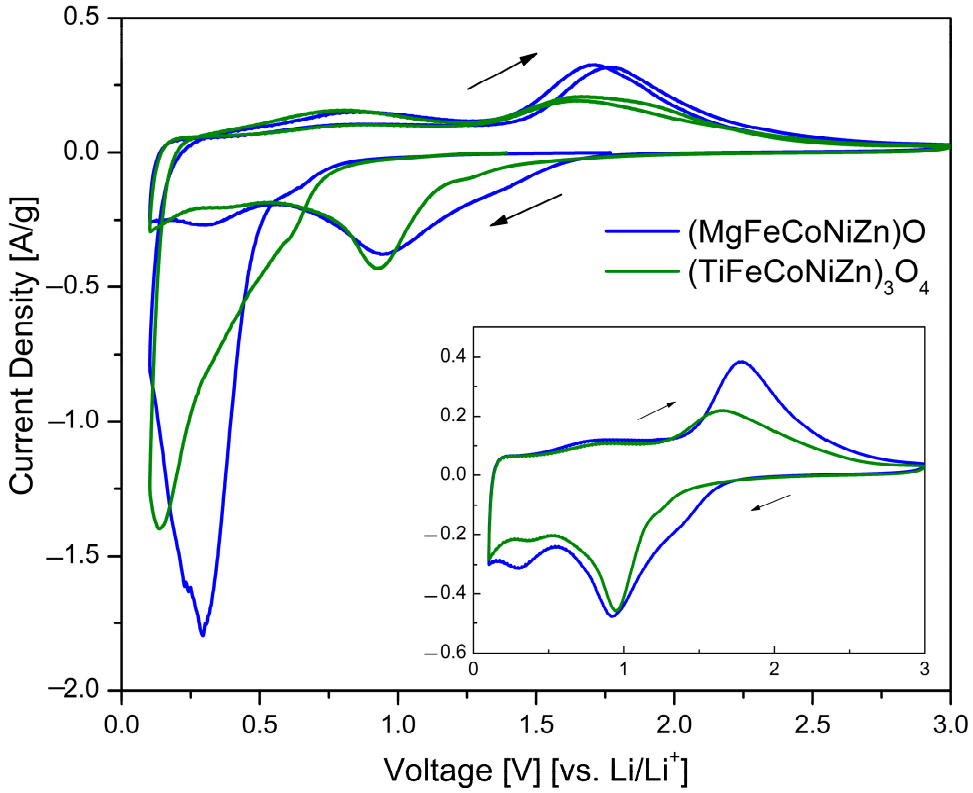

Figure S2: Cyclic-voltammetry at 0.2 mV/s/ for 1st and 2nd cycles of HEOF (in blue) and HS (in green) electrodes. The figure inset shows the 2nd cycle alone.

4. XANES comparisons with standards and cycling states of charge

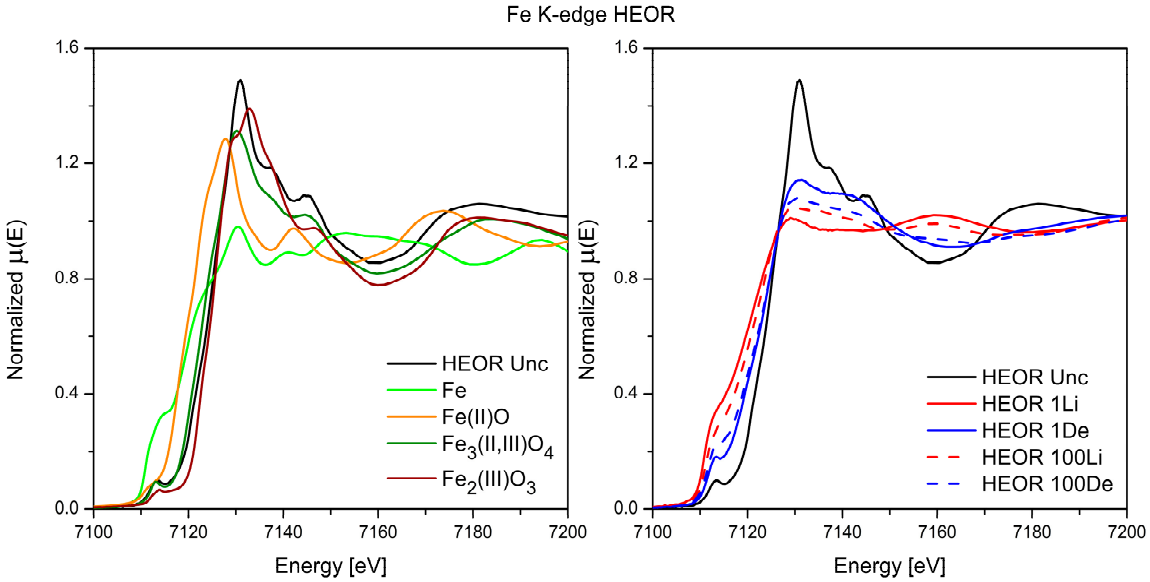

Figure S3: Fe K-edge XANES for OCV HEOR electrode (black) compared to LEFT: standard reference samples Fe (green), FeO (orange), Fe_3O_4 (olive) and Fe_2O_3 (brown); and RIGHT: electrodes at various states of cycle and charge 1st lithiation (solid red), 1st delithiation (solid blue), 100th lithiation (dashed red), and 100th delithiation (dashed blue).

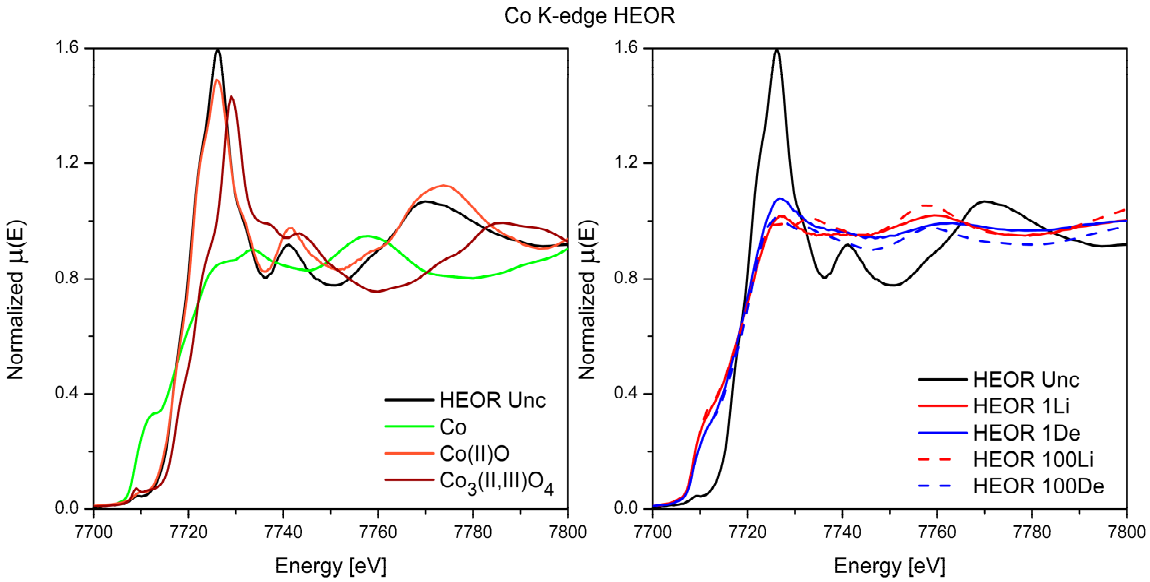

Figure S4: Co K-edge XANES for OCV HEOR electrode (black) compared to LEFT: standard reference samples Co (green), CoO (orange), and Co_3O_4 (brown); and RIGHT: electrodes at various states of cycle and charge 1st lithiation (solid red), 1st delithiation (solid blue), 100th lithiation (dashed red), and 100th delithiation (dashed blue).

