

Spontaneous Solid Electrolyte Interface Formation in Uncycled Sodium Half-Cell Batteries:
Using X-ray Photoelectron Spectroscopy to Explore the Pre-passivation of Sodium Metal by
Fluoroethylene Carbonate Before Potentials are Applied.

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Supporting Information

Experimental Detail

Cu₂Sb and Sb/CNT electrode preparation can be found in our previous publications.^{16,25,35} Battery assembly and sodium metal soaking experiments occurred inside an argon glove box (O₂ <1 ppm). Sodium metal (Aldrich, cubes mineral oil, 99.9%) is cleaned using a toothbrush to remove as much surface oxide as possible. The electrolyte solution comprised of 1 M sodium perchlorate (NaClO₄, Sigma Aldrich nACS Reagent) supporting electrolyte dissolved in 1:1:1 portions of ethylene carbonate (EC, recrystallized), dimethyl carbonate (DMC, Anhydrous Sigma Aldrich ≥99%), and diethyl carbonate (DEC, Sigma Aldrich Anhydrous 99%) by weight, as well as for certain experiments, 5% fluoroethylene carbonate (FEC, Sigma Aldrich ≥99%) by volume. The same FEC is used for presoaking sodium electrolytes. All sodium soaking is done in flame dried scintillation vials, no etching was observed in any experiment. Half-cell batteries are assembled using half inch Swagelok parts and cycled on Arbin BT2000 series battery tester under constant current conditions. Electrochemical impedance spectroscopy was performed using a Gamry Reference 3000 potentiostat between 300,000 and 0.1 Hz with 5 mV AC voltage. Before X-ray photoelectron spectroscopy characterization electrodes are washed with <1mL DMC.

X-ray photoelectron spectroscopy (XPS) was performed using a PE-5800 series Multi-Technique ESCA system. An Al K α monochromatic source operating at 350.0 W is used for all experiments. For each electrode three spectra are collected in different spots for all present elements. For each experimental condition three replicates were performed totaling 9 replicate spectrum. Figures are comprised of all 9 spectra overlaid with an average spectrum created using a previously published Python code (see main text). Repeated from main text: Electrolyte condition **1** 1 M sodium perchlorate (NaClO₄) in 1:1:1 ethylene carbonate (EC):dimethyl

carbonate (DMC):diethyl carbonate (DEC) a common electrolyte system. Condition **2** is **1** with 5% FEC. Finally, condition **3** has sodium metal is soaked in pure FEC for 48 hours before being used with condition **1**.

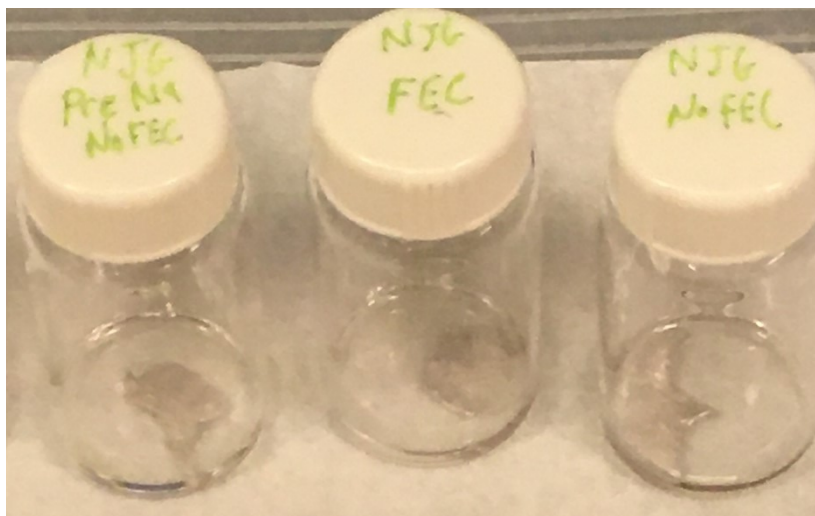


Figure S1. Photograph electrolyte solutions immediately after sodium immersion. Electrolyte solutions are from left to right: **3**, **2**, and **1**.

Images taken immediately after sodium is placed in all three electrolyte (**1**, **2**, and **3**) conditions show that the initial systems all look the same with pristine sodium that is still shiny from being brushed and clear electrolyte solutions (Figure S1).

