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of Sodium Metal by Fluoroethylene Carbonate Before
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COMMUNICATION

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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Testing sodium battery technology relies on a half-cell setup with sodium metal as the counter electrode. Herein, we show that sodium metal reacts with conventional carbonate electrolyte to form the solid electrolyte interface (SEI) on the working electrode spontaneously in a half-cell, without applying any external potential. Fluoroethylene carbonate prevents this spontaneous SEI formation by pre-passivating sodium metal, again before any potentials are applied or current is passed.

Sodium offers an important alternative to lithium for large scale applications in batteries and capacitors due to its natural abundance.^{1–3} Many aspects of sodium systems have been adapted from analogous lithium systems, however there are important chemical differences that make a direct substitution of sodium for lithium challenging. For example, the difference in ionic radius between the two alkali metal ions means that graphite, the successfully commercialized intercalation anode material for lithium ion batteries, is incompatible with sodium. Hence, alternative anodes for sodium batteries are required.⁴

Additionally, reports in the literature indicate that common liquid electrolytes are more reactive when in contact with sodium as compared to lithium.^{5,6} Liquid electrolytes commonly include linear and cyclic organic carbonates to dissolve the supporting alkali salt.⁷ These electrolytes react with lithium or sodium to passivate their surfaces, but the sodium products have a higher solubility, which may help explain the observed enhanced reactivity because the surfaces cant passivate as completely.^{8–10} Despite the many issues caused by the higher reactivity of sodium metal, few studies have examined the effect of sodium reactivity on the working electrode, the material being tested, in a half-cell.^{11–14} If sodium metal reactivity affects the material being tested then true device performance cannot be realized. To effectively improve battery performance all aspects and interactions in the system must be understood. Specifically, in a half-cell, the questions of how the sodium metal reactivity affects the solid electrolyte interface (SEI) formation remains unanswered.

Though the SEI effects battery performance, its formation is still not well understood.^{8,15,16} Previously, we examined reductive electrochemical liquid electrolyte decomposition into the SEI as a function of applied potential on Cu₂Sb in sodium metal half-cells using X-ray photoelectron spectroscopy (XPS).¹⁷ Our results showed that fluoroethylene carbonate (FEC), a small molecule additive that has been widely studied because it improves cycle lifetime in both sodium and lithium batteries, has a significant impact on the SEI species observed at different voltages during the initial discharge of

half-cells, where the SEI is thought to form.¹⁷ The additive FEC is thought to improve cycle lifetime by acting sacrificially, decomposing onto the anode's surface, to build a SEI that benefits the cell.^{18–21} One hypothesis, proposed by Dugas et. al., suggests that FEC may form a stable inner layer and an evolving outer layer on sodium metal with cycling, though no conclusion on the true nature of how FEC passivates and affects sodium metal has been reached.²²

Notably in our previous work, we show that without FEC, there is a significant quantity of SEI species on the surface of Cu₂Sb at potentials where little charge had passed.¹⁷ Subsequently, we hypothesized, and show herein, that the base carbonate electrolyte reacts with sodium metal spontaneously and the products of this reaction diffuse across the half-cell to deposit onto Cu₂Sb as initial SEI species. Furthermore, we hypothesize and demonstrate that FEC works differently than previously thought in the literature: instead of reducing onto the anode during cycling, FEC prevents the previously mentioned initial spontaneous SEI formation through pre-passivating sodium metal prior to any applied electrochemistry. Numerous control experiments are utilized below to test if the SEI is forming spontaneously and to explore the function of FEC in sodium-ion half-cells. Our data indicated that initial SEI species form on the working electrode of a sodium half-cell with no applied potential. The importance of FEC is further highlighted as it can prevent the formation of many of the initial SEI species. These results demonstrate the importance of understanding SEI formation and how electrolyte additives such as FEC impact this process, which will be crucial for effectively developing sodium technologies.

