

# On the electrochemical phase evolution of anti-PbO type CoSe in alkali ion batteries

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## S1: Rietveld refinement model parameters

It should be noted that the weight fractions in the below tables differ from those presented in the main paper, as they include all species including electrochemically inactive materials such as carbon black. These were excluded for clarity in the main text.

Table S1: Rietveld refinement model parameters for CoSe versus Li ex-situ experiments. Abbreviations used are as follows. CoSe Hex: Hexagonal CoSe. CoSe Tetr: Tetragonal CoSe. a,b,c: Crystallographic Lattice parameters. wR: Weighted Residual.

	CoSe Hex a (Å)	CoSe Hex b (Å)	CoSe Hex c (Å)	CoSe Hex Phase Fraction	CoSe Tetr a (Å)	CoSe Tetr b (Å)	CoSe Tetr c (Å)	CoSe Tetr Phase Fraction	March- Dollase Ratio	Axis	Li <sub>x</sub> Co <sub>2</sub> Se <sub>2</sub> a (Å)	Li <sub>x</sub> Co <sub>2</sub> Se <sub>2</sub> b (Å)	Li <sub>x</sub> Co <sub>2</sub> Se <sub>2</sub> c (Å)	Li <sub>x</sub> Co <sub>2</sub> Se <sub>2</sub> Phase Fraction	March- Dollase Ratio	Axis	Li <sub>2</sub> Se a, b, c (Å)	Li <sub>2</sub> Se Phase Fraction	Co a (Å)	Co b (Å)	Co c (Å)	Co Phase Fraction	Overall wR	Zero Offset
Parent	3.599(7)	3.599(7)	5.280(8)	0.230(1)	3.712(2)	3.712(2)	5.330(3)	0.770(1)	0.6607	'001													2.96%	-0.00952
3%	3.601(4)	3.601(4)	5.282(5)	0.328(8)	3.709(2)	3.709(2)	5.337(2)	0.672(8)	0.515	'001													2.46%	0.002225
7.50%	3.610(7)	3.610(7)	5.27(1)	0.300(1)	3.657(4)	3.657(4)	5.373(4)	0.350(3)	0.6011	'001	3.695(5)	3.695(5)	5.509(4)	0.360(3)	0.5121	'001							2.71%	-0.04581
20%	3.65(1)	3.65(1)	5.230(8)	0.390(1)	3.687(6)	3.687(6)	5.383(8)	0.350(2)	0.6421	'001	3.73(1)	3.73(1)	5.605(9)	0.260(2)	0.5109	'001							2.65%	-0.04218
60%																	6.003(8)	1.00					6.59%	-0.082
100%																	6.014(4)	0.66(1)	2.513(6)	2.513(6)	4.08(1)	0.34(1)	2.03%	0.063981

Table S2: Rietveld refinement model parameters for CoSe versus K ex-situ experiments. Abbreviations used are as follows. CoSe Hex: Hexagonal CoSe. CoSe Tetr: Tetragonal CoSe. a,b,c: Crystallographic Lattice parameters. wR: Weighted Residual.

	CoSe Tetr a, b (Å)	CoSe Tetr c (Å)	CoSe Phase Fraction	March- Dollase Ratio	Axis	CoSe Hex a, b (Å)	CoSe Hex c (Å)	CoSe Hex Phase Fraction	K <sub>x</sub> Co <sub>2</sub> Se <sub>2</sub> I4/mmm a, b (Å)	K <sub>x</sub> Co <sub>2</sub> Se <sub>2</sub> I4/mmm c	K <sub>x</sub> Co <sub>2</sub> Se <sub>2</sub> I4/mmm Phase Fraction	March- Dollase Ratio	Axis	K <sub>x</sub> Co <sub>2</sub> Se <sub>2</sub> I4m a, b (Å)	K <sub>x</sub> Co <sub>2</sub> Se <sub>2</sub> I4m c (Å)	K <sub>x</sub> Co <sub>2</sub> Se <sub>2</sub> I4m Phase Fraction	March- Dollase Ratio	Axis	K <sub>x</sub> Co <sub>2</sub> Se <sub>2</sub> P4/nmm a, b (Å)	K <sub>x</sub> Co <sub>2</sub> Se <sub>2</sub> P4/nmm c (Å)	K <sub>x</sub> Co <sub>2</sub> Se <sub>2</sub> P4/nmm Phase Fraction	Carbon Black a, b (Å)	Carbon Black c (Å)	Carbon Black Phase Fraction	Zero Offset	wR		
Parent																												
2%	3.705	5.330	0.29(1)	0.695	001	3.561	5.316	0.188(7)	3.775	14.02	0.25(1)	1.717	002	8.86	15.66	0.135(8)	1.376	002				2.72	6.82	0.13(4)	-0.09229	2.04%		
6%	3.705(3)	5.330(2)	0.111(4)	0.5687	001	3.561(6)	5.316(7)	0.091(4)	3.775(6)	14.02(3)	0.43(2)	1.409	002	8.86(4)	15.66(2)	0.001(2)	0.9014	002				2.72(3)	6.82(2)	0.37(3)	0.022406	1.97%		
30%	3.699(3)	5.31(1)	0.55(4)	1.5974	001				3.773(3)	14.03(1)	0.24(2)	0.6688	002						3.842(3)	9.32(2)	0.21(1)					0.025385	3.29%	
70%	3.72(1)	5.33(4)	0.49(3)	0.8561	001				3.80(2)	13.9(1)	0.51(2)	0.672	002													-0.00472	4.52%	

Table S3: Rietveld refinement model parameters for CoSe versus Na ex-situ experiments. Abbreviations used are as follows. CoSe Hex: Hexagonal CoSe. CoSe Tetr: Tetragonal CoSe. a,b,c: Crystallographic Lattice parameters. wR: Weighted Residual. Cu phase fraction was 0.743(3) and  $a = 3.6159(2)$  Å.