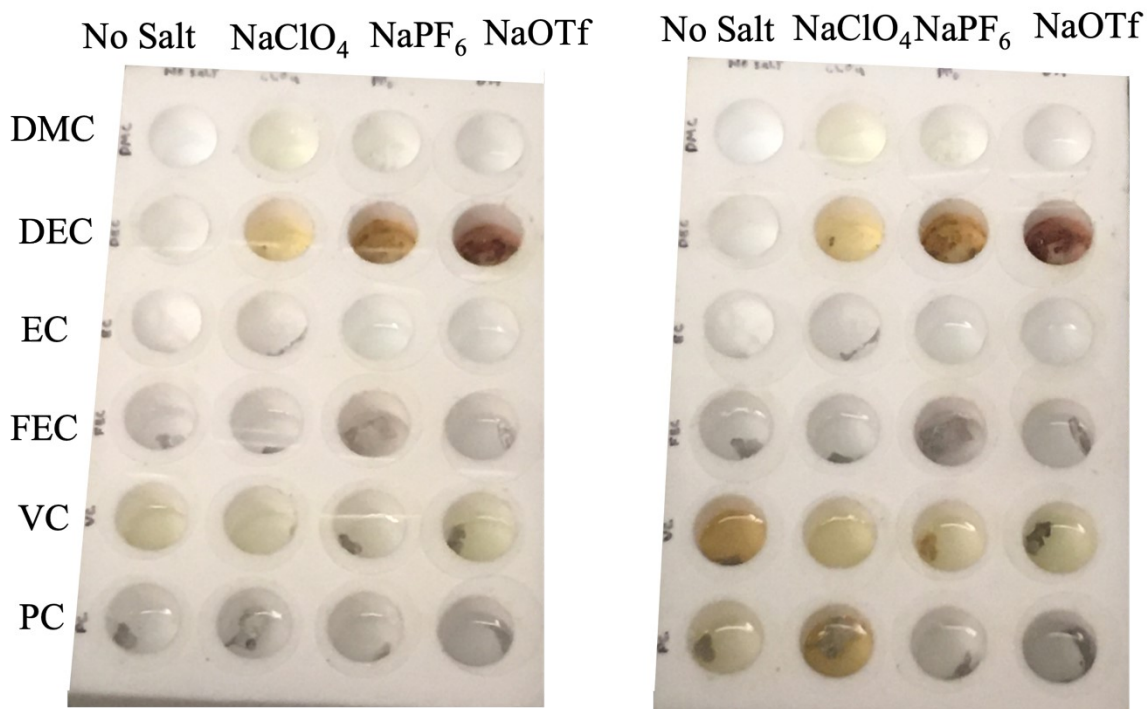


Figure S2. Array of electrolyte component reactions using Teflon reaction wells. DMC, DEC, EC, FEC, VC, and PC, were mixed with No salt, NaClO₄, NaPF₆, or NaOTf and sodium metal. Left is an image within five minute of immersion, the right image is ~72 hours later.

Sodium is soaked in different carbonates with and without different supporting electrolytes (Figure S2.). The first row of DMC samples dried up but the second row DEC shows a significant color change when a supporting salt is present. Third row EC is a solid so no change occurs. Fourth row FEC has no color change with or without salt. Fifth row vinylene carbonate (VC) changes color both with and without salt. Finally, sixth row propylene carbonate (PC) only changed color with NaClO₄

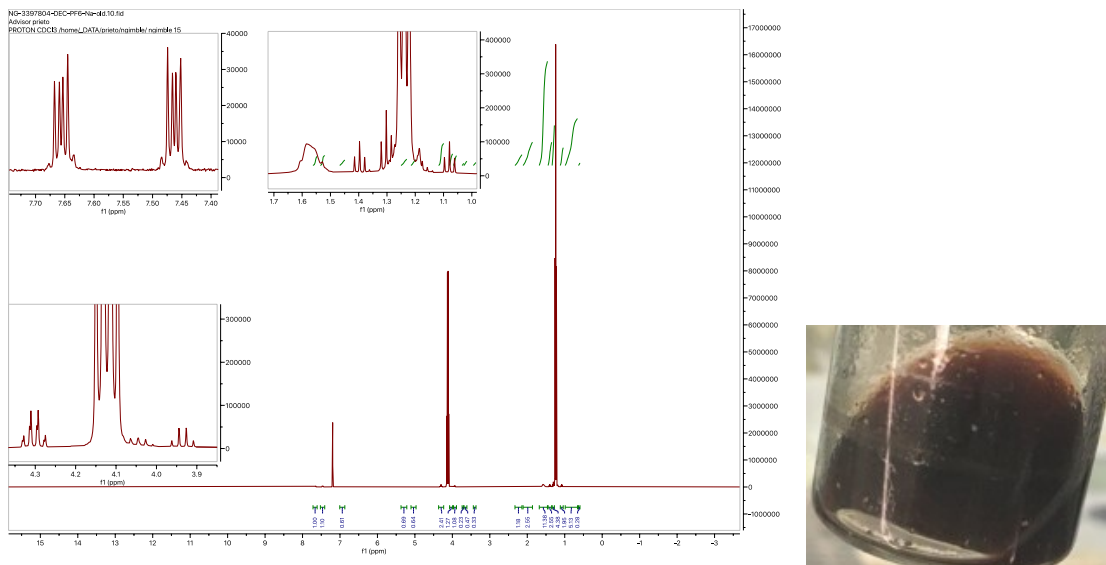


Figure S3. ^1H NMR from solution of 1 M NaPF_6 in diethyl carbonate for ~5 months pictured right.

NMR of different electrolytes soaked with sodium were inconclusive (Figure S3, left). The NMR solvent used was CDCl_3 (Cambridge isotope laboratories, D 99.8%) where the supporting electrolyte salt crashed out but organics are soluble. The example spectra shown is of DEC + 1M NaPF_6 (Figure S3, right), the most extreme example having shown an immediate color change in the Teflon array experiment as well as being left to sit for months to build up the products of the reaction. Unfortunately the NMR spectra is dominated by the signal of DEC. An partially air free distillation was used to attempt to separate the products that caused the color change but the solution had one fraction which condensed as a clear liquid. By NMR the distillation fraction was pure DEC. Leftover from the distillation was a colored solid which by XRD was NaPF_6 . Additional careful air-free separations would need to be carried out to clearly identify any reaction products.