To understand how SEI products are forming, three electrolyte conditions were explored using different experimental methods. Electrolyte condition **1** is 1 M sodium perchlorate (NaClO₄) in 1:1:1 ethylene carbonate (EC):dimethyl carbonate (DMC):diethyl carbonate (DEC), a common simple electrolyte system. Condition **2** is the base electrolyte **1** with 5% FEC added. Finally, condition **3** is sodium metal soaked in pure FEC for 48 hours to accumulate chemical passivation before use with condition **1**.

Over several days of soaking sodium metal in condition **1** in a scintillation vial, a cloudy yellow color change occurred, similar to the changes seen by Pfeifer et. al. (an electrolyte system without FEC) (Figure 1A) (before images shown in Figure S1).⁶

The color change is likely due to a chemical reaction where the products are continuously dissolving into the solution. Condition **2**, with 5% FEC added, resulted in an electrolyte solution that remained clear and exhibited no color change (Figure 1B). Condition **3** also results in no color change (Figure 1C) suggesting, for these

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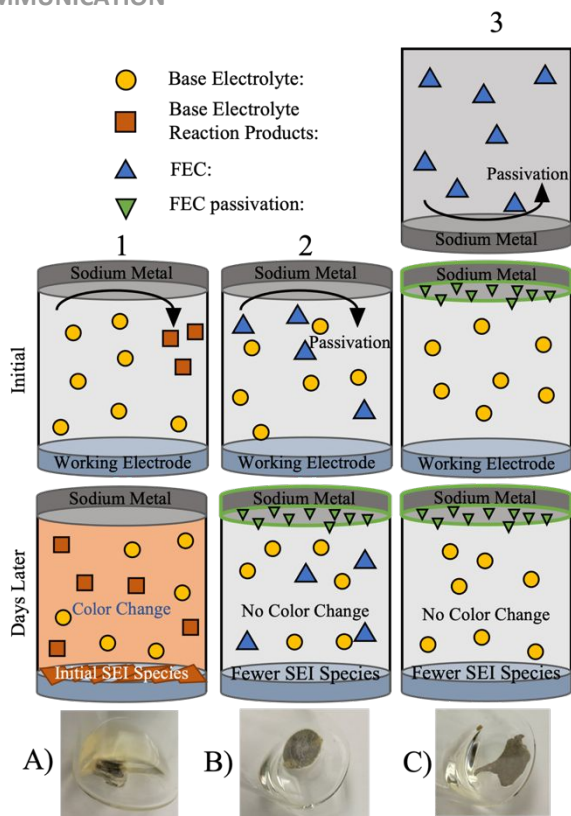


Figure 1. Molecular level diagrams of the three electrolyte conditions (**1**, **2**, and **3**) in half-cells are depicted in columns **1**, **2**, and **3**, respectively. Column **3** begins in the first row showing the 48 hour pre-soak of sodium metal in FEC. The second row represents the initial immersion of sodium metal under each electrolyte condition. The third row shows each system days later. The fourth row has photographs of sodium soaked in each electrolyte condition (A, B, and C) after five days. Shapes used are: Base electrolyte (1 M NaClO₄ EC:DMC:DEC) as yellow circles, base electrolyte decomposition products as orange squares, FEC as blue triangles, and FEC passivation products as green upside down triangles.

soaking experiments, the passivation of sodium by FEC may have the same effect as FEC in solution. Characterization of the source of the color change by NMR proved difficult due to the low concentration of reaction products (Figure S3). Meticulous air-free separation techniques would be required to accurately identify these products. To explore the conditions of the color change, sodium metal was immersed in individual liquid carbonates with and without different supporting salts (Figure S2). The salt NaClO₄ is used as the supporting electrolyte to ensure that FEC is the sole source of fluorine, although other salts caused a more intense color change (Figure S2). A crucial result was that without a salt, no color change is observed. However, the sodium metal surface exhibited different species measured using XPS even when the solution remains colorless (Figure S4), indicating that although there is no color change detected by eye, there is still some surface reactivity and presence of salt may impact reaction product solubility.