	CoSe Hex a (Å)	CoSe Hex b (Å)	CoSe Hex c (Å)	CoSe Hex Phase Fraction	CoSe Tetr a (Å)	CoSe Tetr b (Å)	CoSe Tetr c (Å)	CoSe Tetr Phase Fraction	March- Dollase Ratio	Axis	Na <sub>2</sub> Se a (Å)	Na <sub>2</sub> Se b (Å)	Na <sub>2</sub> Se c (Å)	Na <sub>2</sub> Se Phase Fraction	Na <sub>2</sub> Se <sub>2</sub> a (Å)	Na <sub>2</sub> Se <sub>2</sub> b (Å)	Na <sub>2</sub> Se <sub>2</sub> c (Å)	Na <sub>2</sub> Se <sub>2</sub> Phase Fraction	wR	Zero Offset
Parent																				
2%	3.588(9)	3.588(9)	5.31(1)	0.320(1)	3.709(3)	3.709(3)	5.337(7)	0.680(1)	0.7969	'001									2.16%	0.111567
5%	3.608(6)	3.608(6)	5.251(7)	0.050(3)	3.701(6)	3.701(6)	5.343(4)	0.207(6)	0.6172	001									3.54%	0.036906
50%											6.78(2)	6.78(2)	6.78(2)	44.0(2)%	4.74(7)	4.74(7)	10.47(3)	56.0(2)%	2.29%	-0.11216
100%											6.809(4)	6.809(4)	6.806(4)	100%	5.0(2)	5.0(2)	11.15(1)	0.31(1)	4.72%	-0.05812

## S2: Rietveld Refinement Detailed Plots

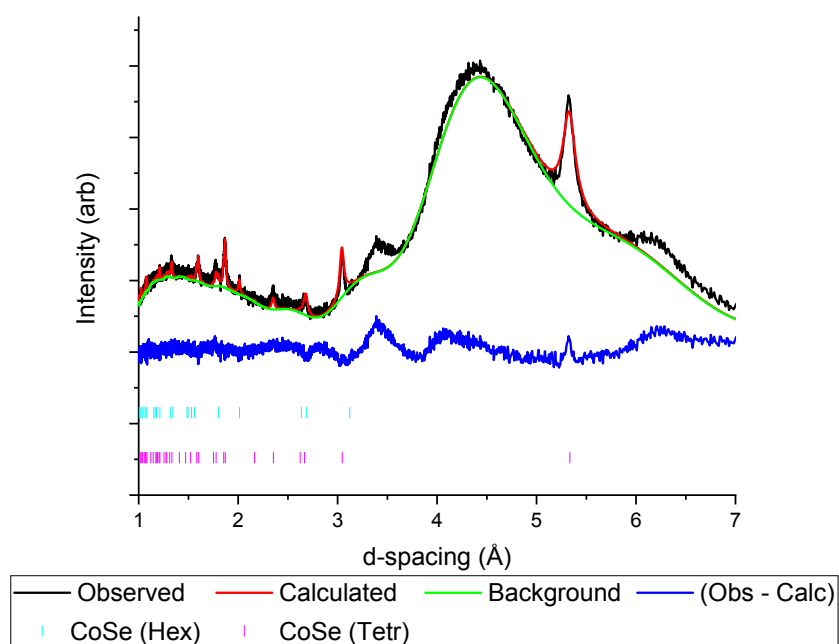


Figure S1: Rietveld analysis of structural models with PXRD data from the CoSe electrode.

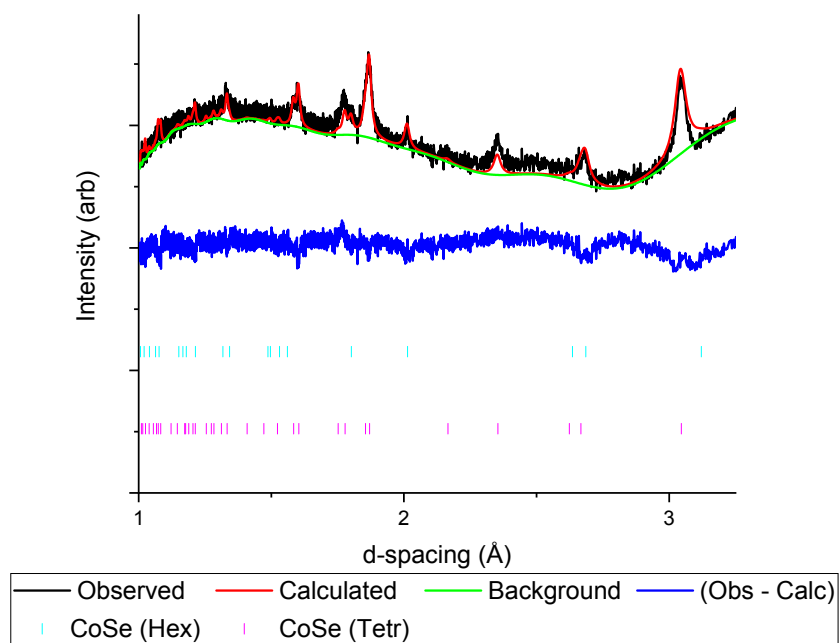


Figure S2: Rietveld analysis of structural models with PXRD data from the CoSe electrode, zoomed to a region of interest.

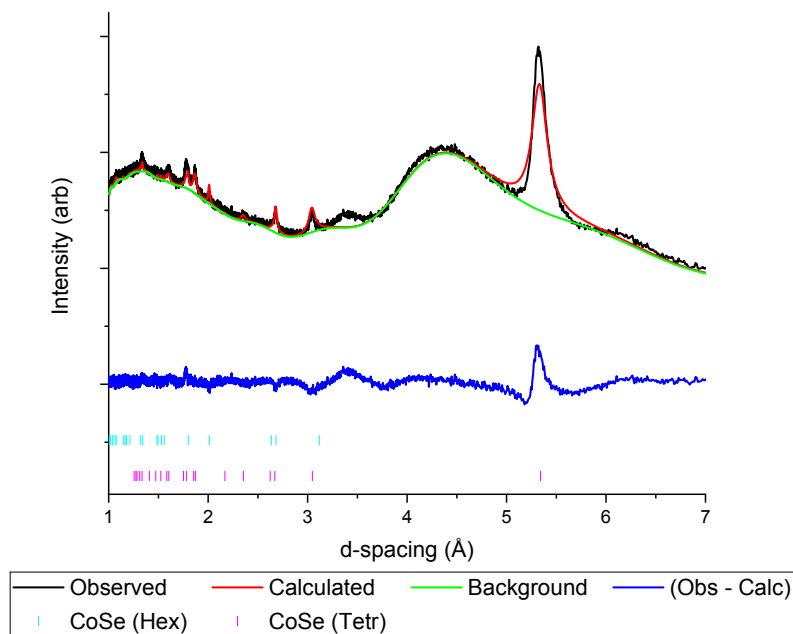


Figure S3: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus Li half cell discharged to 3% of full capacity.

