



New Paradigms on the Nature of Solid Electrolyte Interphase Formation and Capacity Fading of Hard Carbon Anodes in Na-Ion Batteries

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Capacity fading in Na/C half-cells has long been attributed to the continuous formation of the solid electrolyte interphase (SEI). The SEI is often assumed to grow thicker on the carbon anode surface during cycling, eventually rendering it electrochemically inactive. However, the findings here shed new light on this assumption. It is shown that SEI has an inward progression into the anode material, not an outward one. Additionally, it is also reported that the Na-metal counter electrode is hardly an inactive component in the Na/C half-cell. Contrarily, it is a primary source of electrolyte degradation. It is then shown that the combination of SEI formation, along with electrolyte degradation leads to severe kinetic problems at the electrolyte/anode interface, resulting in poor electrochemical performances. However, it is also demonstrated that such negative effects in a Na/C half-cell are easily reversible. By either drastically reducing the current rate, or pairing the carbon electrode with new electrolyte and new Na-metal counter electrode a carbon material with a 70% capacity loss can recover its original performances. These conclusions bring forth valuable insight. This shows that in a Na/C half-cell setting, long-term fading is not due to the carbon material, but caused by electrolyte degradation stemming from interface phenomenon.

## 1. Introduction

Study of Na-ion batteries (NIBs) is of high importance. Their performance coupled with the abundant availability of Na on Earth holds the potential to bring them to the forefront of electrical energy storage (EES) applications.<sup>[1]</sup> The successful deployment of NIBs would be significant. Such breakthroughs in EES technologies are necessary to bridge the gap between energy supply and demand—something currently holding back

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renewable energies, such as wind and solar. However current performance with candidate electrode materials has impeded the development of commercially viable NIBs.<sup>[2]</sup>

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Unlike the better-known Li-ion batteries (LIBs), NIBs cannot use graphite anodes due to the unfavorable thermodynamics of Na-ion insertion in graphite. Unless an electrolyte solvent is used for coinsertion, Na-ions cannot form a graphite intercalation compound.<sup>[3]</sup> As a result, many alternative anodes have been suggested, such as expanded graphite/reduced graphite oxides,<sup>[4]</sup> amorphous carbons,<sup>[5]</sup> alloyingtype materials, such as tin,<sup>[6]</sup> antimony,<sup>[7]</sup> phosphorous,<sup>[8]</sup> conversion oxide/sulfide materials,<sup>[9]</sup> layered oxide materials,<sup>[10]</sup> and organic compounds.<sup>[11]</sup>

Of these candidate anode materials, hard carbon, also known as nongraphitizable carbon, stands out. Its electrochemical performance as an NIB anode is much superior to that of graphite that is close to

be inactive in such a role,<sup>[12]</sup> as the more "open" and defected turbostratic structures<sup>[13]</sup> do not suffer the same thermodynamic constraints during Na-ion insertion. This allows them to be functional anode materials.<sup>[14]</sup> Furthermore, unlike the alloying and conversion type anodes, it does not undergo drastic volume changes, which bodes well for its long-term cyclability. Lastly, amorphous carbon has a distinct economical advantage, as it is readily available through the pyrolysis of nearly any type of organic material. This means that it can be obtained from essentially free precursors, such as agricultural waste and biomass materials, which would otherwise be left to decompose in the environment. With the proper processing techniques, these materials have shown to be very effective in electrochemical energy storage applications.<sup>[15]</sup>

The majority of the current literature on NIB carbon anodes centers around three metrics: capacity, power performance, and long-term cycling. Most studies use a Na/C half-cell setup for electrochemical testing. To those ends, high performance has been published in the literature. While this is encouraging, there are still a few outstanding issues that need to be addressed to accelerate progress, mainly the issues of mass loading and the first-cycle coulombic efficiency (CE@1st). Most reported materials typically use mass loadings of 1.0 to 2 mg cm<sup>-2</sup>, with a few

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recent experiments reporting higher numbers.<sup>[16]</sup> While this is acceptable on the lab bench scale to reveal fundamentals, future commercial NIB batteries may require mass loadings greater than ~5.0 mg cm<sup>-2</sup>, which is a very conservative estimation for the needed values. We have opened commercial Li-ion batteries for brand name cell phones, measured the mass loading of graphite anode, and found the loading is ~10 mg cm<sup>-2</sup>. Additionally, commercial batteries will also require CE@1st to be *at least* greater than 80%. There can be little compromise on these two factors if NIBs are ever to be a viable EES technology. However, high mass loading anodes in Na/C half-cells typically exhibit poor performances with regards to CE@1st and longterm cycling. However, research and insights into these problems have been limited. Unfortunately, there is little incentive to study and analyze poor results.