Replacing the sodium salt with a lithium salt significantly changed the reaction rate, as observed by how quickly the color changed after sodium metal is immersed in electrolyte (Figure S5). In particular, the substitution of Na for Li in the supporting electrolyte significantly *decreases* the rate of electrolyte decomposition. Sodium metal reacts with the electrolyte causing a color change likely due to products that can redissolve in a process facilitated by the presence of a supporting salt. To test the effect on working electrodes, half-cell batteries were assembled using electrolyte conditions **1**, **2**, and **3**, then left to rest in the glove box, *without any applied potential*. To ensure reaction products could form and, according to our hypothesis, diffuse across the cell, half-cells were left for 72 hours. After disassembly, the surface of the working electrode and any initial SEI products could then be analyzed with air free XPS.²³ Following our previous work, electrodeposited Cu₂Sb anode material was used so SEI species can be observed without interference from binders or additives.^{17,24–27} For the interested reader, more information on XPS fitting and presentation can be found in our previous publications.^{17,28} XPS data of all corresponding sodium counter electrodes is present and discussed in the supplemental information (Table S1, Figure S6, and Figure S7). Uncycled Cu₂Sb-sodium metal half-cells with lithium perchlorate-based electrolyte were also characterized by XPS and are discussed briefly in the supplemental material (Figure S9 and S10).

A qualitative examination each set of XPS experiments of uncycled Cu₂Sb/Na half-cell batteries reveals that the profile of each XPS spectra for condition **2** is similar to **3**, which are both different from condition **1** (Figure 2). This supports the hypothesis that the SEI is forming spontaneously and the pre-passivation of sodium metal with FEC exhibits similar properties to having FEC in solution. Quantitative results for average peak position and peak concentration are tabulated in the supporting information (Table S1). Average peak position is extremely consistent, meaning the same environments are present in replicate experiments. The fit peak concentration error is larger, indicating there is heterogeneity in the amount of initial SEI species. Examining the carbon 1s XPS quantitatively (Figure 2A, D, G and Table S1.), the fit peak area of the singly oxygenated carbon environment at ~286.6 eV is two times larger in condition **1** compared to **2** and **3**, an indication of the differing amounts of SEI species. The highest binding energy peak at 290.1 eV in battery samples is usually attributed to carbonate or fluorinated carbon.^{29,30} For all conditions it is carbonate carbon (appearing between 289 and 291.5 eV), not fluorinated carbon, as there is no fluorine in **1** and in the other two systems the fluorine is attributed to NaF (Figure S5).³¹ Samples with and without FEC have the carbonate peak at 290.1eV, but without FEC (**1**) the peak is again roughly about two times larger, while under condition **2** the peak is just above the background. As with singly oxygenated carbon, this difference indicates the increased concentration of SEI species forming spontaneously without the presence of FEC.