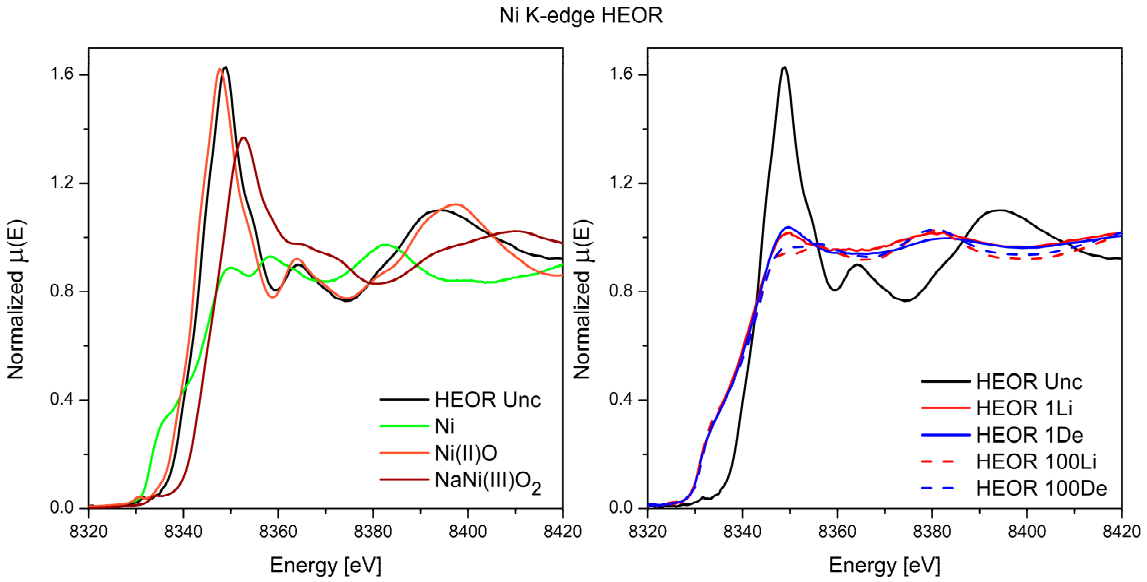

Figure S5: Ni K-edge XANES for OCV HEOR electrode (black) compared to LEFT: standard reference samples Ni (green), NiO (orange), and $NaNiO_2$ (brown); and RIGHT: electrodes at various states of cycle and charge 1st lithiation (solid red), 1st delithiation (solid blue), 100th lithiation (dashed red), and 100th delithiation (dashed blue).

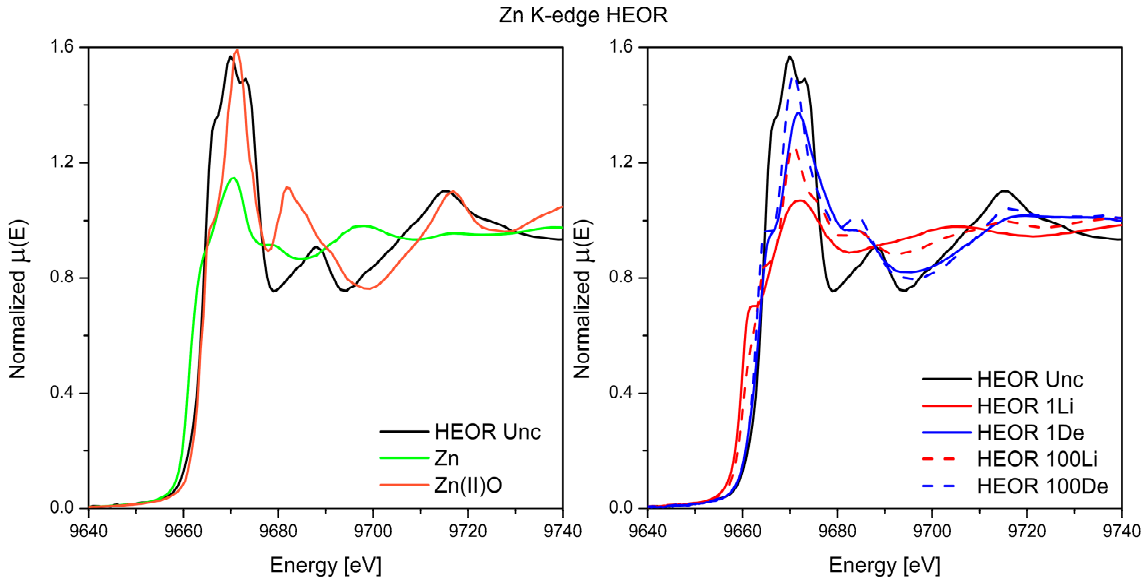

Figure S6: Zn K-edge XANES for OCV HEOR electrode (black) compared to LEFT: standard reference samples Zn (green) and ZnO (orange); and RIGHT: electrodes at various states of cycle and charge 1st lithiation (solid red), 1st delithiation (solid blue), 100th lithiation (dashed red), and 100th delithiation (dashed blue).

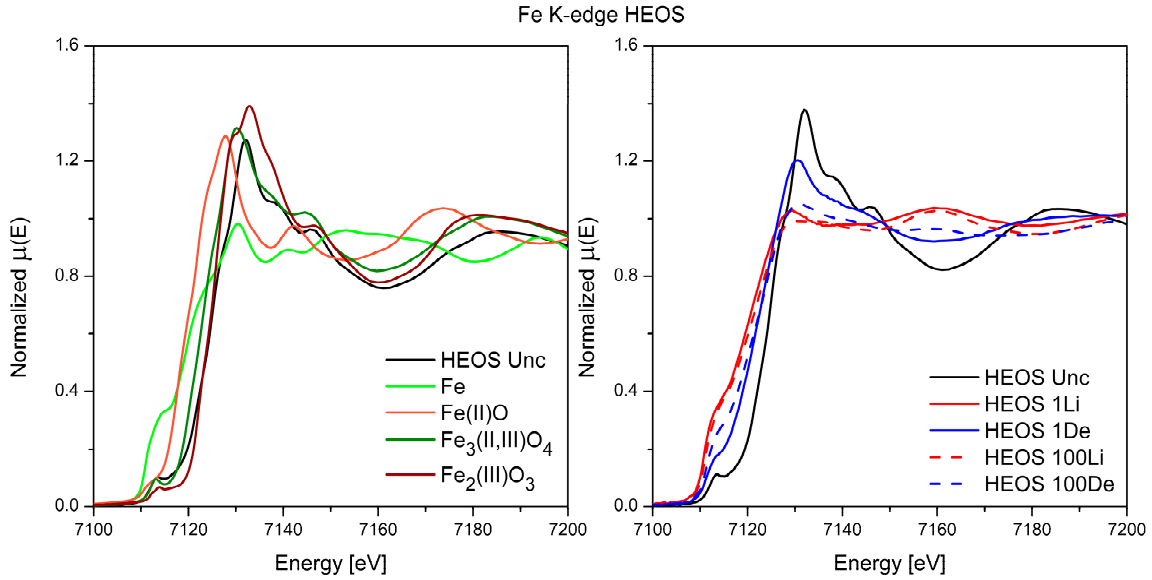

Figure S7: Fe K-edge XANES for OCV HEOS electrode (black) compared to LEFT: standard reference samples Fe (green), FeO (orange), Fe_3O_4 (olive) and Fe_2O_3 (brown); and RIGHT: electrodes at various states of cycle and charge 1st lithiation (solid red), 1st delithiation (solid blue), 100th lithiation (dashed red), and 100th delithiation (dashed blue).

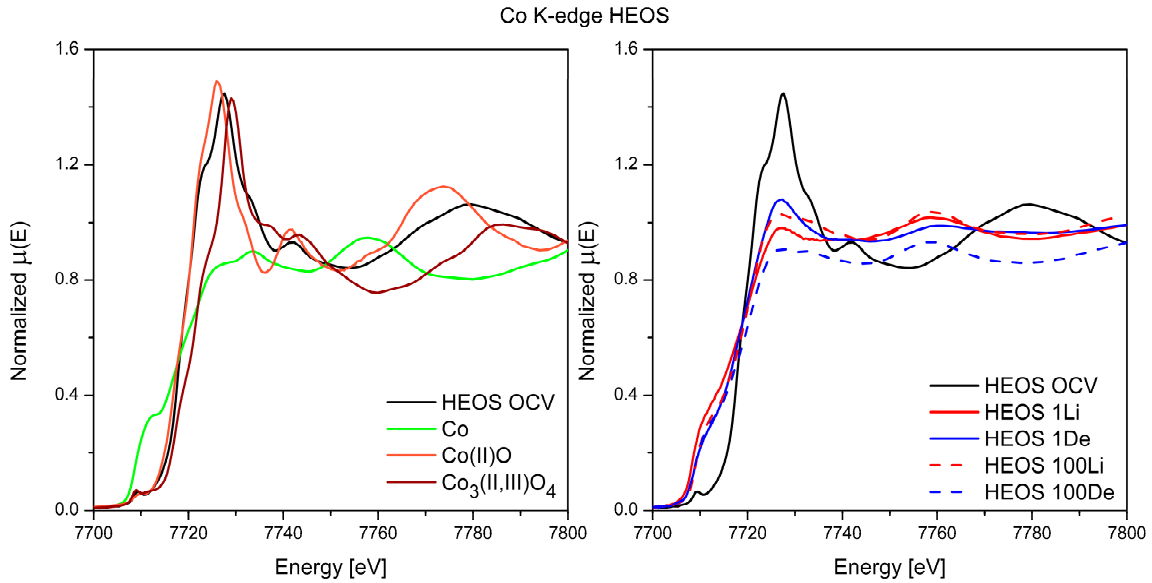

Figure S8: Co K-edge XANES for OCV HEOS electrode (black) compared to LEFT: standard reference samples Co (green), CoO (orange), and Co_3O_4 (brown); and RIGHT: electrodes at various states of cycle and charge 1st lithiation (solid red), 1st delithiation (solid blue), 100th lithiation (dashed red), and 100th delithiation (dashed blue).