Herein, we take on the issues of high mass loading and poor long-term cycling head on. We study the root causes of capacity fading of hard carbon anode with a high active mass loading in a Na/C half-cell. The "high mass loading" referred to here is defined that an areal capacity can be above 1 mAh cm<sup>-2</sup>, an internal arbitrary standard. If the specific capacity is 200 mAh g<sup>-1</sup>, it would require a mass loading above 5 mg cm<sup>-2</sup>. The mass loading of the self-standing cloth carbon is above that with a loading of 7 mg  $cm^{-2}$  in this study. We then probe several crucial questions: is a high-mass-loading carbon anode intrinsically poor at long-term cycling? Or, are external factors, such as electrolyte/carbon surface interactions, i.e., SEI formation, or the presence of a Na-metal counter electrode to blame? Answers to these questions will allow the field to gain valuable insight on its current research approach, as well as the viability of hard carbon as long cycling NIB anode material.

To minimize external, non-carbon influencing factors, we select an additive-and-binder-free self-standing hard carbon cloth as the electrode, derived by pyrolyzing "Lyocell" cloth. Using this self-standing carbon anode, we discover that electrolyte degradation is the primary cause for the capacity fading during long cycling in a Na/C half-cell. The electrolyte degradation mechanism manifests itself in SEI formation, which surprisingly does not grow outward from the carbon interface, but rather inward. We also demonstrate that a severe capacity loss can be recovered in its entirety by either drastically lowering the current rate or pairing the cycled carbon anode with new Na-metal counter electrode and new electrolyte. This latter method also leads to the complete recovery of original rate performance and diffusivity values. Furthermore, we find that in a half-cell setting, the presence of the Na-metal significantly impacts the long-term cycling life by degrading the electrolyte. Lastly, the self-standing carbon anode offers the CE@1st close to 90%, where we identify that the CE@1st is lowered by the addition of polyvinylidene fluoride (PVdF) binder and high-surface-area carbon additives. It is important to remember that such insights on the fading mechanism/capacity recovery are most applicable to Na/C half-cells with a heavy carbon anode. Speculative applications of these findings beyond this system are left up to individual readers, as is further research, which is highly encouraged. It is likely that there are some significant parallels in the degradation mechanism with Li/C and K/C half-cells, and with that of full cells-though full cells also have to contend with



delamination of the electrode from the current collector as

### 2. Experiment and Results

another degradation mechanism.<sup>[17]</sup>

#### 2.1. Material Synthesis

The carbon materials studied are obtained through pyrolysis of commercially available Lyocell cloth. Lyocell fibers are regenerated cellulose filaments, formed from cellulose dissolution in organic solvents, such as N-methylmorpholine N-oxide (NMMO), followed by extrusion through a narrow opening and recrystallization in a coagulation bath.<sup>[18]</sup> In this study, we pyrolyzed light gauge waffle cloth weave Tencel-C, which is a cloth composed of Lyocell fibers of roughly 5 µm diameter threaded into strands close to 100 µm in diameter (Figure S1, Supporting Information). The cloth is pyrolyzed at 1600 °C under Ar gas for 2 h, yielding a self-standing and flexible carbon-fiber cloth. Due to the uneven arrangement of the carbonized threads, a precise thickness was difficult to obtain, however when cut in disks with a radius of 1 cm, the carbon cloth is found to have an areal density of 7 mg cm<sup>-2</sup> (Figure 1a). This cloth material will be referred to as L-1600 hereafter. Closer inspection of pyrolyzed cloth under scanning electron microscopy (SEM) shows that most individual fibers have retained their morphology as their original "bundles".

#### 2.2. Material Characterization

 $\rm N_2$  sorption measurement reveals hard carbon cloth of low surface area and low porosity with a Brunauer–Emmett–Teller (BET) surface area of 1.96 m<sup>2</sup> g<sup>-1</sup> and a density functional theory (DFT) total pore volume of 0.007 cm<sup>3</sup> g<sup>-1</sup> (Figure S2, Supporting Information). TEM imaging along with its noise-filtered-frequency-transformed image shows an amorphous carbon structure consisting of few-layered turbostratic nanodomains and amorphous regions (Figure 1b,c). The fast Fourier transfer image (FFT) shows no appreciable patterns, demonstrating the amorphicity of the material (Figure S3, Supporting Information).