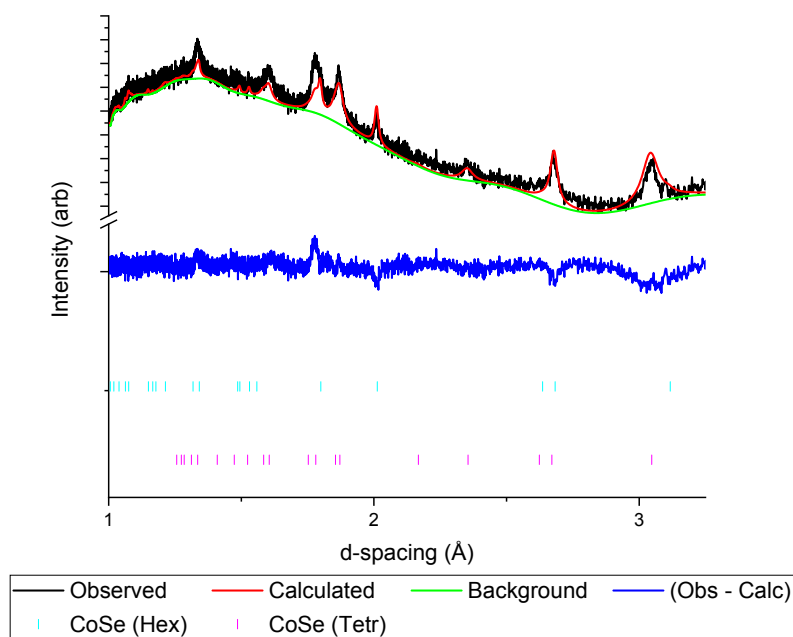


Figure S4: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus Li half cell discharged to 3% of full capacity, zoomed to show region of interest.

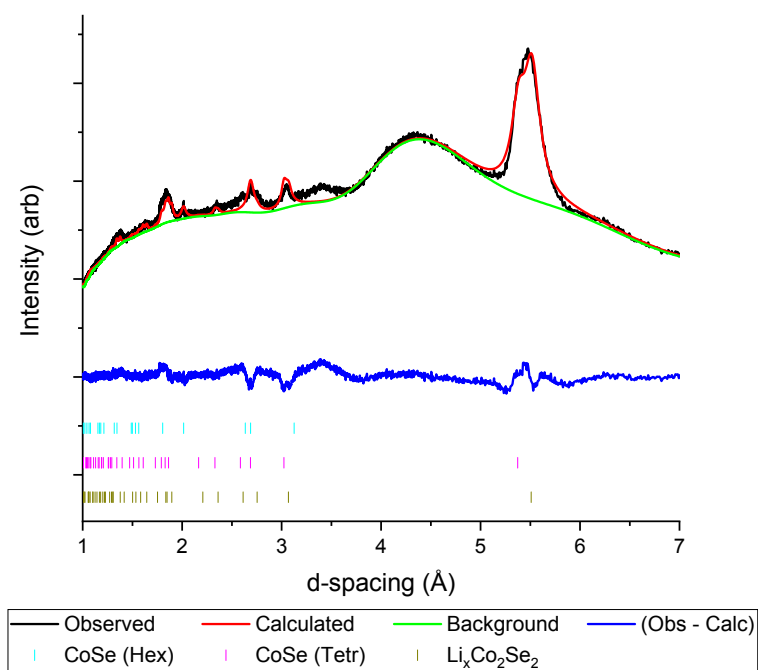


Figure S5: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus Li half cell discharged to 7.5% of full capacity.

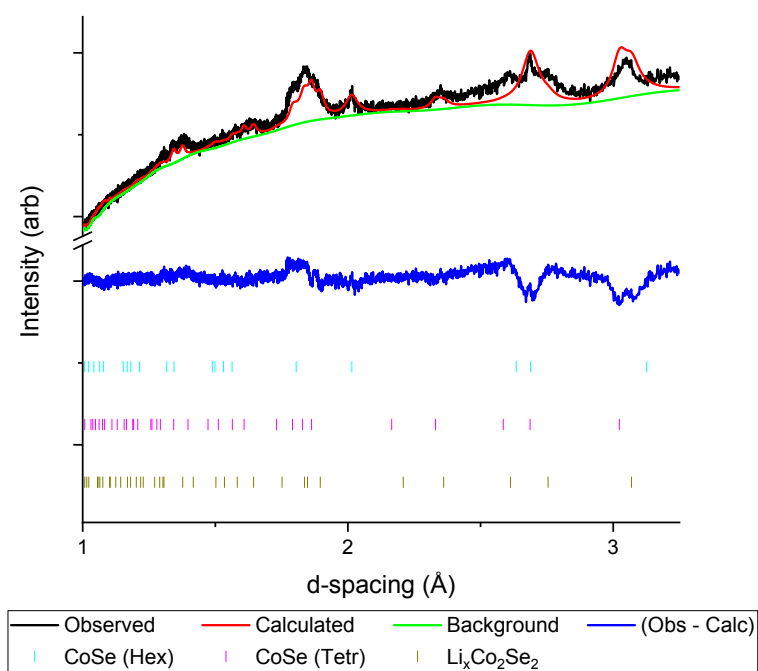


Figure S6: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus Li half cell discharged to 7.5% of full capacity, zoomed to show region of interest.

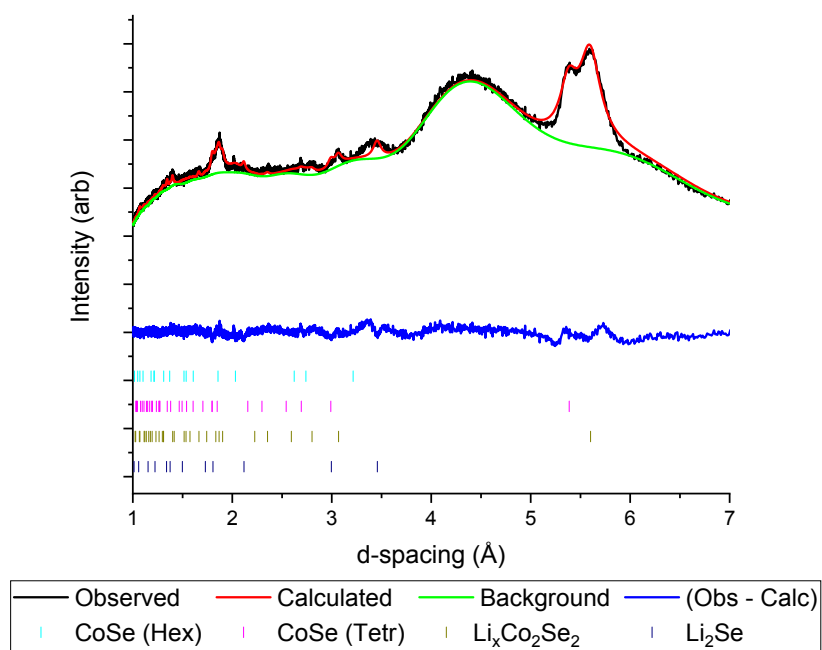


Figure S7: Rietveld analysis of structural models with PXRd data of an electrode extracted from a CoSe versus Li half cell discharged to 20% of full capacity.