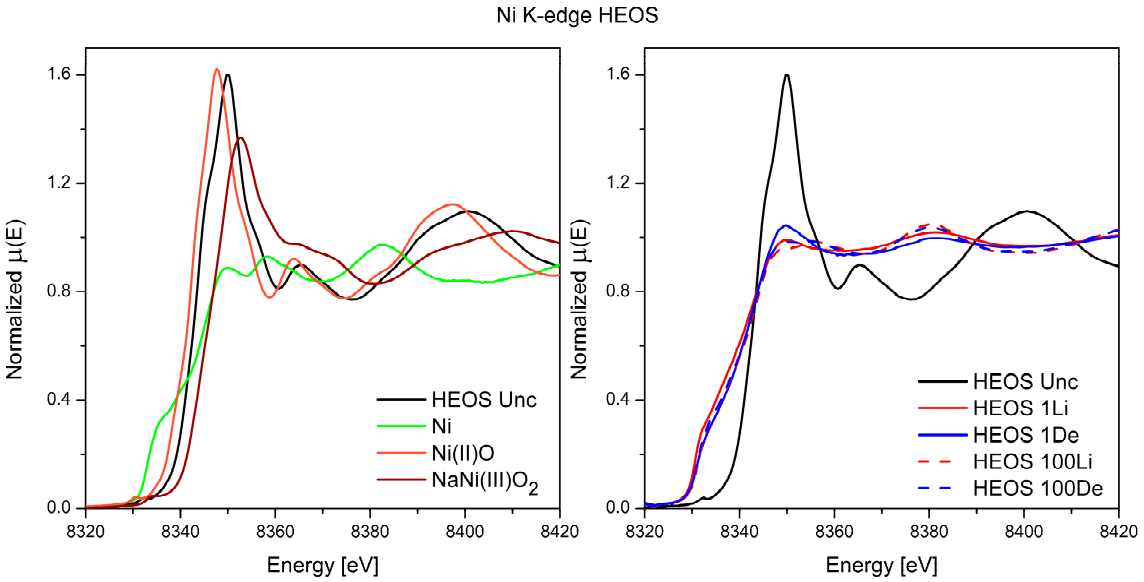

Figure S9: Ni K-edge XANES for OCV HEOS electrode (black) compared to LEFT: standard reference samples Ni (green), NiO (orange), and $NaNiO_2$ (brown); and RIGHT: electrodes at various states of cycle and charge 1st lithiation (solid red), 1st delithiation (solid blue), 100th lithiation (dashed red), and 100th delithiation (dashed blue).

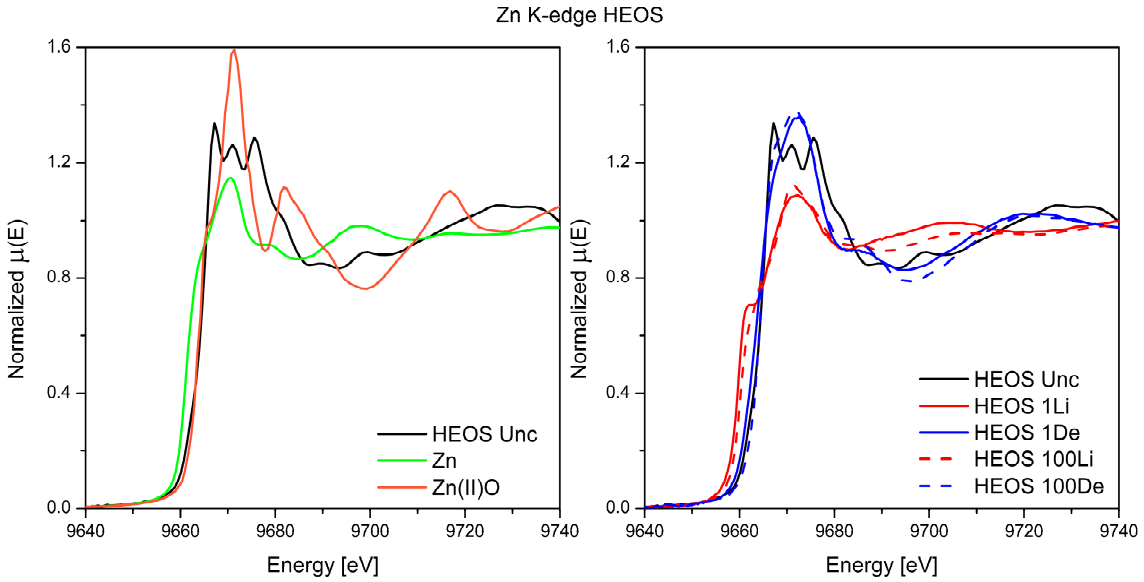

Figure S10: Zn K-edge XANES for OCV HEOS electrode (black) compared to LEFT: standard reference samples Zn (green) and ZnO (orange); and RIGHT: electrodes at various states of cycle and charge 1st lithiation (solid red), 1st delithiation (solid blue), 100th lithiation (dashed red), and 100th delithiation (dashed blue).

5. Details of EXAFS and fitting

The data were fitted using a TM-O path and a TM-M path. Because the metal nearest neighbors are effectively indistinguishable from each other, the Ni atom was used as the generic M in the fits. The fits were performed with k-weight = 2 using Hanning windows with 2 $Å^{-1}$ < k < 10 $Å^{-1}$ (dk = 2) and 1 Å < R < 3 Å (dR = 0.2). The amplitude reduction factors (S_0^2) used in the fits were calculated from fits of standard reference foils (Fe, Co, Ni, and Zn) measured during the same experimental session and held constant. The values differ between data sets because of slightly different beamline setups from one session to the next.

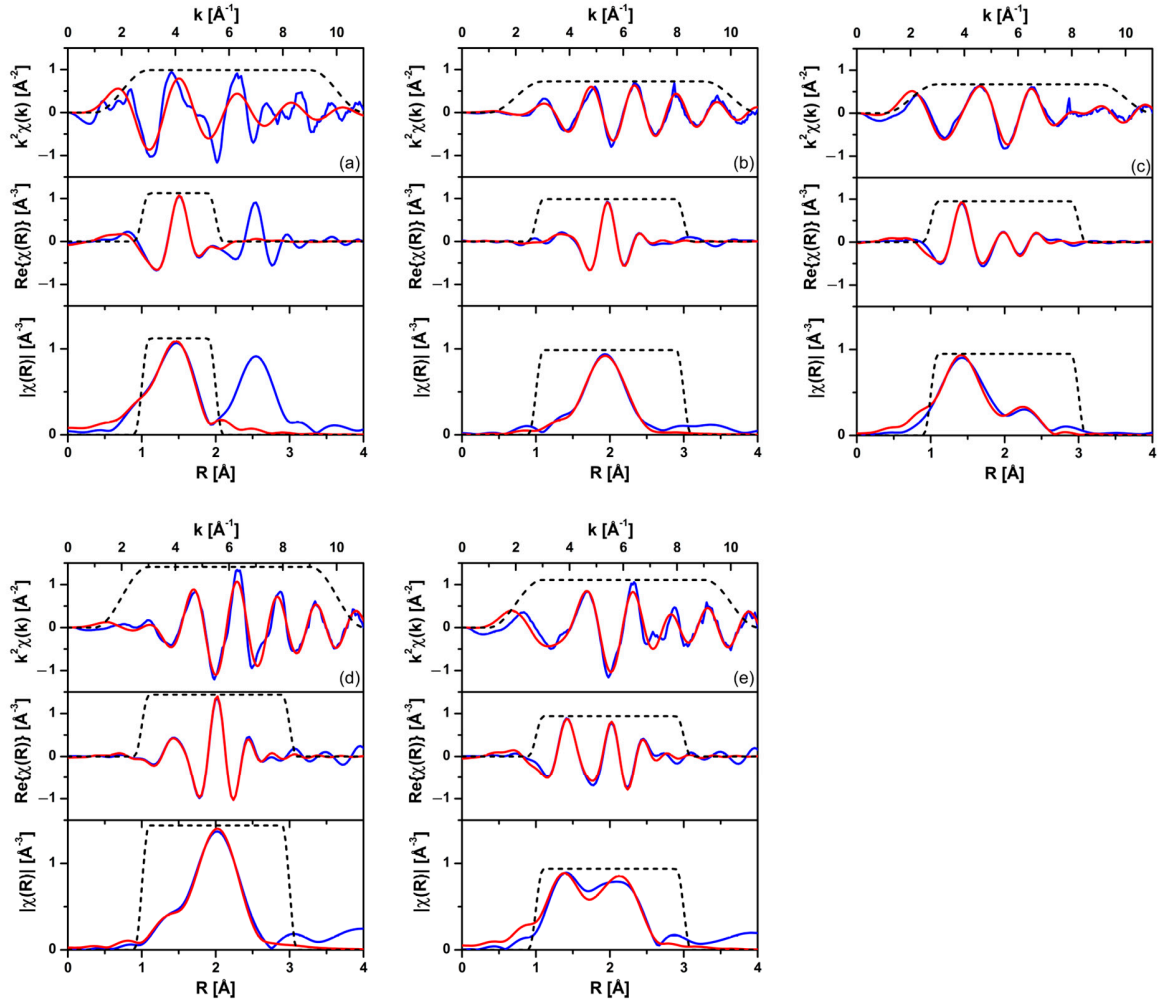

Fig S11: EXAFS fits for the Fe K-edge of the HEOR electrode: (a) Uncycled electrode, (b) 1st lithiation, (c) 1st delithiation, (d) 100th lithiation, and (e) 100th delithiation showing experimental data (blue), fit (red), and windows (black). Bottom panel is the magnitude of the Fourier Transform, middle panel is the real part of the Fourier Transform, and top panel is the k^2-weighted EXAFS.