The Raman spectrum confirms a typical amorphous carbon structure, expressing D-band at 1350 cm<sup>-1</sup> and G-band at 1580 cm<sup>-1</sup>. The D-band is typically ascribed to phonons at the K-point of the Brillouin zone, which stems from the A1g breathing mode of six-carbon rings. Defects must be present in the carbon rings for phonon scattering from this mode to occur. The G-band arises from  $E_{2g}$  phonons emanating at the  $\Gamma$  point, the center of the Brillouin zone. Its intensity is proportional to the number of sp<sup>2</sup>-bonded carbon, which does not require the presence of six-member rings. There is also the presence of a D band overtone-the 2D band at 2700 cm<sup>-1</sup>, a double resonance frequency made possible by the absence of defects.<sup>[19]</sup> The presence of 2D peak indicates that this material has a good degree of graphenic order due to the high annealing temperature during pyrolysis. In addition to the carbon characteristics, the spectrum also reveals the existence of TiO<sub>v</sub> impurity by the peaks around 150, 400, and 600  $cm^{-1}$ , which



**Figure 1.** a) A representative SEM image of L-1600 carbon cloth, showing the individual carbon fibers arranged into the bulk strands. The inset shows the flexibility of the cloth. b) A representative high-resolution TEM image of L-1600. c) The same TEM image that has undergone a 2D Fourier transform and subsequent frequency filtering in order to better show the contrast between the graphene domains and amorphous regions of the material. d) Raman spectrum (top) and XRD pattern (bottom) of L-1600. The index of the TiO hongquite phase is shown. e) A representative high angle angular dark field (HAADF) TEM image of a carbon fiber cross-section. f) An image of the enlarged area marked in the box in (e) on one of the particulates/ pores in the carbon fiber cross-section and corresponding energy dispersive X-ray (EDX) elemental mappings of titanium, oxygen, and carbon.

are similar signals found in other  $\text{TiO}_x$  carbon materials (Figure 1d).  $\text{TiO}_2$  is often added to Lyocell fibers as to increase ultraviolet protection or enhance self-cleaning properties.<sup>[20]</sup> Surprisingly, the X-ray photoelectron spectroscopy (XPS) analysis did not reveal any signals of Ti, but it did show faint traces of Ca, most likely a leftover artifact from the synthetic process (Figure S4, Supporting Information). The failure of XPS to display Ti signals is most likely due to the presence of the TiO particles on the inside of the carbon fibers, where they are too far from the surface to be probed by XPS radiation. Thermogravimetric analysis (TGA) under air to 900 °C reveals an ash mass of 3%, which is attributed to the TiO<sub>x</sub> compound along with the trace Ca (Figure S5, Supporting Information). Energy dispersive X-ray spectroscopy (EDX) revealed a similar mass percentage of TiO<sub>x</sub> (Figure S6, Supporting Information).

X-ray diffraction (XRD) patterns confirm the nongraphitic carbon structure along with the presence of titaniumcontaining impurity. The broad peaks around 24° and 43° represent the (002) and (100) crystallographic planes, respectively, where the (002) *d*-spacing of 0.366 nm is typical for hard carbon (Figure 1d). Using the Scherrer equation,  $L_a$  and  $L_c$ , the coherence lengths along the ab plane and c-axis in the turbostratic nanodomains, are estimated to be 3.97 and 1.10 nm, respectively. Combining the (002) *d*-spacing with  $L_c$  values, we can estimate that the average turbostratic nanodomains are of three-graphene-layers thick. These results may appear different from the TEM image; however, it is important to remember that the values provided by the Scherrer equation serve to give the average length: while there are five-layered domains, and there are also regions that have no order and thus lower the average. The same can be said for the  $L_a$  dimensions.

The additional XRD peaks at 36°, 42°, 61°, 73°, and 77° can be indexed to TiO in the hongquite phase (Figure 1d).<sup>[21]</sup> XRD pattern of the unpyrolyzed cloth fails to show significant crystalline phases; however, Raman spectrum of the unpyrolyzed cloth shows peaks at low wavenumbers consistent with TiO<sub>2</sub> (Figure S7, Supporting Information). It is likely that the titanium species were reduced from Ti(IV) to Ti(II) during the high-temperature annealing under high purity argon gas.<sup>[22]</sup> Looking at the cross section of a carbon fiber, we can spot the presence of several particulates inside of a fiber, which happen to be high in titanium and oxygen content (Figure 1e,f).



The presence of the TiO on the inside of the cloth would explain why the L-1600 sample failed to show any presence of titanium during the XPS analysis. Unlike the other characterization techniques, such as Raman, XRD, EDX, and TGA that give a "whole" length scale of characterization of the sample, XPS radiation is only helpful in probing the first few to 10 nm of a material surface. The location of the TiO particles are well beneath the surface of the carbon fiber, as seen in the SEM liftout, would explain why the presence of Ti is not present on the XPS but present in all the other tests.