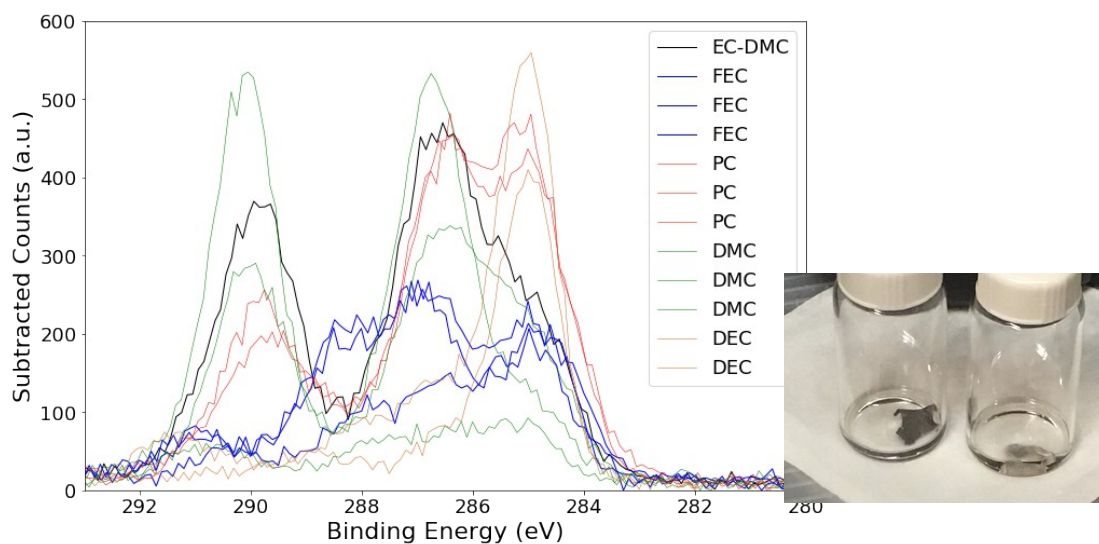


Figure S4. Left: carbon 1s XPS spectra of sodium metal soaked in different carbonates where EC-DMC mixture (black), FEC (blue), propylene carbonate (PC) (red), DMC (green) and DE (orange) are shown. Right: example picture of sodium metal soaked in DEC (left) and FEC (right).

XPS was performed on sodium metal soaked in various individual carbonates (Figure S4.). In all cases, soaking sodium in carbonate without a salt resulted in solutions that remained clear. Many different carbon XPS environments including carbonate, carboxyl, singly oxygenated, aliphatic, and reduced carbon are observed with varying concentrations. This set of experiments shows the complexity of the sodium metal reaction with individual carbonates. These results clearly show the variability in reaction occurring between sodium metal and the different carbonates. Additional experiments are required to identify the products forming, to learn about their solubility, and understand how the presence of a supporting salt is capable of solubilizing these products to form initial SEI species.

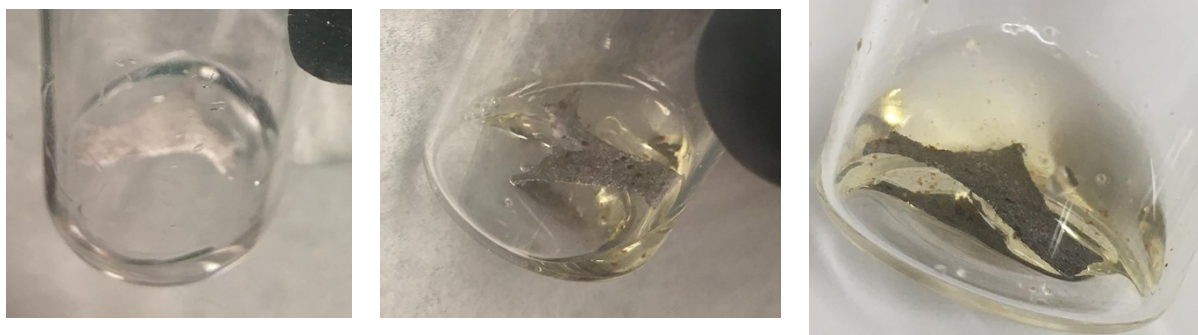


Figure S5. Sodium metal soaked in 1M LiClO₄ 1:1:1 EC:DMC:DEC electrolyte pictured immediately after immersion, 96 hours (4 days), and 144 hours later (6 days).

Soaking sodium metal in a lithium electrolyte still resulted in a color change, but at a slower rate than a sodium electrolyte. It is hypothesized that lithium ions in solution change the solubility of sodium based reaction products affecting the rate of reaction.

Cu₂Sb NoFEC	Avg Position	Stdev Position	Avg Conc.	Stdev Conc.
C 1s C-C	284.99	0.04	15	3
C 1s C-O	286.66	0.06	13	2
C 1s CO ₂	288.3	0.2	2.4	0.6
C 1s CO ₃	290.1	0.1	5	1
Sb ₂ O ₃ 3d 5/2	530.10	0.09	0.3	0.3
Sb ₂ O ₃ 3d 3/2	539.44	0.09	0.2	0.2
Sb 3d 5/2	527.4	0.1	0.10	0.08
Sb 3d 3/2	536.8	0.1	0.06	0.05
O 1s ClO ₄	533.4	0.2	35	7
O 1s O-C	531.6	0.3	12	4
ClO ₄ 2p 3/2	208.5	0.1	3.0	1.0
ClO ₄ 2p 1/2	210.1	0.1	1.5	0.5
F 1s NaF	0		0	
F 1s FEC	0		0	
Na 1s	1072.4	0.2	12	2
Cu 2p 3/2	932.7	0.1	0.5	0.3
Cu 2p 1/2	952.7	0.2	0.21	0.10
Cu₂Sb FEC	Avg	Stdev	Avg	Stdev

	Position	Position	Conc.	Conc.
C 1s C-C	285.02	0.05	28	6
C 1s C-O	286.7	0.1	7	2
C 1s CO ₂	288.6	0.1	7	1
C 1s CO ₃	290.4	0.4	3	2
Sb ₂ O ₃ 3d 5/2	530.5	0.1	2.5	0.6
Sb ₂ O ₃ 3d 3/2	539.9	0.1	1.6	0.3
Sb 3d 5/2	528.0	0.1	0.5	0.1
Sb 3d 3/2	537.3	0.1	0.35	0.06
O 1s ClO ₄	532.8	0.3	18	8
O 1s O-C	531.3	0.5	30	10
ClO ₄ 2p 3/2	208.4	0.2	0.9	0.2
ClO ₄ 2p 1/2	210.0	0.2	0.4	0.1
F 1s NaF	684.8	0.1	1.4	0.4
F 1s FEC	687.2	0.01	1.96	0.02
Na 1s	1072.0	0.1	7	1
Cu 2p 3/2	932.9	0.2	4	2
Cu 2p 1/2	952.7	0.2	2.1	0.8
Cu₅Sb	Avg	Stdev	Avg	Stdev
Presoak	Position	Position	Conc.	Conc.
C 1s C-C	284.99	0.04	23	5
C 1s C-O	286.60	0.10	9	1
C 1s CO ₂	288.55	0.08	9	2
C 1s CO ₃	0		0	
Sb ₂ O ₃ 3d 5/2	530.6	0.1	2.0	0.8