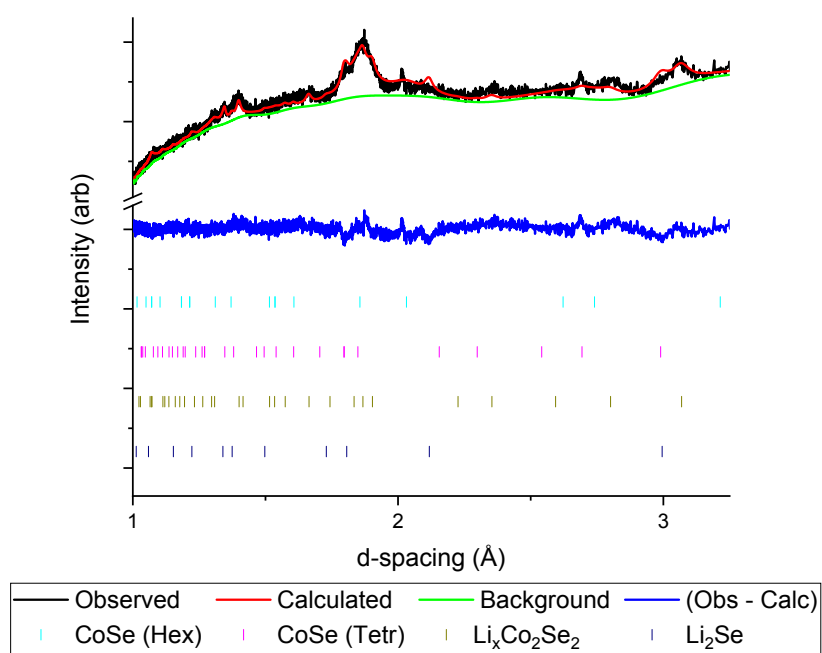


Figure S8: Rietveld analysis of structural models with PXRd data of an electrode extracted from a CoSe versus Li half cell discharged to 20% of full capacity, zoomed to show region of interest.

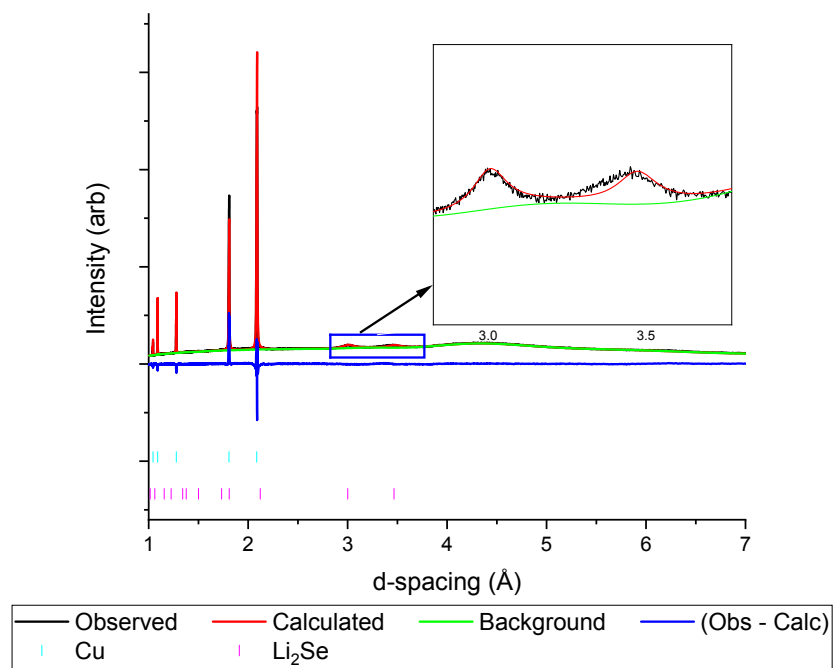


Figure S9: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus Li half cell discharged to 60% of full capacity.

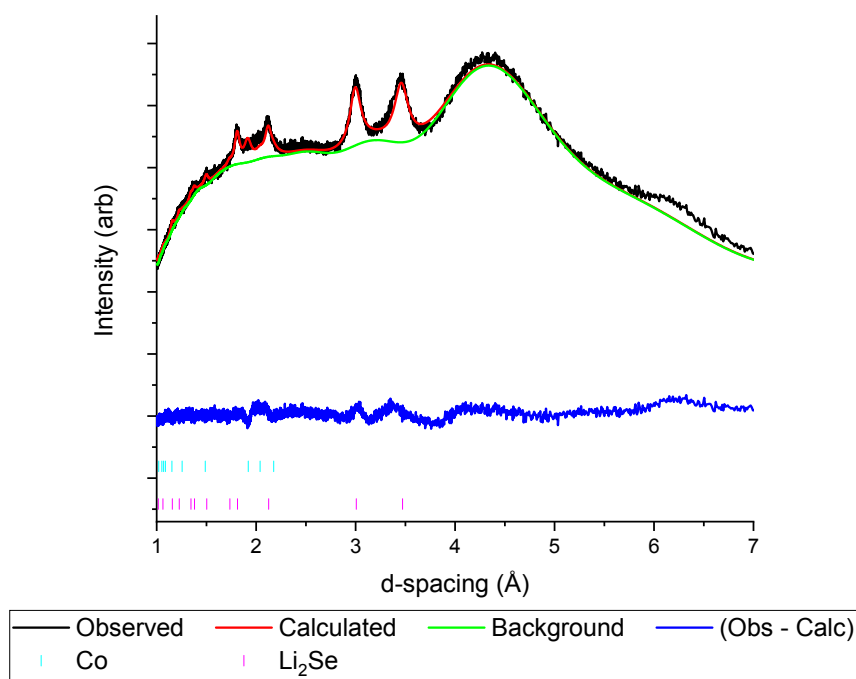


Figure S10: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus Li half cell discharged to 100% of full capacity.