### 2.3. Electrochemical Characterization

To test electrochemical performance, L-1600 cloth was cut into squares weighing around 3–4 mg sq<sup>-1</sup> as the working electrode in Na/C half-cells, where Na foil serves as both counter and reference electrode. For electrochemical testing, the C-rate was set to be 200 mA g<sup>-1</sup>. At a current rate of 20 mA g<sup>-1</sup> (C/10), L-1600 exhibits a reversible desodiation capacity of 210 mAh g<sup>-1</sup> and a CE@1st of 89.4% (**Figure 2a** and Figure S8, Supporting Information). This is one of the highest CE@1st values in literature for hard carbon anodes.<sup>[23]</sup> The combination of the desodiation capacity along with the high CE@1st is important when considering anode materials for a full cell: a full cell is in its fully charged state when the carbon anode is fully sodiated. Thus the capacity available in a NIB is dependent on the amount of

ions that can be reversibly desodiated from the anode material. Furthermore, a high efficiency of sodiation is critical. It is also important to remember that a full cell only possesses a finite amount of Na-ions in the cathode, which makes the high CE@1st important. Some of the cloth was ground into powder and processed into traditional electrodes using PVdF binder and Super-P (C-45) conducting carbon additive. However, these cells exhibited a lower CE@1st, with the L-1600-91 (90 wt% carbon, 10 wt% PVdF binder) having an efficiency of 81.9% with a loading mass of 2.4 mg  $cm^{-2}$  on an aluminum disk with a diameter of 1.0 cm. The L-1600-811 (80 wt% carbon, 10 wt% PVdF binder, 10 wt% C-45) had a CE@1st of 82.1% with a loading mass of 2.1 mg  $cm^{-2}$  on a similar aluminum disk. These results hereby show that PVdF and high surface area C-45 may be responsible for the lower CE@1st, which is reduced by nearly 10% (Figures S9 and S10, Supporting Information).

The potentiogram profiles are typical for a hard carbon material: a steep sloping region followed by a long low-voltage plateau. The sloping region is attributed to the binding of Naions at defect sites in the carbon, while the plateau region is assigned to Na-ion intercalation between turbostratic graphene layers and binding onto the curved graphene wrinkles inside the pores.<sup>[5a,14e]</sup> The potentiogram profiles also reveal the lack of significant contribution of capacity from TiO, as such a contribution would be manifested in the presence of a much shorter low-voltage plateau and longer and more



**Figure 2.** a) The 1st cycle potentiograms of the L-1600. b) Long-term cycling of the L-1600, total capacity (black), capacity contribution over 0.1 V versus Na<sup>+</sup>/Na (red), capacity contribution under 0.1 V versus Na<sup>+</sup>/Na (blue) and coulombic efficiency (gray). The initial climb in capacity from 210 to 235 mAh  $g^{-1}$  in the initial cycles is most likely due to a prolonged "wetting" period. c) Linear regression of the total capacity versus the capacity under 0.1 V versus Na<sup>+</sup>/Na for 350 cycles. d) Potentiograms at current rates of 1 and 20 mA  $g^{-1}$  after 350 cycles. e) Impedance spectra collected after the 1st cycle and after the 350th cycle. Inset shows the equivalent circuit. f) A zoomed-in view of the semicircle comparing the anode materials. The inset shows the difference in ESRs.



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pronounced sloping region from 0.15 V to the upper cutoff voltage.  $\ensuremath{^{[24]}}$ 

Long cycling tests are conducted at a current rate of 20 mA g<sup>-1</sup> (C/10). In 350 cycles, the observed capacity decreased from the maximum of 235 to 70 mAh g<sup>-1</sup>—a retention rate of only 30% (Figure 2b). While such poor cycling results are not desirable, it is a great opportunity to investigate the causes of capacity fading in these half-cells.

We notice that the overall capacity fading is primarily due to the capacity loss from the low-voltage plateau region below 0.1 V versus Na<sup>+</sup>/Na. The capacity retention is only 15% for the lowvoltage plateau, but 80% for the sloping region. After 350 cycles, negligible capacity contribution is from the low voltage plateau (Figure 2b). This is further supported by a linear regression comparing the total capacity versus that obtained under 0.1 V, which yields an R<sup>2</sup> value of 0.998 (Figure 2c). Intriguingly, when the current rate is lowered to 1 mA g<sup>-1</sup> (C/200) after 350 cycles, the capacity rises to 260 mAh g<sup>-1</sup>—even higher than the original capacity at 20 mA g<sup>-1</sup> (C/10) (Figure 2d). Furthermore, the entire low-voltage plateau reappears. This shows that capacity fading is not due to a structural breakdown of carbon anode, but rather due to kinetic limitations. This suggests that hard carbon does not exfoliate on the basis of its unique structure.