Sb ₂ O ₃ 3d 3/2	539.91	0.10	1.3	0.5
Sb 3d 5/2	528.0	0.2	0.6	0.2
Sb 3d 3/2	537.3	0.2	0.4	0.1
O 1s ClO ₄	532.9	0.6	15	5
O 1s O-C	531.6	0.7	30	10
ClO ₄ 2p 3/2	208.8	0.7	2	1
ClO ₄ 2p 1/2	210.4	0.7	1.0	0.6
F 1s NaF	0		0	
F 1s FEC	687.4	0.1	2	1
Na 1s	1072.3	0.1	8	4
Cu 2p 3/2	933.2	0.1	2.3	0.9
Cu 2p 1/2	953.0	0.1	1.0	0.5
	Avg	Stdev	Avg	
Na NoFEC	Position	Position	Conc.	
C 1s C-C	294.99	0.07	23	6
C 1s C-O	286.5	0.2	4.7	0.8
C 1s CO ₂	288.3	0.2	2.7	0.5
C 1s CO ₃	289.8	0.1	2.9	0.8
C 1s Cred	283.46	0.10	4	5
O 1s ClO ₄	533.4	0.3	7	5
O 1s O-C	531.6	0.2	16	7
O 1s Na ₂ O	530.0	0.3	13	4
F 1s NaF	0		0	
F 1s FEC	0		0	
ClO ₄ 2p 3/2	208.8	0.4	0.6	0.7

ClO ₄ 2p 1/2	210.4	0.4	0.3	0.3
ClO ₄ * 2p 3/2	207.2	0.3	1	1
ClO ₄ * 2p 1/2	208.8	0.3	0.7	0.5
Na 1s	1071.7	0.3	30	10
Na 1s Na ₂ O	1070.3	0.1	1.7	0.7
Na 1s NaF	0		0	
Na FEC	Avg Position	Stdev Position	Avg Conc.	Stdev Conc.
C 1s C-C	285.02	0.07	26	7
C 1s C-O	286.73	0.08	4	2
C 1s CO ₂	288.9	0.3	5	3
C 1s CO ₃	290.3	0.7	1.6	0.7
C 1s Cred	283.66	0.04	2.74	0.08
O 1s ClO ₄	533.13	0.26	25	8
O 1s O-C	531.1	0.3	12	5
O 1s Na ₂ O				
F 1s NaF	684.50	0.08	3.8	0.7
F 1s FEC				
ClO ₄ 2p 3/2	208.5	0.3	3	1
ClO ₄ 2p 1/2	210.1	0.3	1.5	0.6
ClO ₄ * 2p 3/2				
ClO ₄ * 2p 1/2				
Na 1s	1071.9	0.08	17	5
Na 1s NaF	0		0	
Na Presoak	Avg	Stdev	Avg	Stdev

	Position	Position	Conc.	Conc.
C 1s C-C	285.01	0.07	18	5
C 1s C-O	286.8	0.3	3.3	0.9
C 1s CO ₂	288.6	0.2	2.3	0.7
C 1s CO ₃	289.8	0.4	2	1
C 1s Cred	283.7	0.2	3	1
O 1s ClO ₄	533.2	0.4	16	10
O 1s O-C	531.2	0.4	10	7
O 1s Na ₂ O	0		0	
F 1s NaF	684.6	0.1	10	5
F 1s FEC	687.2	0.4	7	4
ClO ₄ 2p 3/2	208.4	0.3	2.6	0.8
ClO ₄ 2p 1/2	210.0	0.3	1.2	0.5
ClO ₄ * 2p 3/2				
ClO ₄ * 2p 1/2				
Na 1s	1072.0	0.2	26	7
Na 1s NaF	1073.2	0.1	4.0	0.9

Table S1. Quantification for all XPS data. Contains average peak position and % concentration as well as the corresponding standard deviation for all fit environments for no FEC (1), FEC (2), and Presoaked Na systems (3), both the Cu₂Sb and the Na counter electrode. The error in peak position is low (<0.5 eV) meaning for replicate samples each peak fit is representing the same chemical environment. Peak position can then be correlated across different experiments to examine if the same chemical environments are in different samples. Percent concentration of each chemical environment has more error compared to peak position. This makes many comparisons the same within error across different samples, however, the important observations discussed in the main text are statistically significant.