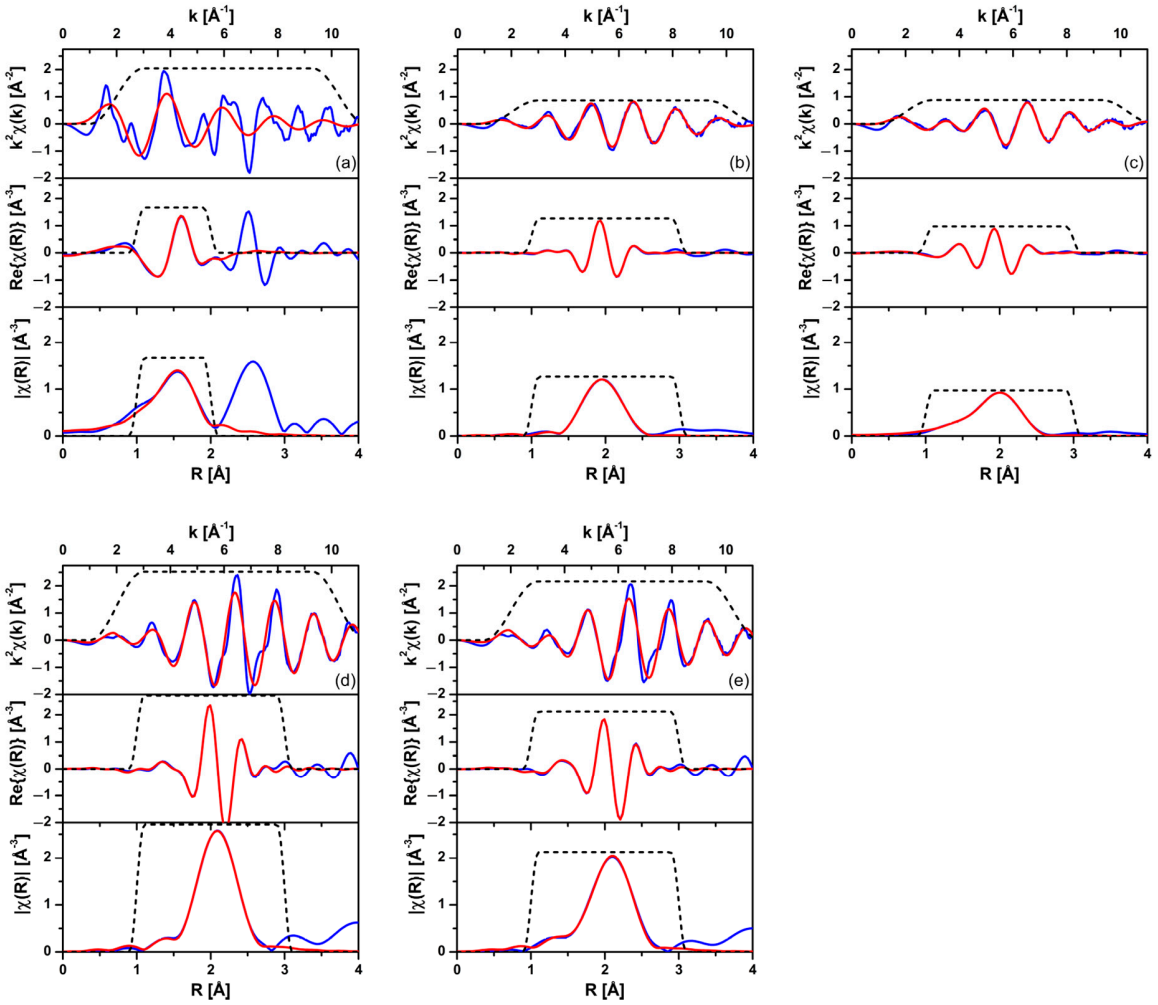

Fig S12: EXAFS fits for the Co K-edge of the HEOR electrode: (a) Uncycled electrode, (b) 1st lithiation, (c) 1st delithiation, (d) 100th lithiation, and (e) 100th delithiation showing experimental data (blue), fit (red), and windows (black). Bottom panel is the magnitude of the Fourier Transform, middle panel is the real part of the Fourier Transform, and top panel is the k^2-weighted EXAFS.

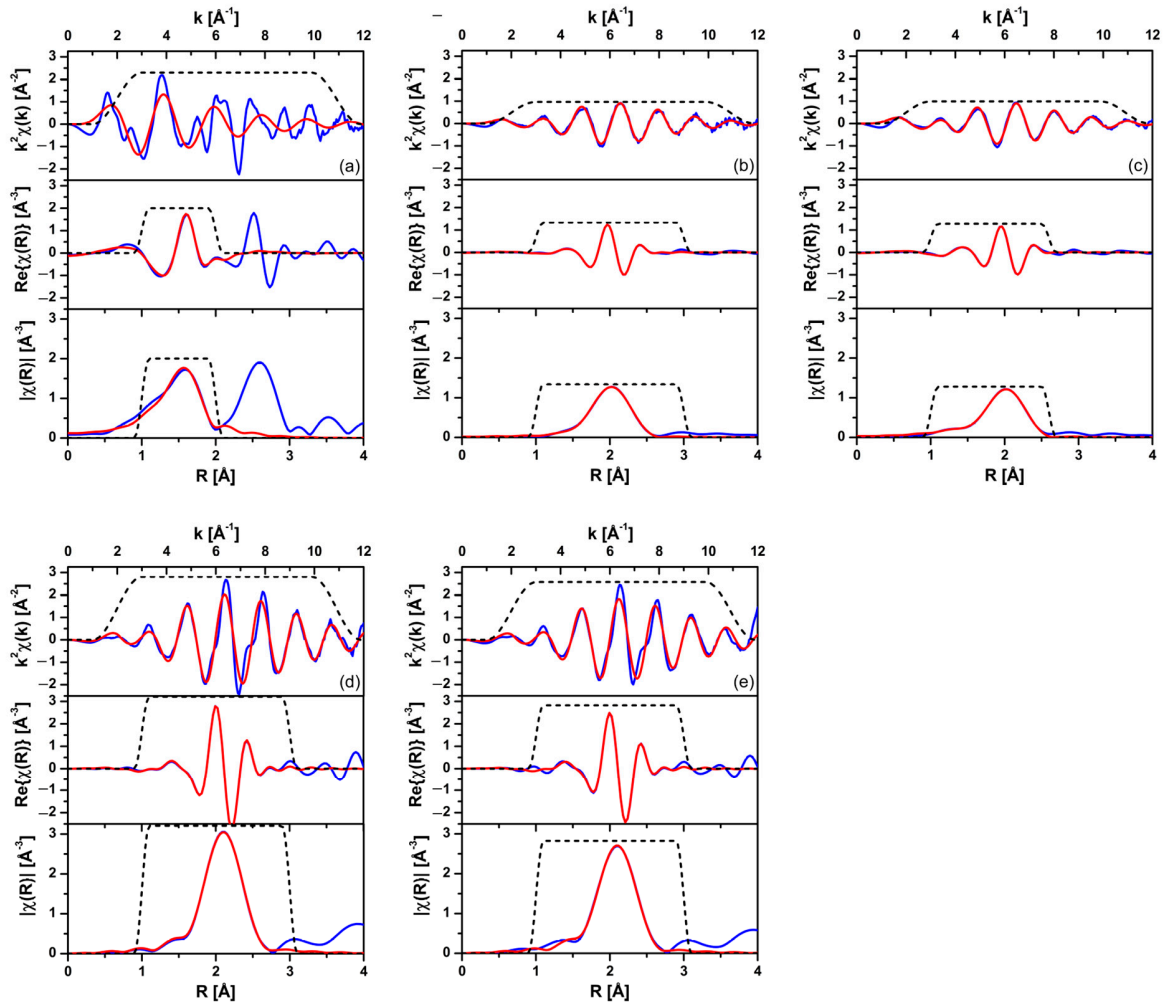

Fig S13: EXAFS fits for the Ni K-edge of the HEOR electrode: (a) Uncycled electrode, (b) 1st lithiation, (c) 1st delithiation, (d) 100th lithiation, and (e) 100th delithiation showing experimental data (blue), fit (red), and windows (black). Bottom panel is the magnitude of the Fourier Transform, middle panel is the real part of the Fourier Transform, and top panel is the k^2-weighted EXAFS.