To study the kinetic limitation, we first compare electrochemical impedance spectra (EIS) between the 1st and the 350th cycle, along with the fitted circuit (Figure 2e and Figure S11, Supporting Information). From the Nyquist plot, equivalent series resistance (ESR), the x-axis intercept, increases from 7.42 to 95.02  $\Omega$  (Figure 2f). The semicircle is due to the resistance of the solid electrolyte interphase (SEI) and the charge-transfer resistance, which should be attributed to both carbon and Na-metal electrodes.<sup>[25]</sup> The sum of the two resistive elements that makes up the semicircle,  $R_{\rm SEI} + R_{\rm CT}$ , rises from 243  $\Omega$  for the 1st cycle to 754  $\Omega$  for the 350th cycle. This confirms the presence of severe kinetic problems developing in the cell in the course of long cycling.

Having established the presence of a kinetic problem, the next challenge is to reveal its root causes: whether it is due to the intrinsic properties of the carbon material, or other factors in the Na/C cells.

#### 2.4. Visual Analysis of SEI

Our first hypothesis was that increased SEI formation on the surface of the individual carbon fibers is the cause for kinetic problems. Thus, we analyzed two representative L-1600 electrodes at two different cycling-life stages in capacity retention: one that has had 75% capacity retention after 150 cycles and the other that has 35% capacity retention after 250 cycles (Figure S12, Supporting Information). To visualize the SEI layer, we used a focused ion beam (FIB) to carve cross-sectional slices of carbon fibers. We collected oxygen EDX elemental mappings to profile the extent of SEI formation as a function of oxygen concentration (Figure 3a,c). The images are displayed on an enhanced color scale to sharpen the contrast between oxygen signals and the background, where the dark blue represents no oxygen signal. We also plot both profiles and 3D pixel intensity maps to better identify the concentration gradients (Figure 3b,d,e,f), where the pixel values are plotted on the vertical axis, with a high value corresponds to a high oxygen concentration, and thus a high presence of SEI.

It must be pointed out that in our visualization of the SEI, we do not characterize and identify individual SEI components. Rather, we look at the SEI as a broad-based entity quantified through the presence of oxygen as a marker, as our ultimate goal is to elucidate the relationship between the scale of the SEI formation and long-term cycling performance. Since we could not control the formation of the SEI, we consider it would be best to treat it as a single entity that could be quantified and imaged by the amount of oxygen content. Prior to the cross-sections being cut with the FIB, the electrodes were removed from



**Figure 3.** Cross-sectional EDX oxygen mappings of cycled L-1600 carbon. a) An electrode after 150 cycles with 75% capacity retention. c) An electrode after 250 cycles with 35% capacity retention. b,d) Corresponding plots of the pixel values from a profile view. e,f) Corresponding 3D pixel intensity plots of the L-1600-75% and L-1600-35% carbon fibers, respectively. The labeled axis is the z-axis, where the pixel values are plotted on a scale of 0–200. The basis for the pixel plots is the sheered images of (a) and (c).



the Na/C half-cells in an Ar-filled glovebox, and washed and briefly sonicated in ethanol before being vacuum dried. The intent of the washing and sonication was to rid the electrodes of remaining liquid electrolyte. Thus, with such preparation, the majority of the oxygen signals present in the characterization should emanate from the remaining SEI deposits. It is likely that the washing affected the concentration of the oxygen content. However, it is important to note that both samples were subjected to the same preparation, yet both yielded vastly different distributions of oxygen signals, thus validating our experimental approaches.

Comparing L-1600-75% to L-1600-35% reveals a surprising phenomenon: the SEI growth on hard carbon has not been an outward growth as one would expect, but an inward growth. L-1600-75% shows a high oxygen concentration near the surface, which tapers off when moving toward the fiber center. L-1600-35% displays a nearly uniform oxygen concentration through the entire cross section of carbon fiber. This is significant as it shows that the SEI is not the traditional "interphase" as is the case with graphite anodes in LIBs. The unique inward growing Na-SEI in hard carbon may have to do with the innate microporous structure of hard carbon despite its low BET surface area measured by  $N_2$  sorption.

#### 2.5. Effect of Replacing Battery Components

To investigate whether such inwardly grown SEI would cause slower diffusion of Na-ions inside hard carbon, we measured the diffusivity values using galvanostatic intermittent titration technique (GITT) (Figure S13, Supporting Information). After 350 cycles, the diffusivity values of half-cells are three orders of magnitude lower in the low-voltage plateau region than the freshly made cells with the same carbon cloth electrode material (**Figure 4**a and Figure S14, Supporting Information). However, it seems likely that the lowered diffusivity values can be related to other components in the Na/C cells than the hard carbon anode. When opening a cycles cell, we notice the yellow tint of the separator indicating the degradation of the electrolyte over cycling. This could play a large factor in poorer electrochemical performances (Figure S15, Supporting Information).