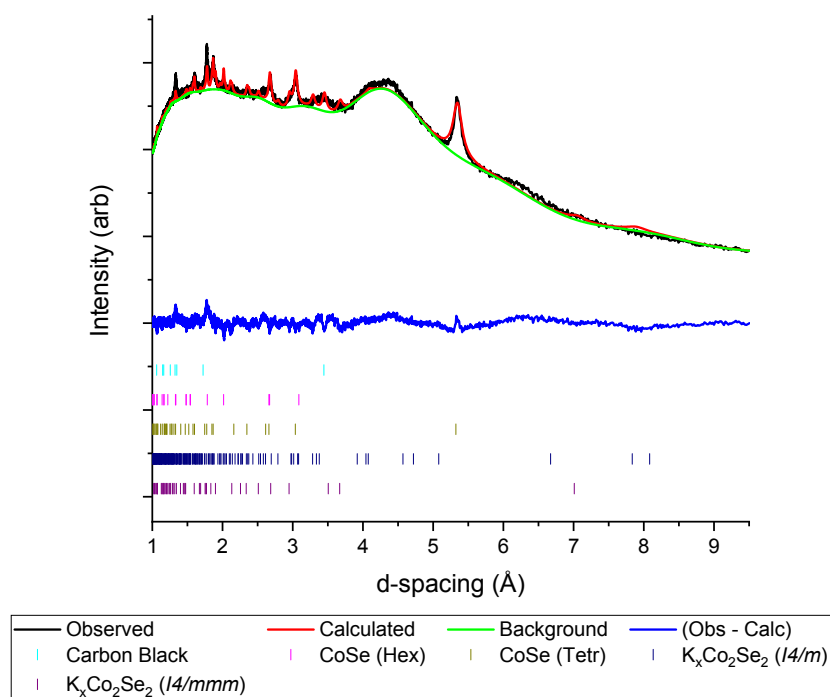


Figure S11: Rietveld analysis of structural models with PXRd data of an electrode extracted from a CoSe versus K half cell discharged to 2% of full capacity.

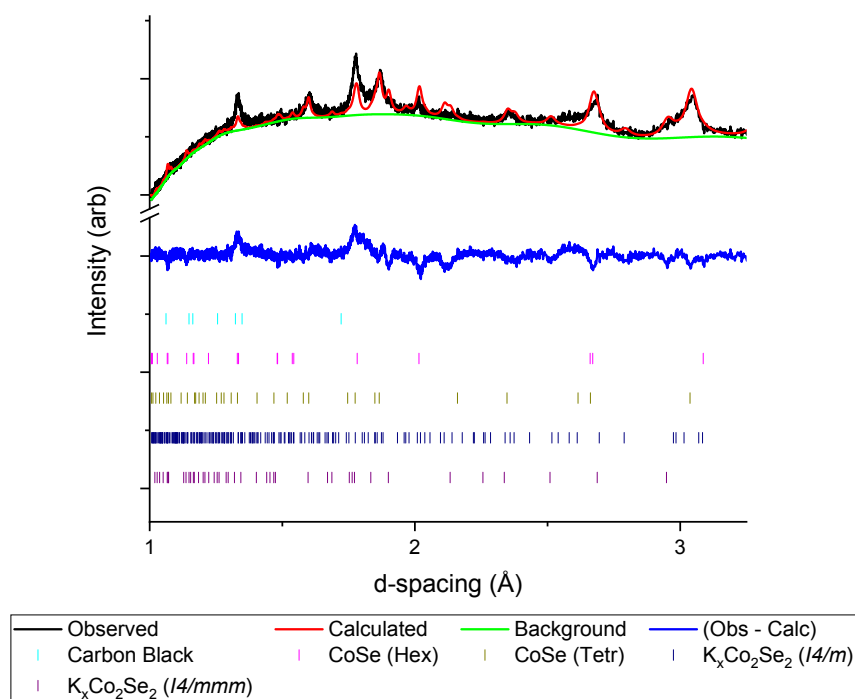


Figure S12: Rietveld analysis of structural models PXRd data of an electrode extracted from a CoSe versus K half cell discharged to 2% of full capacity, zoomed to region of interest.

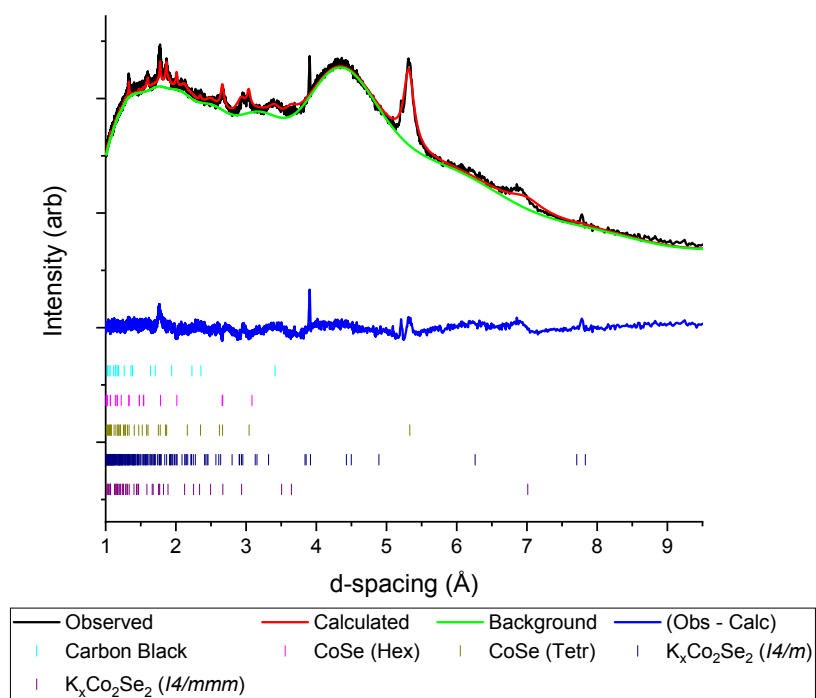


Figure S13: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus K half cell discharged to 6% of full capacity.