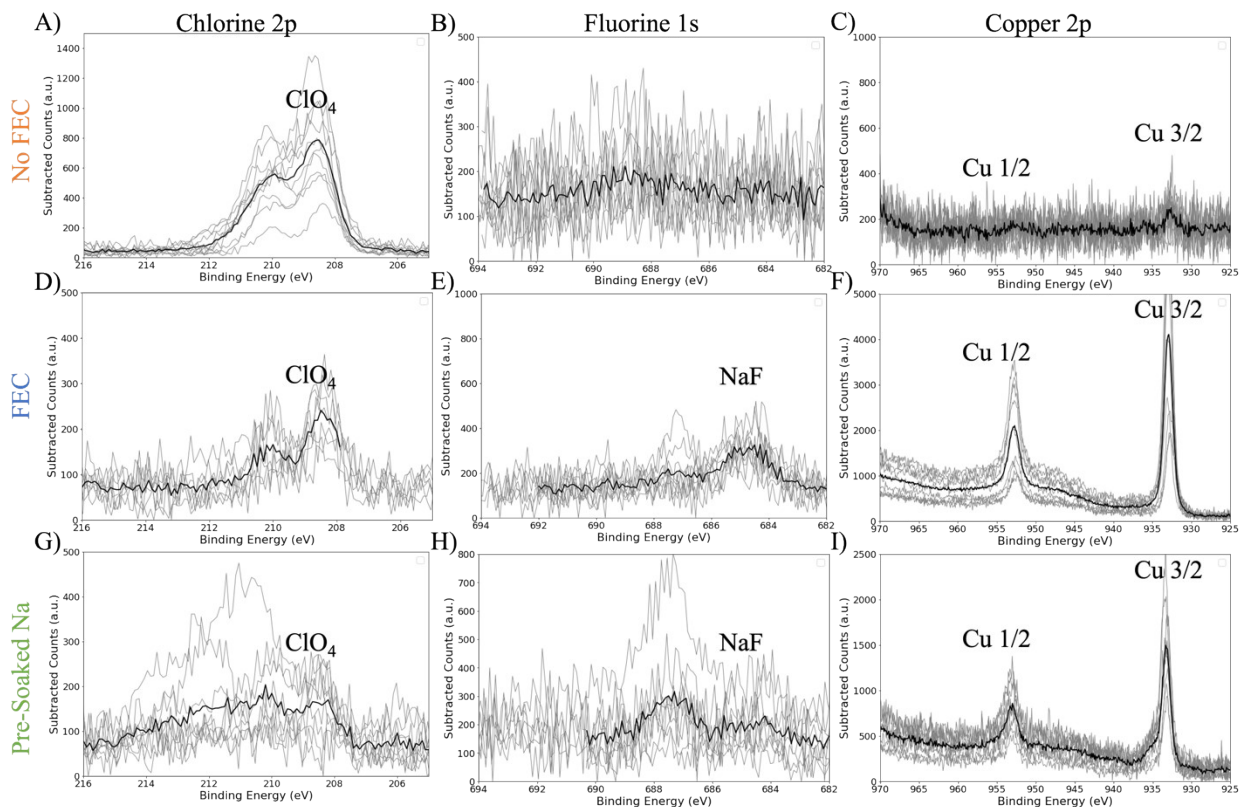


Figure S6. Overlaid of XPS spectra of all spots on replicate uncycled Cu_2Sb from uncycled half-cells. Black line represents an average spectra. The elements photoelectrons present are chlorine 2p (A, B, C), fluorine 1s (D, E, F) and copper 2p (G, H, I). The electrolyte systems in the uncycled batteries are the base electrolyte: 1M NaClO_4 1:1:1 EC:DMC:DEC (A, D, G), base electrolyte with 5% FEC (B, E, H), and the base electrolyte with a the FEC pretreated sodium counter electrode (C, F, I).

The remaining XPS spectra for the other elements present in the uncycled Cu_2Sb half-cell sample are perchlorate chlorine, a small amount of sodium fluoride (condition **2** and **3** none for **1**), and copper metal where the SEI is thin enough for it to be exposed (conditions **2** and **3** not **1**) (Figure S6).

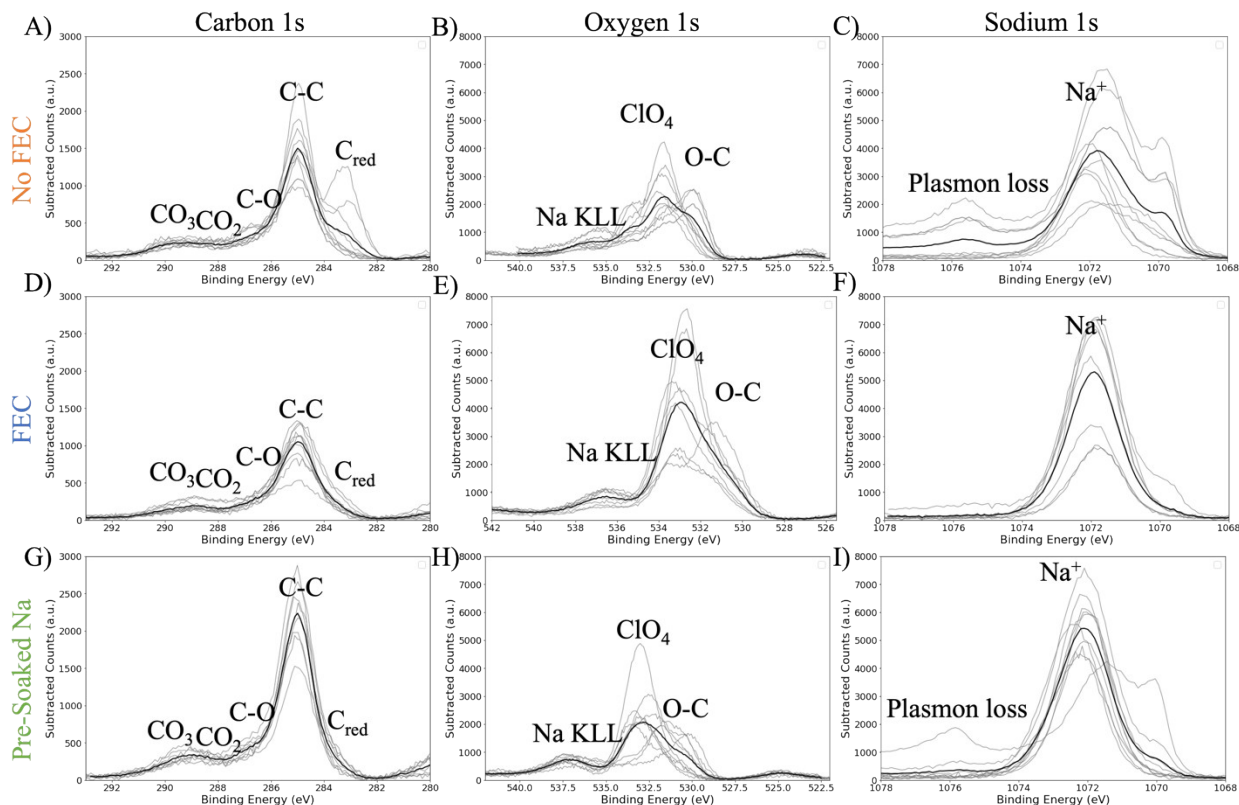


Figure S7. Overlaid of XPS spectra of all spots on replicate sodium metal from uncycled half-cells. Black line represents an average spectra. The elements photoelectrons present are carbon 1s (A, B, C), oxygen 1s and antimony 3d (D, E, F) and sodium 1s (G, H, I). The electrolyte systems in the uncycled batteries are the base electrolyte: 1M NaClO₄ 1:1:1 EC:DMC:DEC (A, D, G), base electrolyte with 5% FEC (B, E, H), and the base electrolyte with a the FEC pretreated sodium counter electrode (C, F, I).