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Therefore, we conducted GITT tests on the *same* carbon cloth anode at four sequential stages: (1) as a pristine anode, (2) after 300 cycles (cycling performance and EIS are shown in Figures S16–S19, Supporting Information), (3) after replacement of cycled electrolyte with new electrolyte, and (4) after replacing all cycled cell components with new ones, including electrolyte, separator, and Na counter electrode except for the cycled hard carbon electrode (Figure S20, Supporting Information). This 4-tiered diffusivity/rate cycling studies allow us to track the changing electrochemical behavior of hard carbon anodes, electrolyte, and Na electrode.

We discover that the diffusivity values of a new cell drop precipitously after 300 cycles, recover slightly when new electrolyte is added, and recovers to nearly its full extent when the electrolyte, the Na-metal counter electrode and the separator are replaced with new ones (Figure 4b and Figure S21, Supporting Information). The capacity values display a similar trend. After long cycling, the capacity at a current rate of 20 mA  $g^{-1}$  (C/10) is 44% of the original; replacement of the electrolyte increases the capacity to 74% of the original value, while the replacement of the electrolyte, separator, and Na-metal counter electrode yields a capacity close to 95% that of the original (Figure 4c). The results show a surprising fact: the capacity fading of hard carbon has nothing to do with hard carbon even kinetically, as a poorly performing electrode can easily be rejuvenated into its former self. This shows that the inward "SEI" formation in a carbon anode may not negatively affect its Na-ion storage properties, which, in fact, causes more questions about the Na-ion storage mechanism in hard carbon-whether the oxygen decorated micropores can store Na-ions or not. To answer this guestion is beyond the focus of this study. This leaves there two causes to the fading of Na/C half-cells: degradation of the electrolyte and passivation of the Na-metal counter electrode.

### 3. Discussion

#### 3.1. Analysis of the Electrolyte and Na-Metal Counter Electrode

To understand the relationship between the degradation of electrolyte and the role that Na counter electrode plays, we



Figure 4. a) GITT diffusivity measurements comparing a pristine anode material and one that has undergone 350 cycles. b) GITT diffusivity measurements on the same carbon cloth at four different stages in the cycle life. c) Rate cycling at the four different stages. Full GITT information is available in the Supporting Information.



**Figure 5.** a) Digital image of Na-metal disk being soaked in a 1 NaPF<sub>6</sub> EC:DEC electrolyte for three months in an argon glovebox. b) Close-up image of the Na-metal disk. c,d) FTIR and Raman spectra of new electrolyte in glass fiber separator, cycled electrolyte in glass fiber separator, which has undergone 350 cycles at 20 mA g<sup>-1</sup> and Na-metal surface soaked in 1 NaPF<sub>6</sub> EC:DEC electrolyte for three months. e) Magnification of Raman EC ring bending mode at 720 cm<sup>-1</sup> and PF<sub>6</sub><sup>-</sup> stretching mode close to 750 cm<sup>-1</sup>. f) Magnification of Raman EC ring-breathing mode close to 900 cm<sup>-1</sup>. g) Overpotential versus cycle number over 350 cycles at 20 mA g<sup>-1</sup>. The outlying points correspond to the values obtained during the first 20 cycles where the anode has not been properly wetted. h) Net current on a log scale versus voltage jump at the beginning of desodiation, leading to a Tafel-like plot. The dashed lines were used to analyze exchange currents.

conducted experiments to reveal the reactivity of Na-metal with the electrolyte. We also investigated the chemical composition of electrolyte trapped in the glass-fiber separator of a cycled Na/C half-cell.

After being soaked in the electrolyte for three months, Na foil is covered by a passivation layer, while the electrolyte turns slightly yellowish (**Figure 5**a,b). When exposed to air, the passivation layer on Na foil prevents its surface from being oxidized to sodium oxide, as the soaked Na foil does not turn white as a fresh piece of Na-metal rapidly does (Figure S22, Supporting Information).