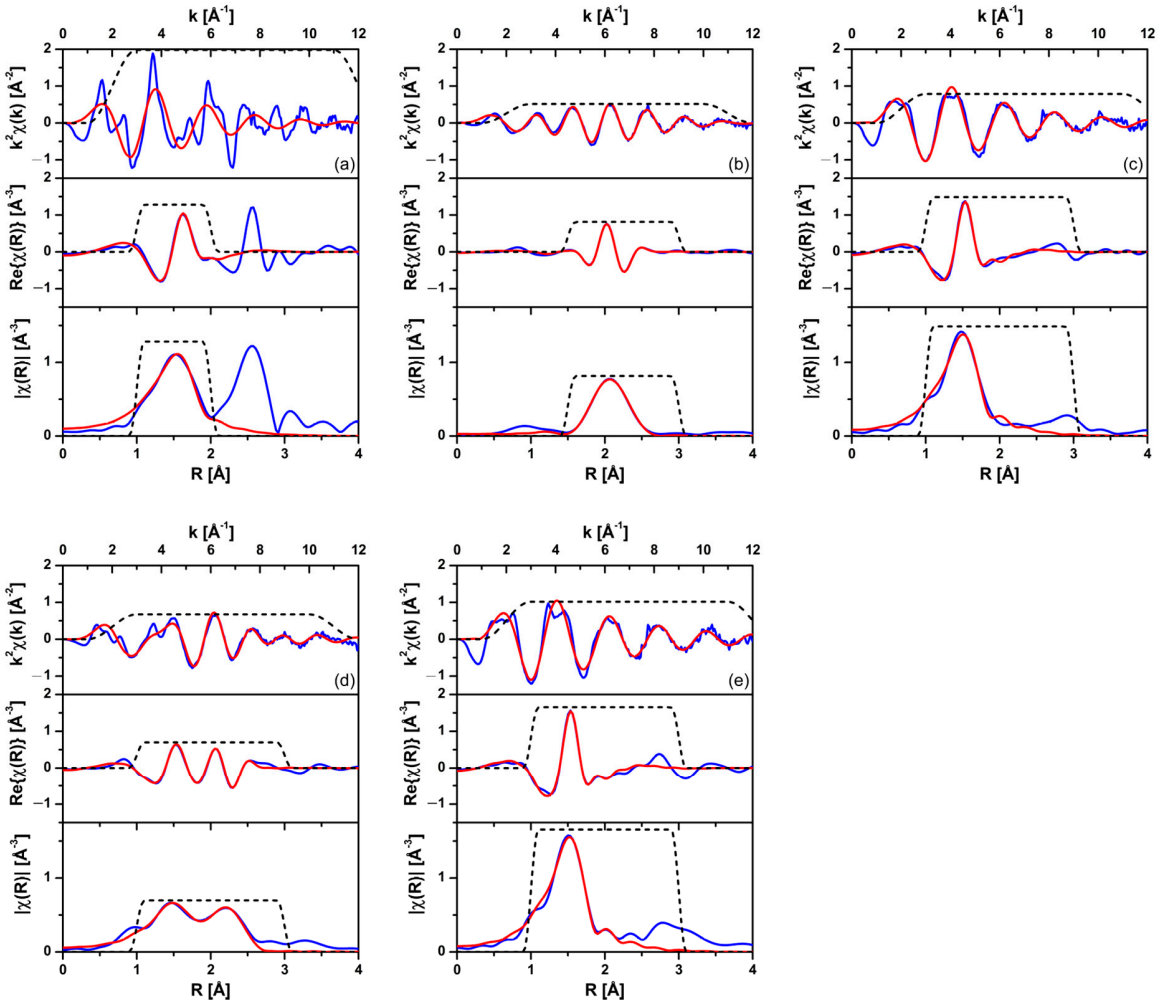

Fig S14: EXAFS fits for the Zn K-edge of the HEOR electrode: (a) Uncycled electrode, (b) 1st lithiation, (c) 1st delithiation, (d) 100th lithiation, and (e) 100th delithiation showing experimental data (blue), fit (red), and windows (black). Bottom panel is the magnitude of the Fourier Transform, middle panel is the real part of the Fourier Transform, and top panel is the k^2-weighted EXAFS.

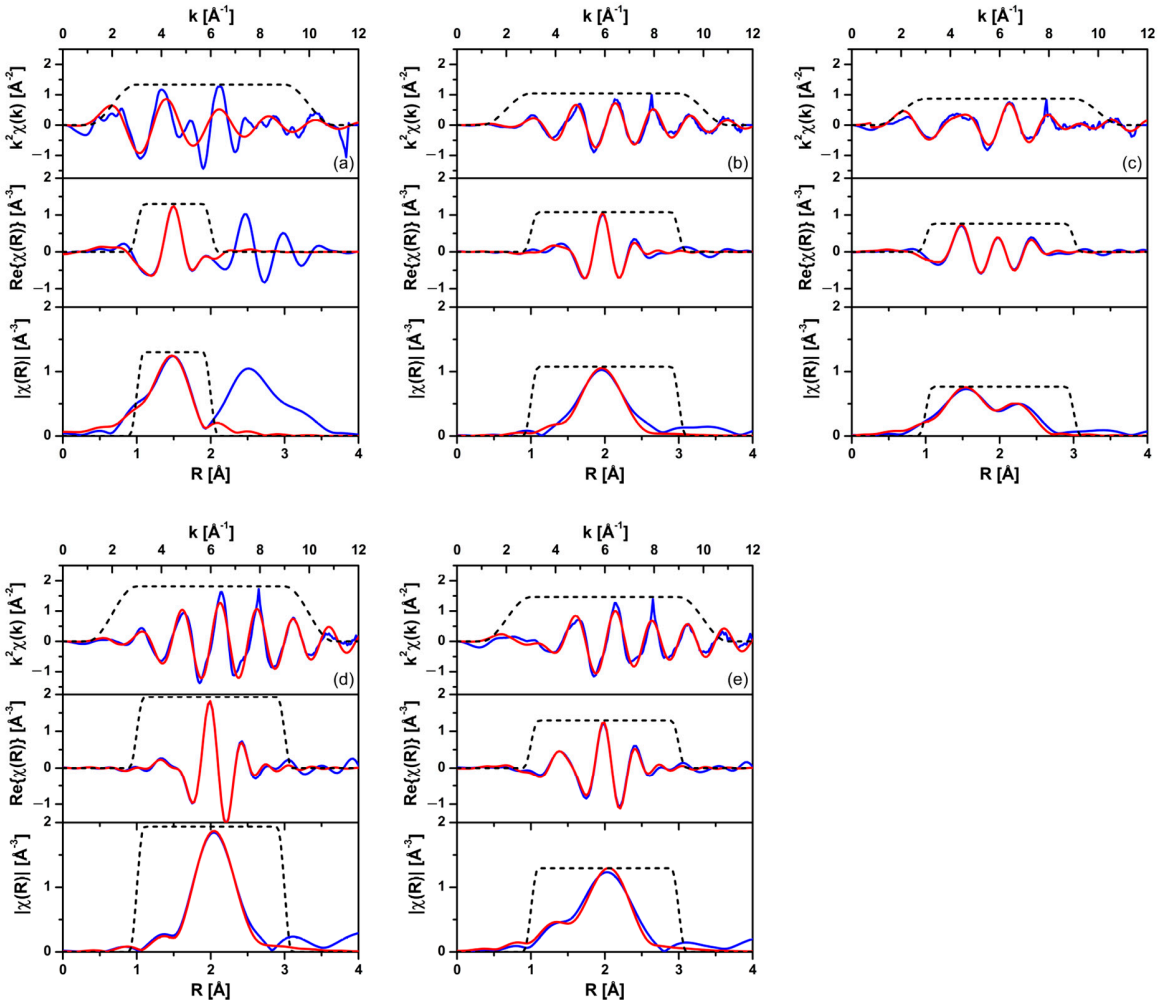

Fig S15: EXAFS fits for the Fe K-edge of the HEOS electrode: (a) Uncycled electrode, (b) 1st lithiation, (c) 1st delithiation, (d) 100th lithiation, and (e) 100th delithiation showing experimental data (blue), fit (red), and windows (black). Bottom panel is the magnitude of the Fourier Transform, middle panel is the real part of the Fourier Transform, and top panel is the k^2-weighted EXAFS.