XPS spectra for carbon, oxygen, and sodium on the surface of the sodium counter electrodes from the uncycled half-cell experiments using electrolyte conditions **1**, **2**, and **3** (Figure S7). Unlike the surface of the Cu₂Sb the sodium metal surface does not have as many clear differences between the electrolyte conditions. The carbon spectra has five environments in all samples assigned as aliphatic, singly oxygenated, carboxyl, carbonate, and a reduced carbon (Cred) environments. Peak positions are the same for the five carbon environments in the different conditions except for carboxyl, CO₂, carbon. Analogous with Cu₂Sb carbon XPS spectra, this environment is at 288.3 eV for **1** and at 288.6 for **2** and **3**. Further examining SI Table 1 where quantification values are presented, the different electrolyte conditions have the

same respective percent concentration of the five chemical environments within error. The presence of the reduced carbon environment is hypothesized to be a result of the highly reducing sodium metal surface. Oxygen contains a lot of heterogeneity but was for the majority of spectra fit with the same two environments: perchlorate, and carbon oxygen. Finally there is a large sodium peak in all scans and a plasmon loss feature, showing the presence of metallic sodium, in certain spectra.

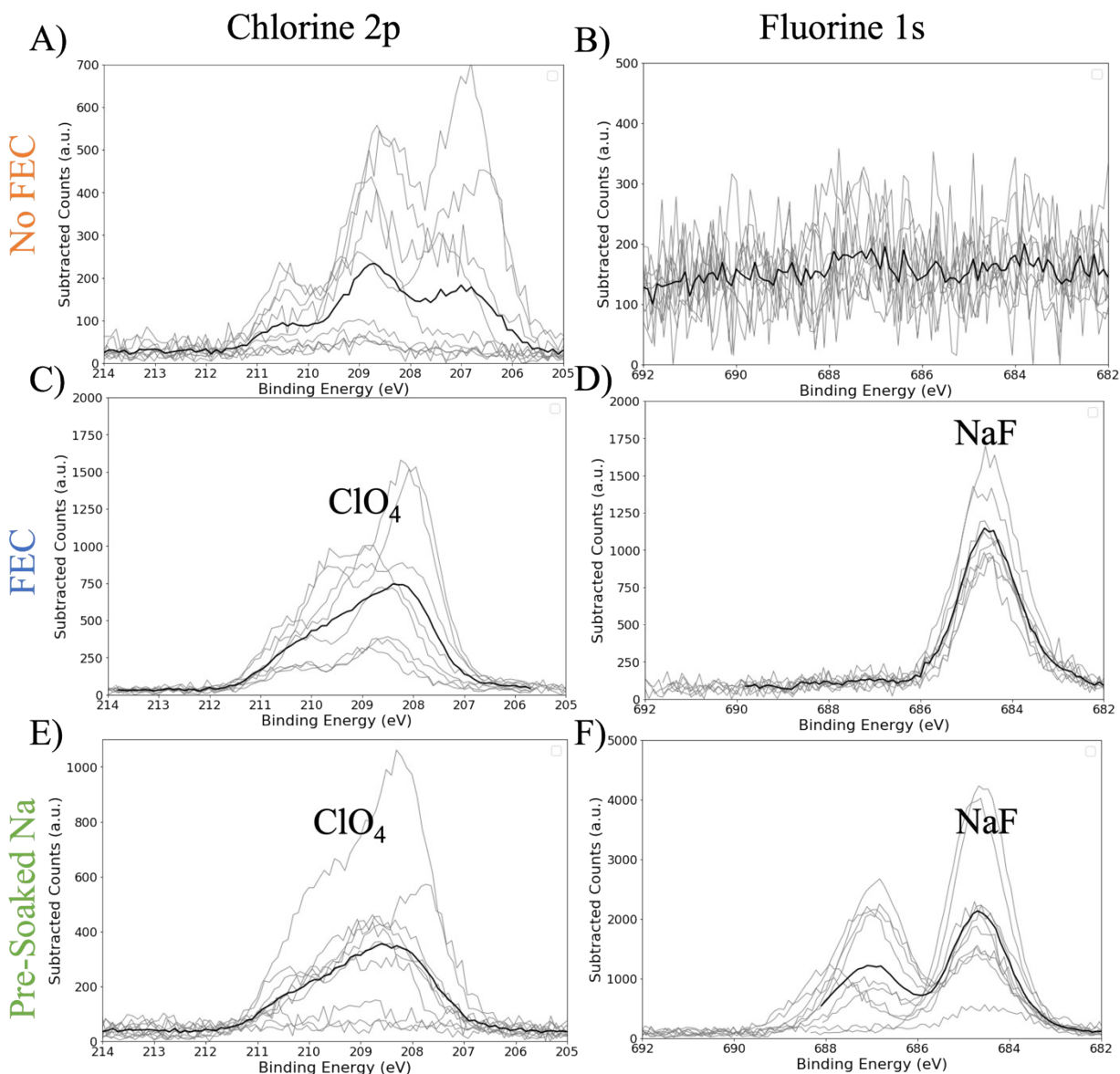


Figure S8. Overlaid of XPS spectra of all spots on replicate sodium metal from uncycled half-cells. Black line represents an average spectra. The elements photoelectrons present are chlorine 2p (A, B, C) and fluorine 1s (D, E, F). The electrolyte systems in the uncycled batteries are the

base electrolyte: 1M NaClO₄ 1:1:1 EC:DMC:DEC (A, D), base electrolyte with 5% FEC (B, E), and the base electrolyte with a the FEC pretreated sodium counter electrode (C, F).