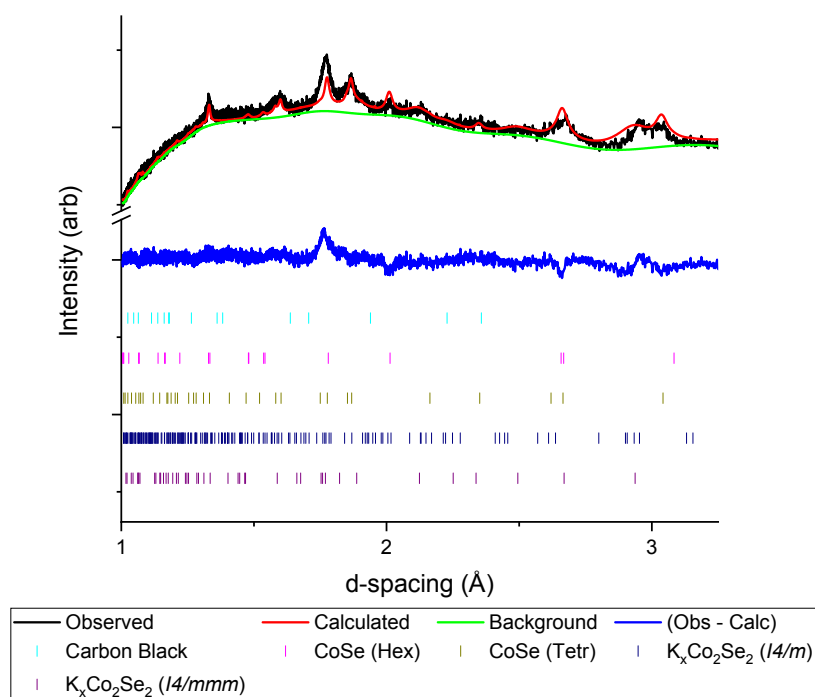


Figure S14: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus K half cell discharged to 6% of full capacity, zoomed to region of interest.

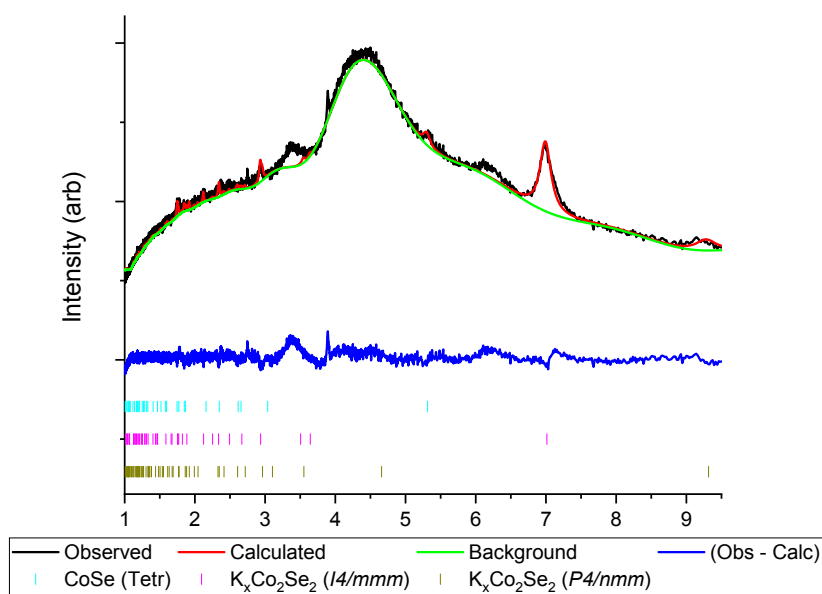


Figure S15: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus K half cell discharged to 30% of full capacity.

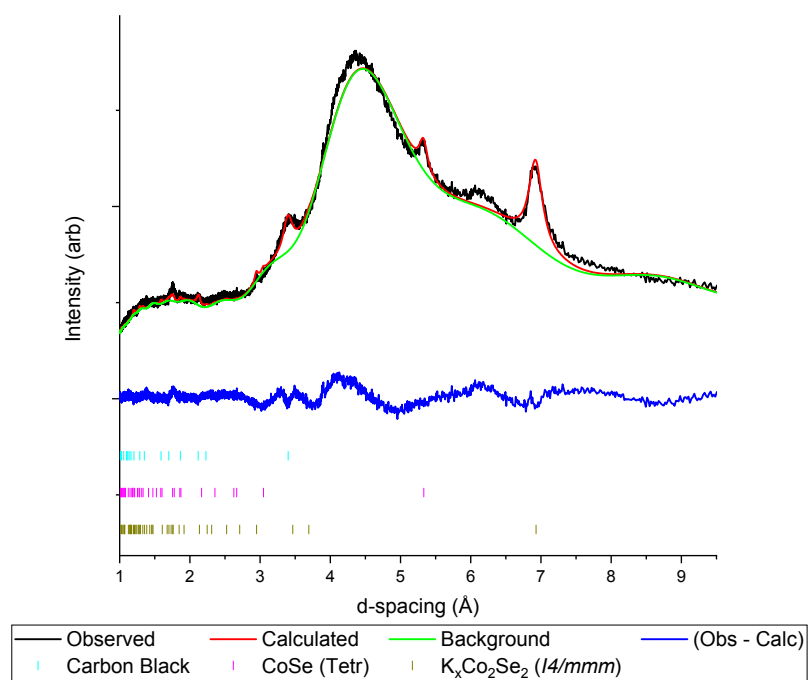


Figure S16: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus K half cell discharged to 70% of full capacity.

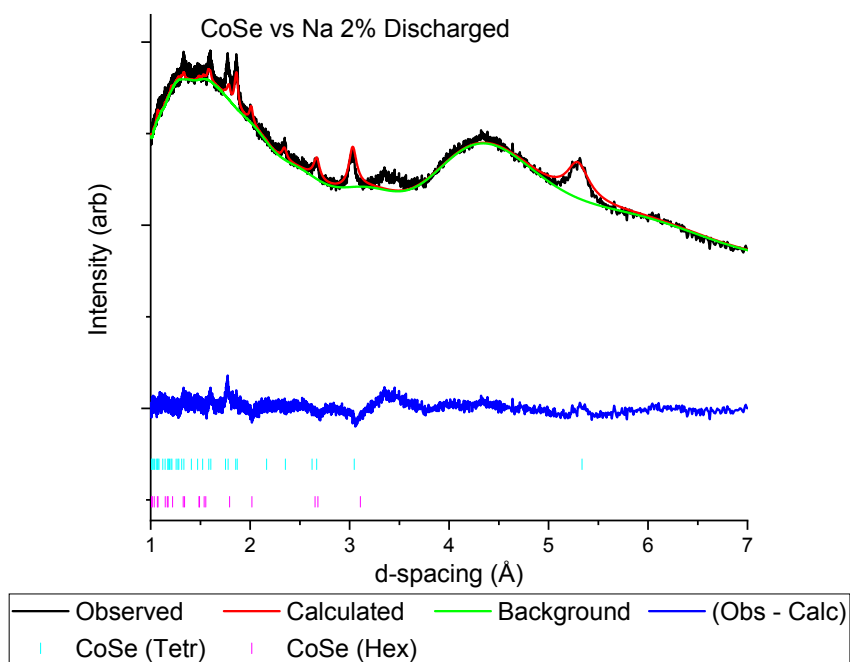


Figure S17: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus Na half cell discharged to 2% of full capacity.