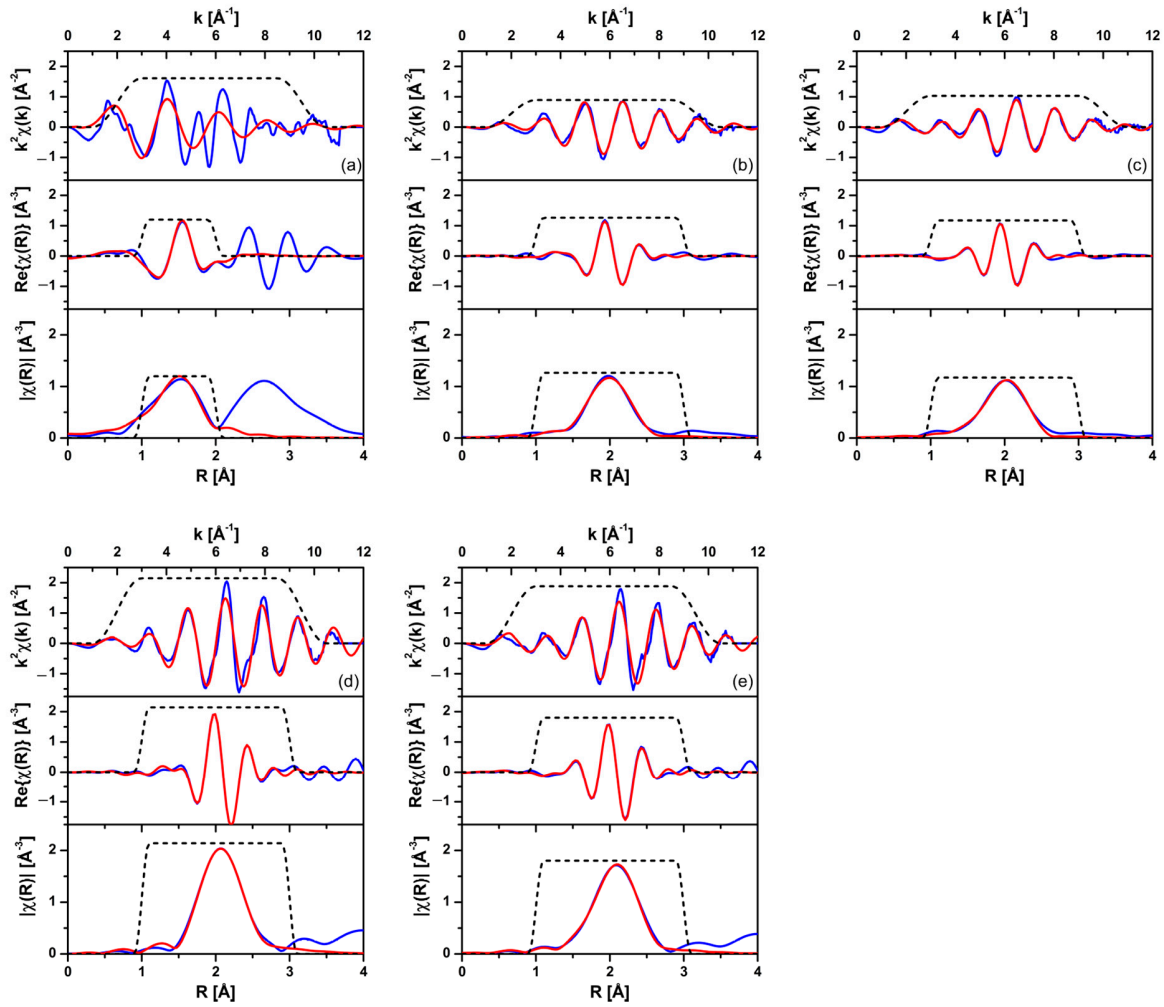

Fig S16: EXAFS fits for the Co K-edge of the HEOS electrode: (a) Uncycled electrode, (b) 1st lithiation, (c) 1st delithiation, (d) 100th lithiation, and (e) 100th delithiation showing experimental data (blue), fit (red), and windows (black). Bottom panel is the magnitude of the Fourier Transform, middle panel is the real part of the Fourier Transform, and top panel is the k^2-weighted EXAFS.

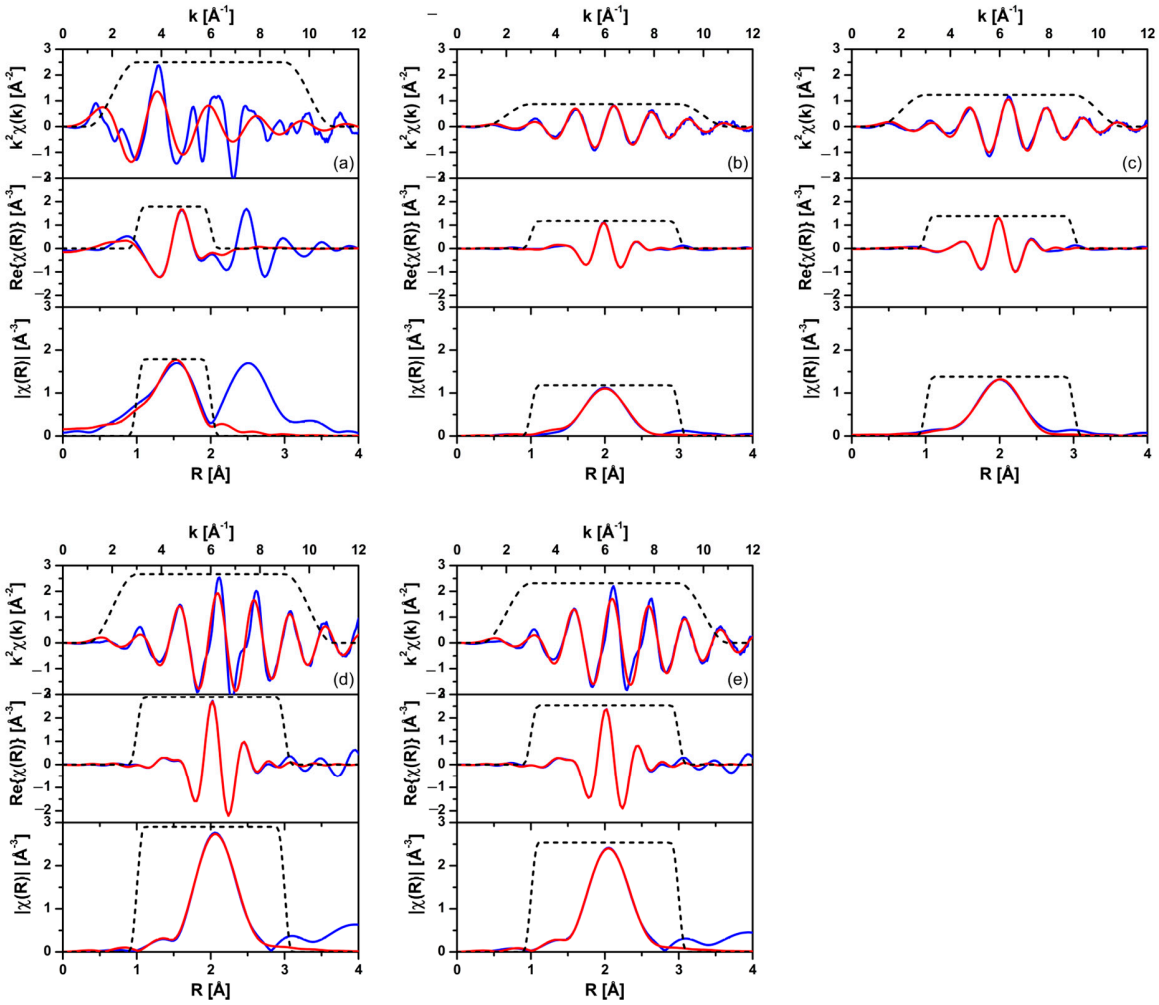

Fig S17: EXAFS fits for the Ni K-edge of the HEOS electrode: (a) Uncycled electrode, (b) 1st lithiation, (c) 1st delithiation, (d) 100th lithiation, and (e) 100th delithiation showing experimental data (blue), fit (red), and windows (black). Bottom panel is the magnitude of the Fourier Transform, middle panel is the real part of the Fourier Transform, and top panel is the k^2-weighted EXAFS.