XPS spectra for chlorine and fluorine on the surface of the sodium counter electrodes from the uncycled half-cell experiments (Figure S8). The chlorine spectra only contains perchlorate from the supporting salt. The fluorine is interesting as for condition **3** spectra there is a FEC fluorine environment in addition to the NaF in condition **2**. There is left over FEC from the presoak that was not removed when the sodium was dried. As this environment represented 7% very little FEC would not be able to change the bulk electrolyte and compromise the experiment.

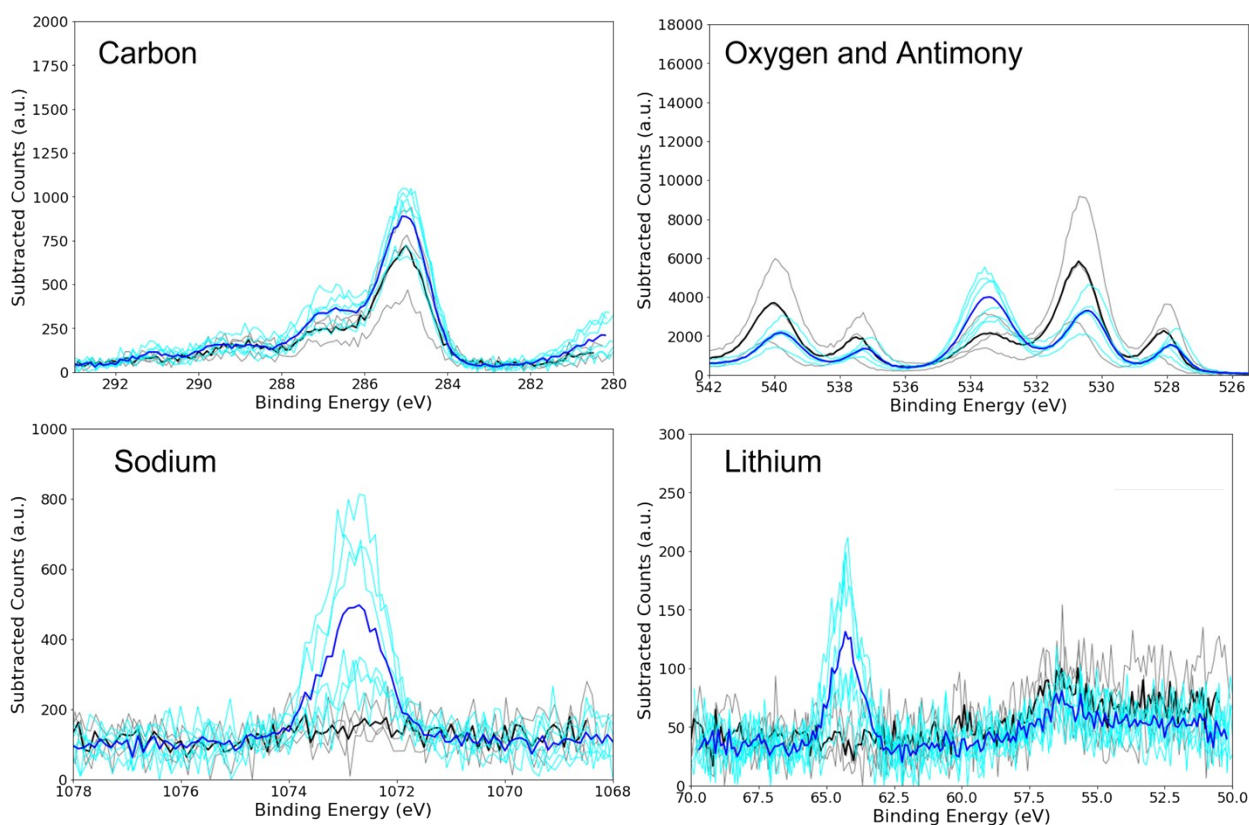


Figure S9. Overlaid XPS spectra from the surface of Cu₂Sb from Cu₂Sb-Na metal half cells with 1M LiClO₄ 1:1:1 EC:DMC:DEC electrolyte left uncycled for 72 hours and 144 hours (black and blue).

The different elements measured on the surface of Cu₂Sb with XPS included carbon, oxygen, antimony, chlorine, copper, and occasionally sodium and lithium (chlorine and copper not presented). As the color change was proceeding slowly, it was hypothesized that the lithium

electrolyte was slowing the reaction creating the initial SEI species measured with the sodium electrolyte. Thus, batteries were left 144 hours to allow more time for the reaction to progress and change the surface of Cu_2Sb . The carbon 1s spectra of Cu_2Sb in the lithium electrolyte with a sodium metal counter electrode does not contain the singly-oxygenated and carbonate carbon environments to the degree observed with the sodium electrolyte, however, given more time, the peaks may evolve. The antimony and copper photoelectrons are present meaning very few initial SEI species are present on the surface and have not built up to the degree needed to obscure the substrate. Interestingly, after 72 hours sodium is not detected but after 144 a sodium cation peak is detected at ~ 1072 eV (as well as sodium 2s at ~ 64 in the lithium spectra). Finally, lithium is barely measured on the surface of Cu_2Sb at ~ 56 eV when a lithium electrolyte is used in a sodium half-cell. The sodium metal counter electrode is the sole source of sodium in this system and measuring sodium species on the surface of Cu_2Sb supports the hypothesis that initial SEI species form at the sodium metal surface, solubilize, and then diffuse across the cell to deposit on the surface of the working electrode without any applied potential.