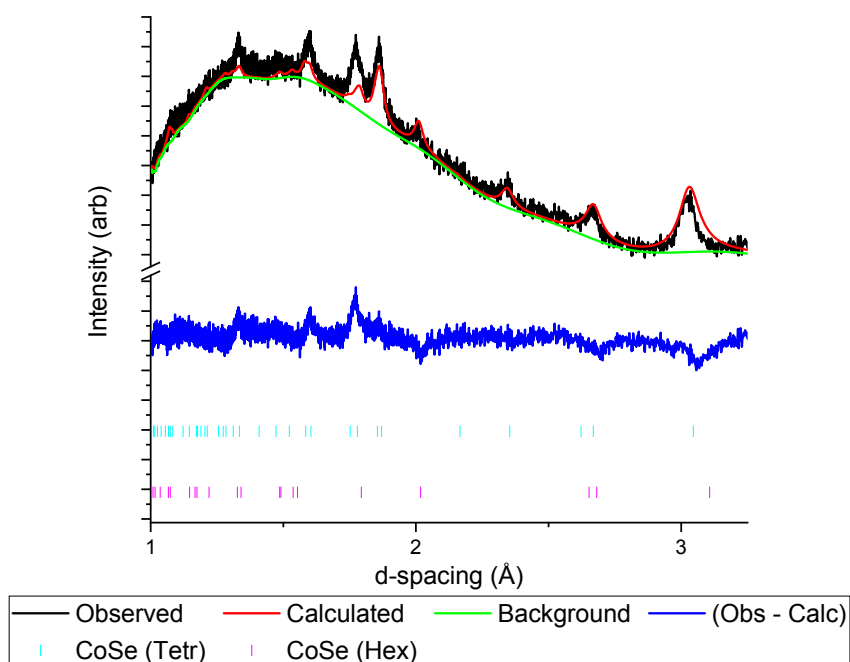


Figure S18: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus Na half cell discharged to 2% of full capacity, zoomed to region of interest.

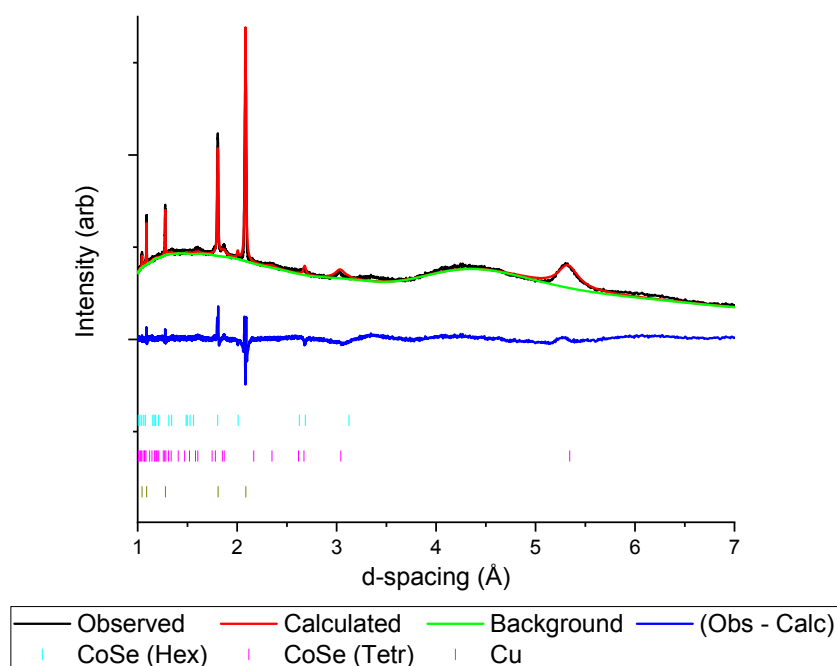


Figure S19: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus Na half cell discharged to 5% of full capacity.

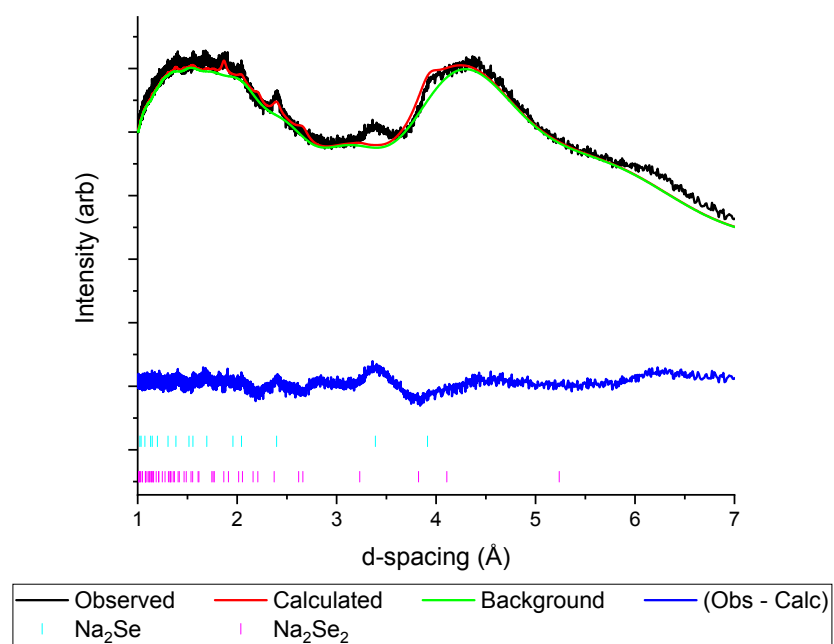


Figure S20: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus Na half cell discharged to 50% of full capacity.

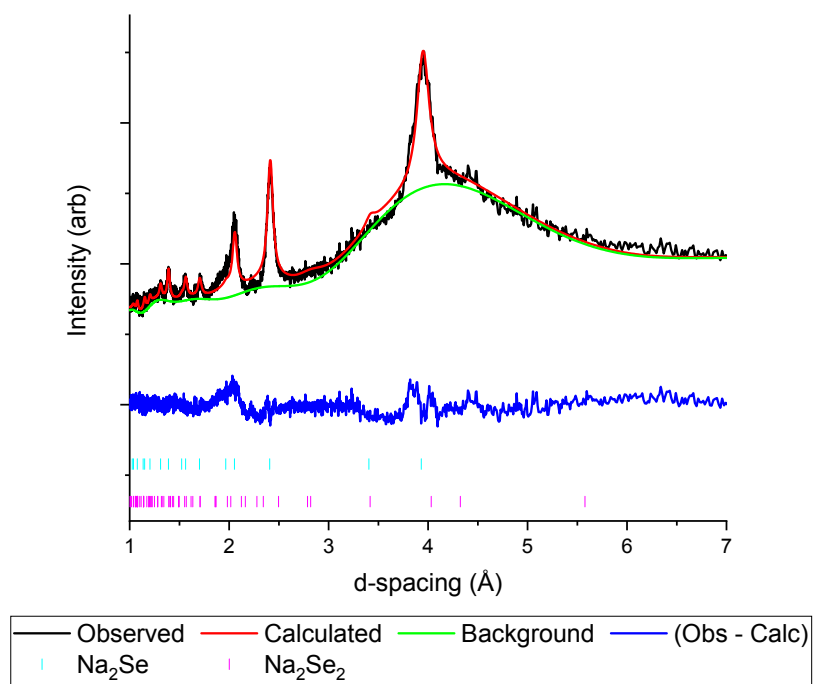


Figure S21: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus Na half cell discharged to 100% of full capacity.