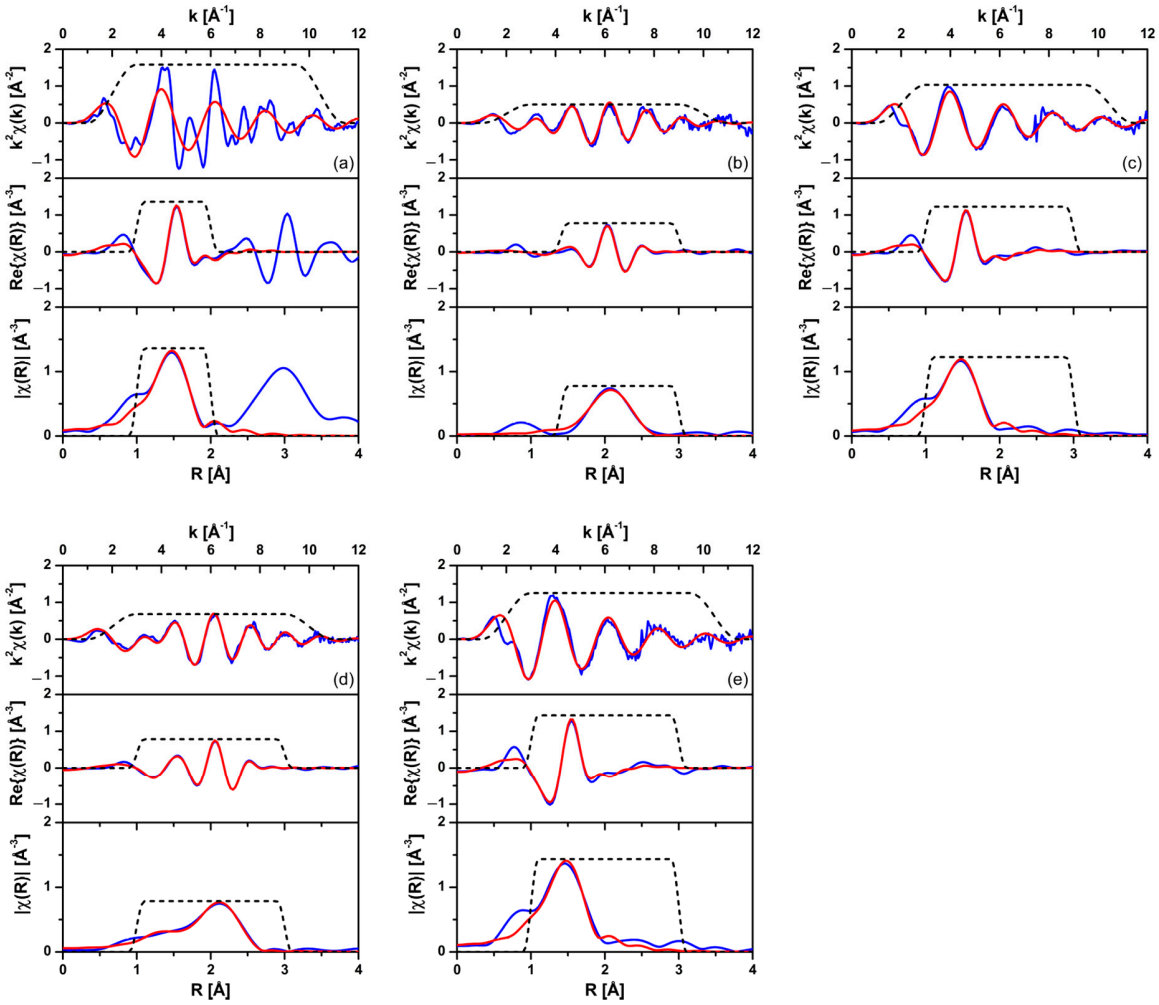

Fig S18: EXAFS fits for the Zn K-edge of the HEOS electrode: (a) Uncycled electrode, (b) 1st lithiation, (c) 1st delithiation, (d) 100th lithiation, and (e) 100th delithiation showing experimental data (blue), fit (red), and windows (black). Bottom panel is the magnitude of the Fourier Transform, middle panel is the real part of the Fourier Transform, and top panel is the k^2-weighted EXAFS.

Table S3: Bond length and number of near neighbors fit results for Fe, Co, Ni, and Zn K-edge fits for HEOR TM–O and TM–M models. The empty cells indicate that the specific path was not used in the fit.

EXAFS Fitting Models			TM–O			TM–M		
Element	(S_0^2)	State	R (Å)	N	$\sigma^2 \times 10^3$ (Å^2)	R (Å)	N	$\sigma^2 \times 10^3$ (Å^2)
Fe	0.65	OCV	1.97 ± 0.01	4.4 ± 0.6	6.5 ± 2.0	-	-	-
	0.72	1Li	-	-	-	2.43 ± 0.01	3.9 ± 0.5	9.3 ± 1.3
	0.72	1De	1.90 ± 0.02	2.6 ± 0.5	4.4 ± 2.9	2.50 ± 0.02	1.4 ± 0.8	7.2 ± 5.7
	0.65	100Li	1.89 ± 0.03	0. 8 ± 0.5	1.9 ± 7.0	2.49 ± 0.01	5.4 ± 0.7	6.6 ± 1.3
	065	100De	1.89 ± 0.03	2.5 ± 0.7	3.5 ± 4.0	2.51 ± 0.02	3.2 ± 1.0	5.6 ± 2.9
Co	0.75	OCV	2.07 ± 0.01	5.9 ± 0.6	8.6 ± 1.9	-	-	-
	0.75	1Li	1.97 ± 0.02	0.3 ± 0.3	5.0 ± 6.8	2.40 ± 0.01	6.5 ± 0.9	13.6 ± 1.5
	0.75	1De	1.93 ± 0.01	0.9 ± 0.3	2.9 ± 3.0	2.43 ± 0.01	5.0 ± 0.6	12.6 ± 1.1
	0.75	100Li	-	-	-	2.48 ± 0.01	8.3 ± 0.5	7.2 ± 0.5
	0.75	100De	1.96 ± 0.3	0.8 ± 0.5	5.4 ± 9.0	2.48 ± 0.01	7.0 ± 0.7	7.8 ± 0.5
Ni	0.78	OCV	2.06 ± 0.01	6.6 ± 0.8	6.7 ± 2.0	-	-	
	0.78	1Li	2.02 ± 0.06	0.6 ± 0.8	13.3 ± 2.0	2.44 ± 0.01	6.9 ± 0.7	12.5 ± 0.9
	0.75	1De	1.97 ± 0.03	1.5 ± 1.1	19.0 ± 1.5	2.42 ± 0.02	6.9 ± 0.6	12.6 ± 0.9
	0.78	100Li	-	-	-	2.49 ± 0.01	10.7 ± 0.5	8.0 ± 0.3
	0.75	100De	-	-	-	2.48 ± 0.01	10.7 ± 0.8	8.6 ±0.6
Zn	0.76	OCV	2.05 ± 0.01	4.7 ± 0.6	9.5 ± 2.0	-	-	-
	0.72	1Li	2.09 ± 0.02	0.5 ± 0.4	2.0 ± 0.8	2.45 ± 0.01	9.0 ± 1.0	19.7 ± 1.5
	0.76	1De	1.96 ± 0.01	3.9 ± 0.5	5.0 ± 2.0	-	-	-
	0.82	100Li	1.96 ± 0.02	1.8 ± 0.4	6.9 ±3.0	2.53 ± 0.02	4.6 ± 1.3	15.3 ± 3.2
	0.76	100De	1.97 ± 0.01	4.0 ± 0.6	4.2 ± 2.0	-	-	-

Table S4: Bond length and number of near neighbors fit results for Fe, Co, Ni, and Zn K-edge fits for HEOS TM–O and TM–M models. The empty cells indicate that the specific path was not used in the fit.

EXAFS Fitting Models			TM–O			TM–M		
Element	(S_0^2)	State	R (Å)	N	$\sigma^2 \times 10^3$ (Å^2)	R (Å)	N	$\sigma^2 \times 10^3$ (Å^2)
Fe	0.72	OCV	1.97 ± 0.01	4.2 ± 0.5	4.9 ± 1.6	-	-	-
	0.72	1Li	-	-	-	2.44 ± 0.01	4.1 ± 0.1	8.4 ± 4.6
	0.72	1De	1.98 ± 0.02	2.1 ± 0.5	2.7 ± 3.0	2.52 ± 0.02	1.8 ± 0.8	2.7 ± 3.0
	0.57	100Li	-	-	-	2.49 ± 0.01	7.0 ± 0.6	5.6 ± 0.7
	0.57	100De	1.87 ± 0.03	1.4 ± 0.8	4.6 ± 8.0	2.48 ± 0.01	4.6 ± 0.9	4.8 ± 1.9
Co	0.67	OCV	2.02 ± 0.02	5.6 ± 1.5	8.5 ± 4.8	-	-	-
	0.67	1Li	-	-	-	2.43 ± 0.01	6.5 ± 0.9	11.8 ± 1.5
	0.67	1De	1.97 ± 0.03	0.7 ± 0.6	6.0 ± 8.0	2.45 ± 0.02	5.2 ± 1.2	10.1 ± 2.3
	0.72	100Li	-	-	-	2.48 ± 0.01	7.0 ± 0.8	6.7 ± 1.0
	0.72	100De	2.01 ± 0.04	0.8 ± 0.7	9.4 ± 11.1	2.49 ± 0.02	6.7 ± 1.3	8.1 ± 2.0
Ni	0.75	OCV	2.05 ± 0.02	7.6 ± 1.3	7.3 ± 2.7	-	-	-
	0.75	1Li	-	-	-	2.45 ± 0.01	6.3 ± 0.6	11.9 ± 0.9
	0.75	1De	1.95 ± 0.05	0.6 ± 0.6	1.3 ± 1.3	2.45 ± 0.01	6.9 ± 1.5	11.0 ± 2.0
	0.74	100Li	-	-	-	2.49 ± 0.01	11.1 ± 0.8	8.1 ± 0.6
	0.74	100De	-	-	-	2.48 ± 0.01	10.3 ± 0.7	8.7 ± 0.6
Zn	0.79	OCV	1.96 ± 0.01	3.6 ± 0.6	4.2 ± 2.1	-	-	-
	0.72	1Li	-	-	-	2.47 ± 0.01	8.0 ± 1.3	18.6 ± 1.8
	0.79	1De	1.97 ± 0.01	3.5 ± 0.3	5.3 ± 1.4	-	-	-
	0.82	100Li	1.91 ± 0.02	0.9 ± 0.3	9.6 ± 6.2	2.50 ± 0.01	7.0 ± 0.8	17.1 ± 1.2
	0.79	100De	1.97 0.01	4.7 ± 0.5	6.8 ± 1.7	-	-	-