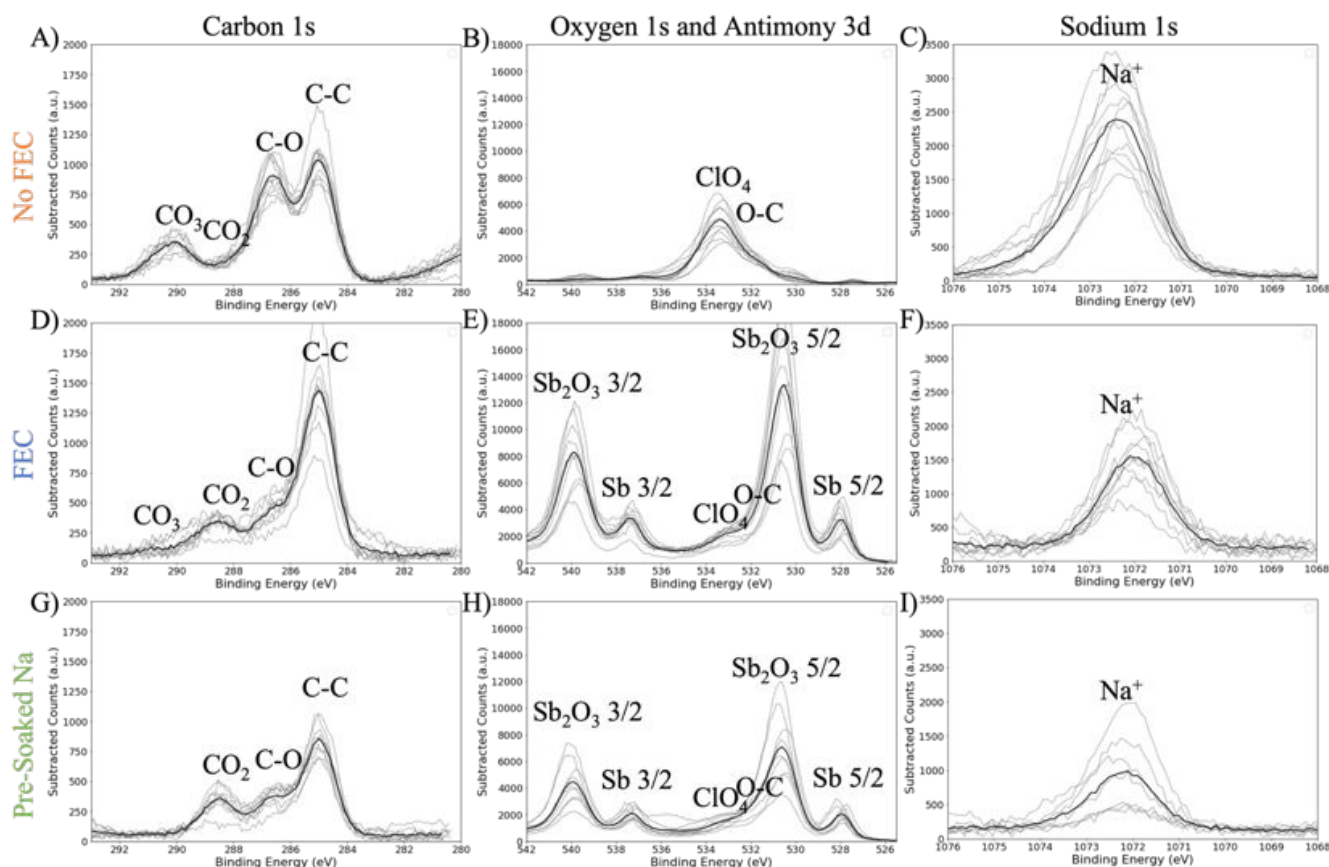


Figure 2. Overlay of XPS spectra of all spots on replicate uncycled $\text{Cu}_2\text{Sb}/\text{Na}$ battery samples. Black lines are an average representative spectrum made from all of the individual replicate grey spectra. The carbon 1s (A, D, G), oxygen 1s and antimony 3d (B, E, H) and sodium 1s (C, F, I) are presented. The electrolyte systems in the uncycled batteries are **1** (A, B, C), **2** (D, E, F), and **3** (G,

The highest binding energy in the **3** samples is at 288.55 eV, which is the same with in error as **2** samples at 288.6 eV, while the third peak in **1** samples is different at 288.3 eV indicating different carboxylate species which appear between 288–289.6 eV.³¹ The concentration of this CO_2 environment is larger under conditions **2** and **3** compared to **1**. Pre-soaking sodium in FEC, (**3**), has similar effects on the carbon environments as when FEC is a part of the electrolyte, (**2**), supporting the hypothesis that FEC is benefiting the cell through passivation of sodium metal. The carbon environments in the sample without FEC (**1**) can be related to the stoichiometry of the SEI species. For example, the singly oxygenated carbon and carbonate species have a 2.5:1 ratio, meaning molecules with that ratio of functional groups may be included in the SEI such as sodium diethylene di-carbonate, a potentially detrimental SEI product identified in other systems.^{32–34} This data, in conjunction with additional control experiments, may help to identify the initial SEI species.