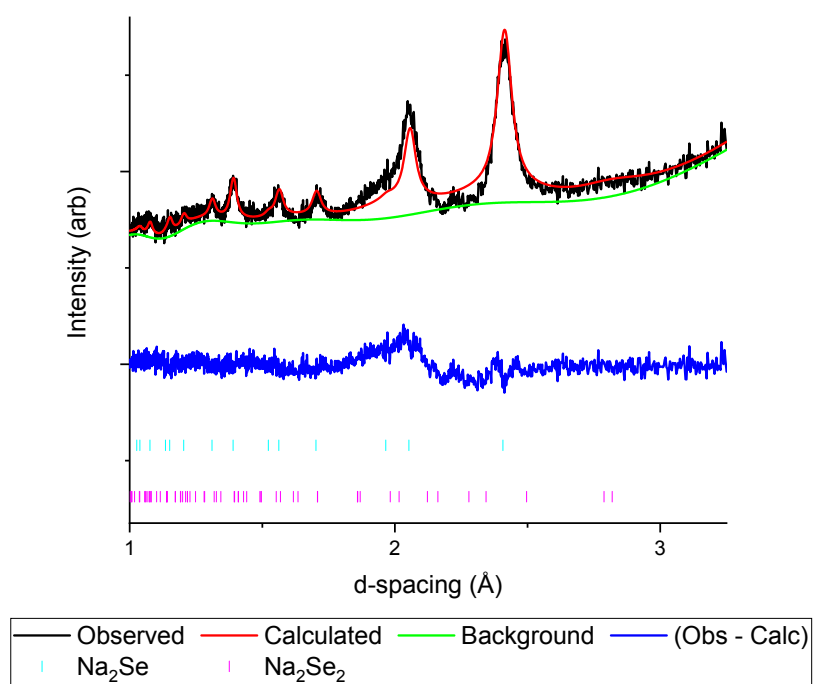


Figure S22: Rietveld analysis of structural models with PXRD data of an electrode extracted from a CoSe versus Na half cell discharged to 100% of full capacity, zoomed to region of interest.

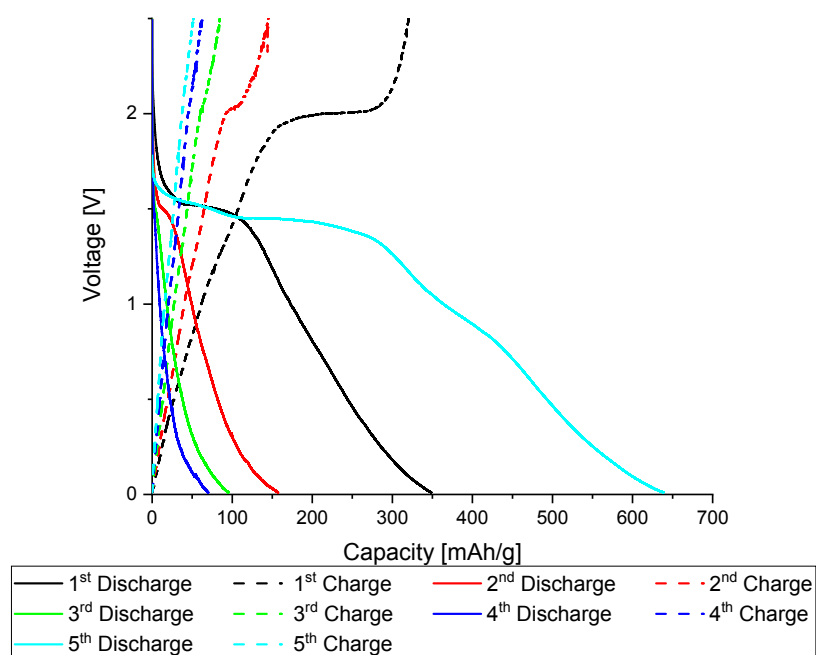


Figure S23: Capacity-voltage curves of CoSe versus Li cell, cycled (discharged, then charged) 5 times.

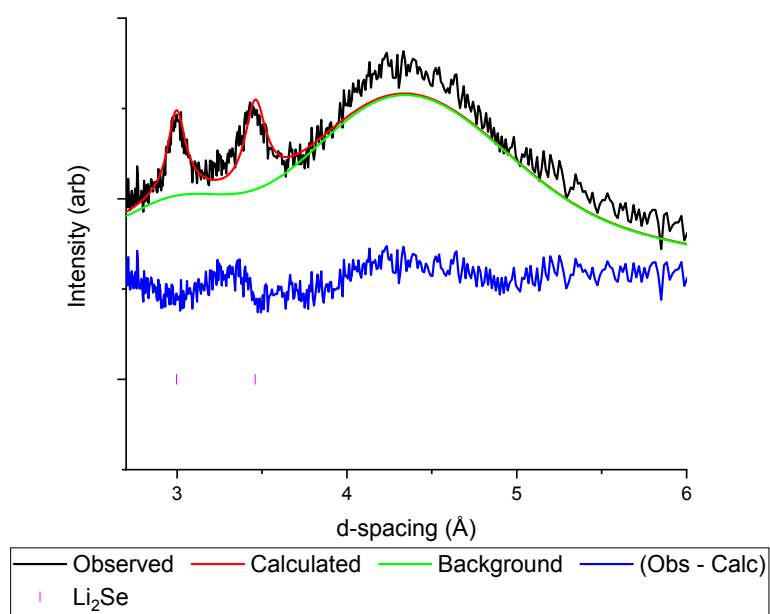


Figure S24: Rietveld analysis of structural models with PXRD data collected from CoSe versus Li sample, cycled (discharged, then charged) 5 times.