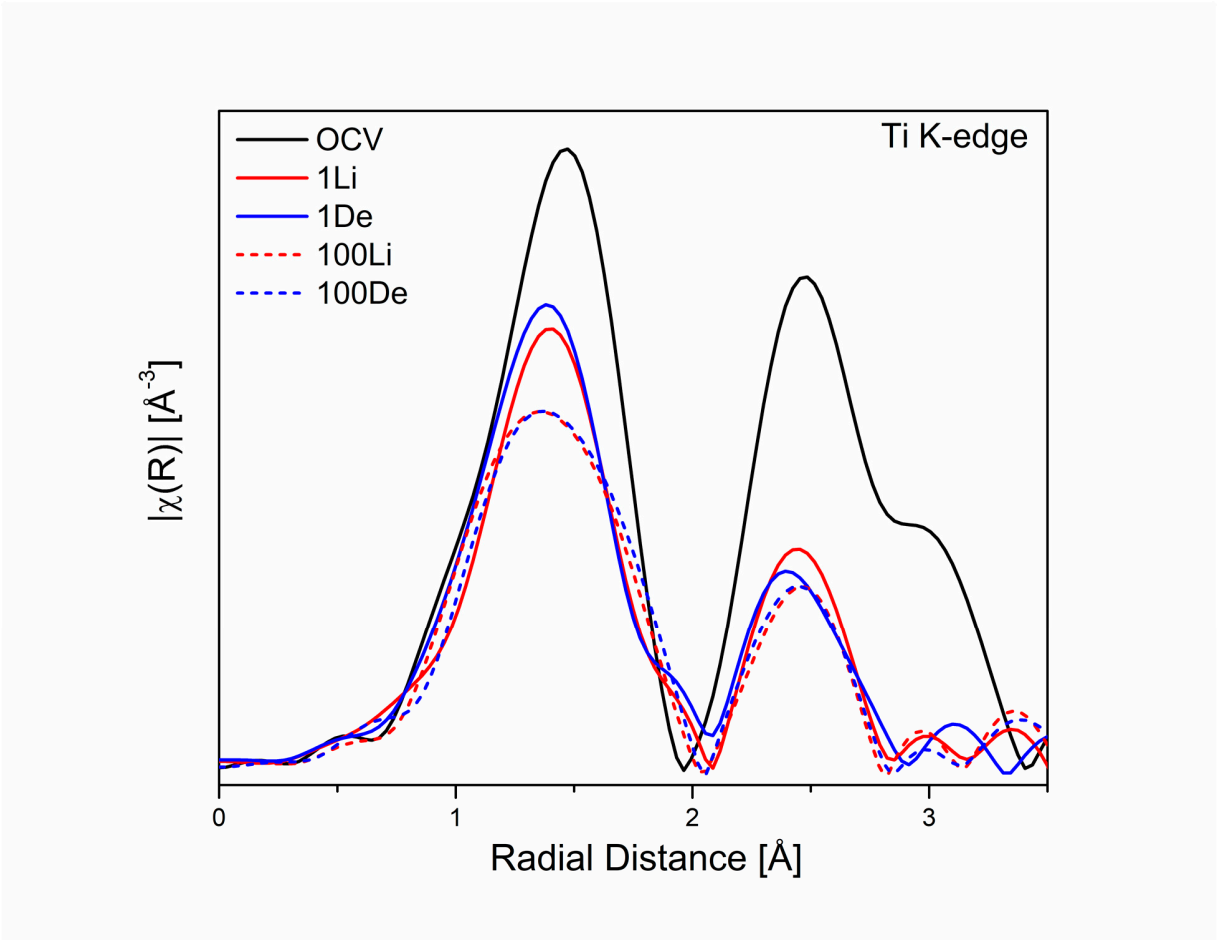

Figure S19: Fourier Transform EXAFS of HEOS electrode Ti K-edge for OCV (black), 1st lithiation (solid red), 1st delithiation (solid blue), 100th lithiation (dashed red), and 100th delithiation (dashed blue).

Table S5: EXAFS fit results for HEOS Ti K-edge.

	OCV	1Li	1De	100Li	100De
N_{Ti-O}	6.9 ± 1.0	5.7 ± 1.2	6.4 ± 1.4	9.7 ± 3.2	9.4 ± 3.4
R_{Ti-O} (Å)	1.95 ± 0.01	1.92 ± 0.02	1.90 ± 0.02	1.93 ± 0.03	1.95 ± 0.04
$\sigma^2_{Ti-O}\times10^3$ (Å^2)	4.6 ± 2.1	7.0 ± 3.5	8.5 ± 3.6	14.0 ± 6.5	13.6 ± 7.2
(S_0^2)	0.47	0.47	0.47	0.35	0.35

6. Calculation of molar capacity

In order to compute the capacity per mole of metal atoms, the specific capacity in mAh/g is multiplied by the molecular weight of the active material for one formula unit of metal atoms

HEOR: $(Mg_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2})O$ with molecular weight 68.635 g/mol, thus the conversion factor to obtain Ah/mol is 0.068635.

HEOS: $(Ti_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2})_3O_4$ with molecular weight 236.052 g/mol and the molecular weight per one formula unit of metal atoms is 236.052/4 = 78.684 g/mol, thus the conversion factor to obtain Ah/mol is 0.078684.

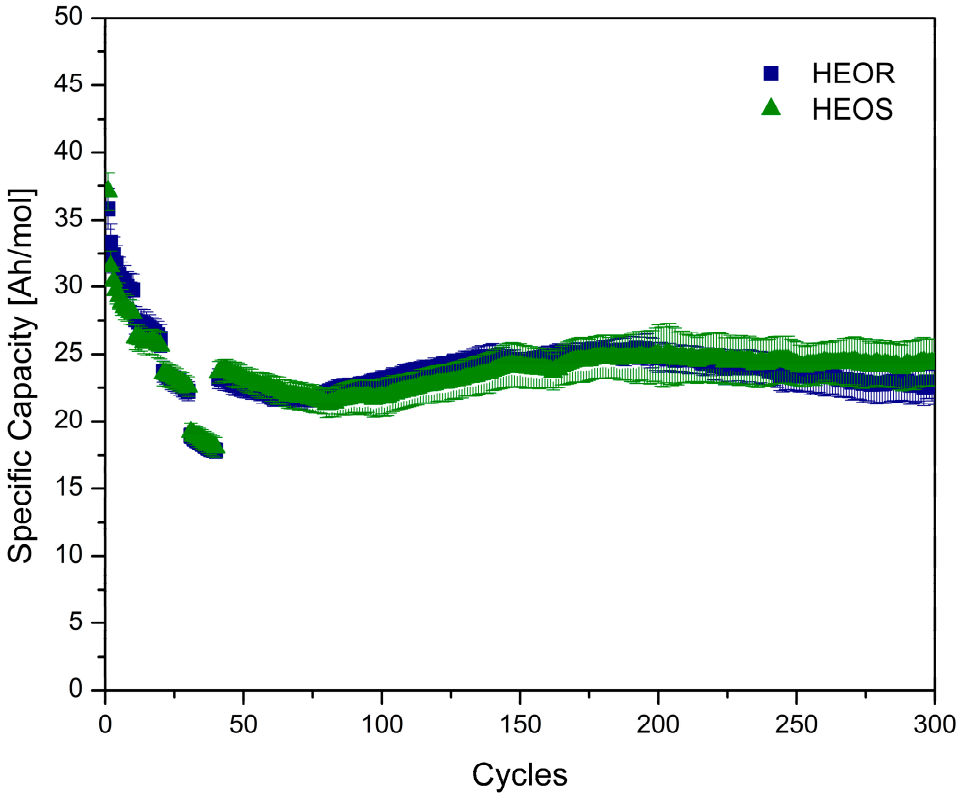

Figure S20: Specific capacity per mole of metal atoms in HEOR and HEOS compounds.