The Fourier-transform infrared (FTIR) spectra of the soaked Na foil and the cycled electrolyte (350 cycles) in the separator are very similar, much different from the new electrolyte (Figure 5c). The measurements of the cycled electrolyte were obtained by cutting a piece of the yellow tinted separator, which acted as "electrolyte sponge." Thus we take the measurements from the separator to be representative of the state of the electrolyte in the Na/C half-cells. Measurements of the new electrolyte were also done by using a separator as "electrolyte sponge", which was then characterized. The background of the glass-fiber separator as well as the sodium-metal factor little in the measurements (Figure S23, Supporting Information). The adsorption bands at 1640  $\rm cm^{-1}$  and 1320  $\rm cm^{-1}$  correspond to the asymmetric (v AS) and symmetric (v S) C=O stretches, respectively, of CH<sub>3</sub>CH<sub>2</sub>OCOONa, also referred to as ROCO<sub>2</sub>Na, which is known to be a main breakdown product in ethylene carbonate (EC)-containing electrolytes due to the ring opening of EC.<sup>[26]</sup> The peak near 1400 cm<sup>-1</sup> is due to the formation of a carbonate compound, though it has also been ascribed to the CH<sub>2</sub> bending mode ( $\delta$  CH<sub>2</sub>) of the carbon chain in the ROCO<sub>2</sub>Na breakdown product.<sup>[27]</sup> Specifics aside, it is yet another sign of electrolyte breakdown.

The FTIR results show that the passivation layer on the soaked Na-metal has the same fingerprint as the SEI electrolyte breakdown species that are found in the cycled electrolyte. This indicates that such breakdown products do not adhere to the Na-metal surface well and could leach throughout the cell. Similar results were reported by Ponrouch and co-workers who explored the surface of Na-metal electrodes after conducting CV cycling in a symmetric cell.<sup>[28]</sup> However, for the soaked Na-metal, the SEI is formed without electrochemical cycling, showing the inherent instability of the Na-metal with conventional carbonate electrolytes.

To further understand the electrolyte degradation, we also collected Raman spectra of the cycled electrolyte (350 cycles) and compared them to a fresh, uncycled electrolyte. The spectrum peak intensity was normalized using the peak at 1224 cm<sup>-1</sup>, as this peak represents the C–H bonding mode of EC, which is not affected by the addition of electrolyte salts.<sup>[29]</sup> We specifically focus on the peaks around 720 and 900 cm<sup>-1</sup>. The peak at 720 cm<sup>-1</sup> is assigned to the ring deformation mode of EC, which reflects the cation-solvent interaction.<sup>[30]</sup> For this peak, first, the peak intensity is much smaller for the cycled electrolyte, meaning that the EC molecules have been consumed in the SEI build up (Figure 5d). Second, there is a



blueshift to a higher wavenumber, meaning that the ratio of coordinating EC molecules in EC-Na<sup>+</sup> over free EC molecules has increased (Figure 5e). The peak near 740 cm<sup>-1</sup>, ascribed to the stretching vibration of  $PF_6^-$  anions,<sup>[31]</sup> is nearly unchanged. Lastly, the peak at 900 cm<sup>-1</sup> is due to the ring breathing mode of EC, which blueshifts when there are cation interactions, i.e., forming EC-Na<sup>+,[29]</sup> Again, the cycled electrolyte exhibits an attenuated peak along with a blueshift when comparing to the new electrolyte (Figure 5f). The lower peak intensity indicates the electrolyte degradation along with the blueshift, shows that the concentration of ionic species has increased after cycling. Comparison between the Raman spectra of the cycled electrolyte and the surface of the electrolyte-soaked Na-metal reveals similar profiles-as is the case with FTIR (Figure S24, Supporting Information). The insights that cycling increases ionic concentration via electrolyte degradation from Raman results were verified through a controlled trial by taking Raman readings of EC:DEC electrolyte solutions with molarities of 0.5, 1, 2, and 4 M of NaPF<sub>6</sub> (Figure S25, Supporting Information).

#### 3.2. Effect of Electrolyte Degradation on Sodiation

The increase in salt concentration causes greater ion pairing between the Na<sup>+</sup> and  $PF_6^-$  ions, thus making it more difficult for the Na-ions to be desolvated from the electrolyte before insertion into hard carbon. This could slow down the reaction kinetics, especially in the case of Na-ion intercalation between graphene layers in hard carbon. It has been shown experimentally and computationally that desolvation is a rate-limiting step as partially solvated ions diffuse much faster into graphitic domains than naked ions.<sup>[32]</sup> This explains why the diffusivity values of the cycled Na/C half-cells obtained via GITT drop so precipitously. If there is a greater energy penalty for an ion to desolvate from the electrolyte, a greater voltage must be applied during GITT to move the same number of ions into the carbon structure in a unit time. This results in a greater polarization. However, this greater polarization causes the battery tester to hit the cut-off potential prematurely, which subsequently switches it into a desodiation mode, before a full sodiation can be obtained. This explains the disappearance of the low-voltage plateau after long cycling, along with its recovery if low current rates are used, or the degraded electrolyte is replaced.