The oxygen 1s photoelectron appears at the same binding energy as antimony 3d (Figure 2B, E, and H). Due to the XPS detection

depth of ~ 10 nm the presence of antimony and copper from the Cu_2Sb substrate is an indicator of SEI thickness (Figure S5). Without FEC (**1**), antimony peaks are barely above the background while antimony and antimony oxide concentration is $\sim 4\%$ with FEC (**2**) an $\sim 5\%$ with FEC pre-soaked (**3**). The SEI from condition **1** is thick enough to obscure the substrate in an uncycled battery clearly showing that SEI is forming in a higher quantity than under conditions **2** and **3**. Oxygen is a complicated element to differentiate via XPS due to multiple chemical environments occurring at similar binding energies, thus the minimum number of peaks were assigned. Condition **1** had more perchlorate chlorine (Figure S5) and therefore the larger perchlorate oxygen peak at ~ 533 eV compared to **2** and **3**. The remaining second oxygen environment was fit to oxygen on carbon at ~ 531 eV. Finally, a sodium auger KLL peak is fit at ~ 536 eV.

Like oxygen, sodium has small binding energy shifts for different chemical environments. For these experiments one sodium environment was fit, representing all potential sodium cations at ~ 1072 eV (Figure 2C, F, and I). The concentration of sodium in each

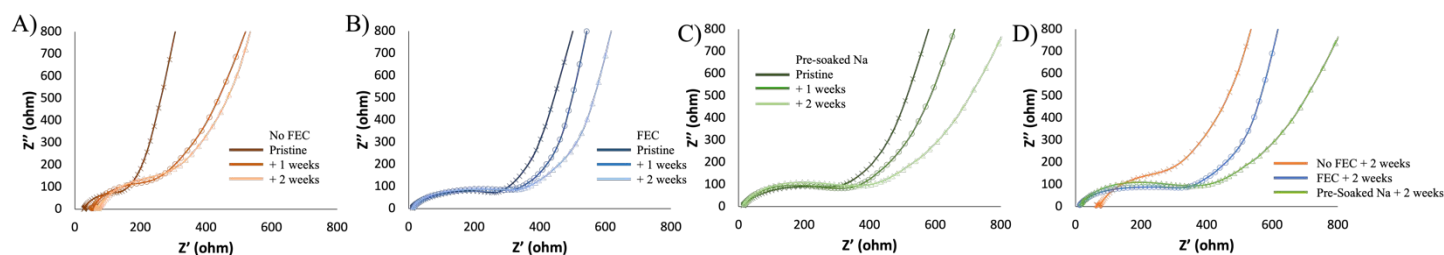


Figure 3. Electrochemical impedance spectroscopy Nyquist spectra, without any fit, of $\text{Cu}_2\text{Sb}/\text{Na}$ half-cell batteries in A) **1** (orange), B) **2** (blue), and C) **3** (green). The dark line in each plot is the half-cell after assembly, intermediate line is one week after assembly, and the light line is two weeks after assembly. Overlaid D) is each EIS spectra after two weeks.

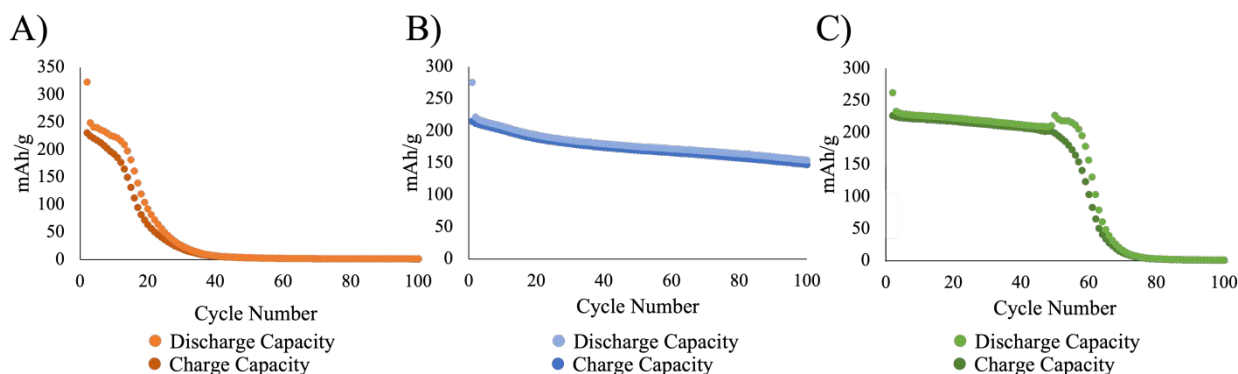


Figure 4. Cycle lifetime plots of Sb-CNT/Na half-cells with, left to right, **1** (orange), **2** (blue), **3** (green).