These results studying a lithium electrolyte in a sodium half cell are preliminary, and is the focus of ongoing research to learn more about the properties of sodium metal reaction products where it is clear the supporting electrolyte is playing a role.

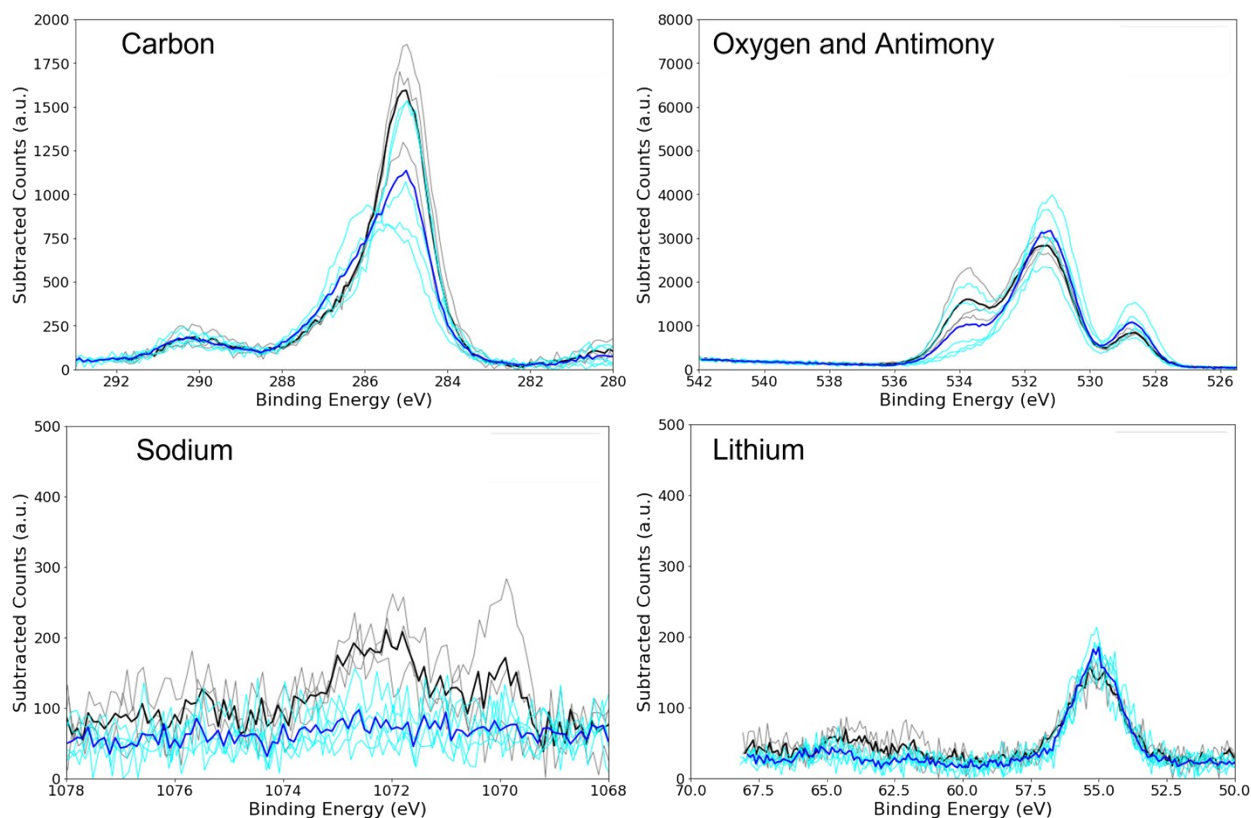


Figure S10. Overlaid XPS spectra from the surface of Na metal from Cu_2Sb -Na metal half cells with 1M LiClO_4 1:1:1 EC:DMC:DEC electrolyte left uncycled for 72 hours and 144 hours (black and blue).

The surface sodium counter electrode in a Cu_2Sb -sodium metal half-cell with a lithium-based electrolyte as measured by XPS contained carbon, oxygen, sodium, lithium, and chlorine (not presented). Interestingly, on the surface of sodium metal, much less sodium is detected compared to lithium. This shows how much the sodium metal reacts with the electrolyte, forming a passivation layer. The lithium electrolyte passivation layer while more effective than the conventional sodium-based electrolyte passivation, is not as capable as FEC based passivation in preventing solubilization of reaction products. Overtime, sodium species diffused across the cell to deposit on the working electrode and a color change is observed. More research is required to understand how best to passivate sodium metal to have it function effectively in half cell and for sodium metal batteries.

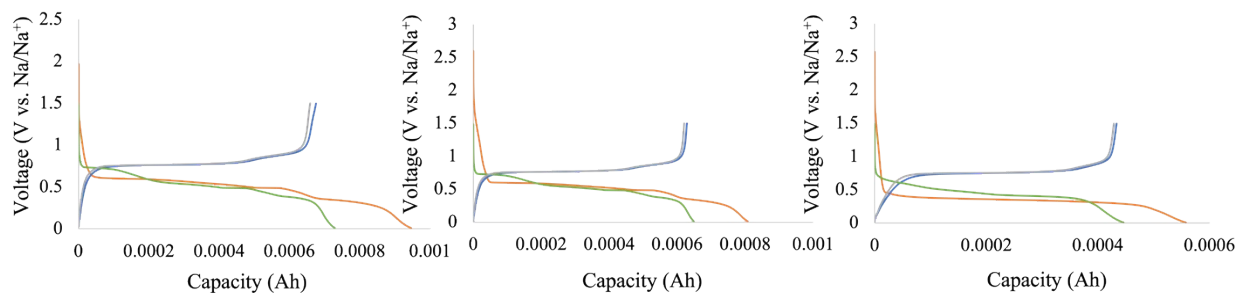


Figure S11. Voltage capacity plots for the first two cycles of the lifetime plots for half cell batteries cycled under conditions **1**, **2**, and **3** (left to right) (Orange discharge 1, blue charge 1, green discharge 2, and grey charge 2).