half-cell for **1** is $12 \pm 2\%$, **2** is $7 \pm 1\%$, while **3** is $8 \pm 4\%$, within error of **1** and **2**. This result supports the other XPS data, suggesting more SEI species are deposited onto the surface of Cu_2Sb without FEC (**1**), while the surface of the FEC (**2**) and presoaked (**3**) systems are similar.

Next, $\text{Cu}_2\text{Sb}/\text{Na}$ half-cells were assembled using the same electrolyte conditions **1**, **2**, and **3** and like the XPS experiments, no electrochemistry is applied. Electrochemical impedance spectroscopy (EIS) was collected after assembly, then collected again after both one week and two weeks to observe how the systems changed over time while no voltage is applied (Figure 3). Analogous to the XPS spectra, qualitatively, the impedance spectra of samples with electrolyte **2** and **3** are similar to each other, while **1** is different. This supports the hypothesis about the role of FEC in initial SEI formation as the reaction products on the surface of sodium metal in pretreated samples (**3**) resembles the impedance of a cell containing FEC in the electrolyte (**2**). The samples without FEC (**1**) show an increase in solution impedance over time, which can be correlated with the chemical reaction that induced the color change highlighted in Figure 1A, as well as the SEI components measured using XPS (essentially, more SEI is formed, which has higher impedance than a well-passivated electrode surface).

Lifetime battery performance of half-cells in each electrolyte condition **1**, **2**, and **3** are compared (Figure 4). Voltage capacity plots for these batteries is presented in the SI (Figure S11). These experiments utilized an antimony carbon nanotube anode material instead of Cu_2Sb , as it was able to obtain longer cycle lifetime.³⁵ The battery with electrolyte **1** exhibits poor cycle life while **2** and **3** have more stable lifetimes. However, the cycle lifetime of **3** exhibits a sudden loss in capacity at approximately cycle 60. This may be due to the importance of SEI repair through available FEC in solution.³⁶ This lifetime experiment further supports the hypothesis that important performance benefits of FEC occur through its pre-passivation of sodium metal rather than decomposing onto the surface of the anode material in half-cell sodium batteries.

Conclusions

Sodium ion batteries and other sodium technologies are increasingly important as alternatives to lithium. Many emerging sodium technologies are tested using half-cell set ups using sodium metal as a counter electrode. While previous work has demonstrated that sodium metal counter electrodes are more reactive than their lithium metal counterpart, no work has been

conducted examining the effect of sodium's heightened reactivity on the working electrode.^{5,6,13,22} Using uncycled sodium half-cells, SEI species are observed to form spontaneously on the working electrode, impacting its performance. This supports our first hypothesis that initial SEI products form from a chemical reaction with sodium metal and the electrolyte to *diffuse across the cell* and deposit on the working electrode. Additionally, we show that the solubility and thus the rate of the formation of these initial SEI products is dependent on the presence of the supporting electrolyte. We show that the passivation layer of sodium metal by FEC alone is capable of preventing the SEI species from forming. This supported our second hypothesis that the benefits of FEC occur through its own chemical passivation reaction with sodium metal, not its electrochemical reduction on the anode during cycling. These results are an important step in understanding the interactions occurring in a sodium battery and provide valuable insights for testing new sodium materials and developing sodium technology.

Author Contributions

Nathan Gimble conducted the chemical experiments and was the primary writer. Amy Prieto assisted with experimental design and edited and improved the manuscript.

Conflicts of interest

There are no conflicts to declare.

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