#### 3.3. Effect of Electrolyte Degradation on Desodiation

The degradation of electrolyte also causes an increase in overpotentials during the desodiation sweeps. When the Na-ions are removed from the carbon anode, they need to be resolvated by EC molecules. If the concentration of free EC molecules is low, there will be greater polarization on the carbon surface—this is much like the concept of overpotential ( $\eta$ ) in Butler–Volmer reaction kinetics.

As further proof of this, we plot the voltage "jump" (Figure 5g inset) that occurs when the battery switches from sodiation to desodiation mode. Looking at Figure 5g, we see that aside from the initial cycles this voltage jump increases steadily along with cycling, and is well correlated with the desodiation capacity



during cycling—when the voltage jump is higher the capacity is lower (Figure S26, Supporting Information). The initial voltage jump decreases most likely due to the electrolyte/carbon anode wetting process.

Initially, we took this voltage jump to be a sign of an increasing ESR. However, when running a rate-cycling test at current rates ranging from 1 mA  $g^{-1}$  (C/100) to 1500 mA  $g^{-1}$  (7.5C), we failed to see a linear trend of the voltage jump, especially at low current rates, thereby showing that this voltage jump is not entirely a function of ESR (Figure 5h). This was the case in multiple cycled cells.

Thus, we postulate this voltage jump to be a pseudo-overpotential: an activation overpotential is needed to desodiate the hard carbon, where upon a higher current rate, a greater overpotential is necessary to sustain the desodiation process. When plotting these overpotential values versus a logarithm-scaled version of their current rates, we see that the resulting plot shares many similar characteristics with a typical Tafel plot, thereby indicating that the onset of desodiation has a Tafel-like behavior (Figure 5h). When taking this into the context of the electrolyte solution, a clear picture begins to emerge. When Naions become desodiated from the carbon material, they must be coordinated by EC molecules. If the ratio of free EC molecules over EC-Na<sup>+</sup> coordinating EC molecules is small, the frequency of newly released Na-ions pairing up with EC molecules will be diminished, which will cause the system to become more polarized, thereby leading to a higher initial voltage jump.

We model the behavior in Figure 5h by the Tafel equation (Equation (1))

$$\eta = \mathbf{a} + \mathbf{b}\log\left(i\right) \tag{1}$$

where  $\eta$  is overpotential, *i* is the applied constant current (the current density can be referred to as *j*), *a* is the y-intercept of the  $\eta$  versus log(*i*) plot and *b* is the Tafel slope (Equation (2)), which equals to

$$(-\alpha F)/(2.3RT) \tag{2}$$

where  $\alpha$  term represents the transfer coefficient, *F* is Faraday constant while *R* is a thermodynamic parameter, and *T* is temperature in Kelvin.

Here, we plot log(i) as a function of  $\eta$ , where the slope is found to be extremely similar in both cases, thereby showing that the overall nature of the electrochemical reaction has not changed. However the y-intercept that expresses  $log(i_0)$  is vastly different with  $i_0$  representing the exchange current when  $\eta$  is zero. Under Butler-Volmer kinetics, this is the current at which both the cathodic and anodic reactions proceed at the same rate. A smaller  $i_0$  implies more sluggish reaction kinetics, and as a result, a higher activation overpotential is needed to drive the reaction. Extending this to the Na/C cell, a smaller  $i_0$  means that it is slower to transport the Na-ions to sodiate/desodiate the carbon anode, especially in the region near the cutoff potential (≈0.01 V vs Na<sup>+</sup>/Na). When comparing the cycled anode (350 cycles) with old electrolyte/old Na-metal versus the same cycled anode paired with new electrolyte and new Na-metal, the measured  $i_0$  is much greater for the new electrolyte/new Na cell. This proves that the degradation in electrolyte and



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passivation of Na-metal lead to much slower kinetics, which adversely affects the performance. This in turn shows that the capacity fading during long cycling is primarily a function of the electrolyte and Na-metal counter electrode. Furthermore, the improved kinetics can lead to much-improved capacities, especially at current rates between 10 mA  $g^{-1}$  (C/20) and 100 mA  $g^{-1}$  (0.5C) (Figure S27, Supporting Information).

It is important to note that our intent of the electrochemical analysis is not a direct analysis of a Tafel-slope, overpotential  $\eta$ , exchange current  $i_0$  and exchange coefficient  $\alpha$ . Rather, we are trying to show how our current systems follow behaviors highlighted in basic electrochemical principals, and that such comparisons help to show that degrading electrolyte causes severe kinetic problems, which lead to poor battery performances.

## 4. Conclusion

We have demonstrated five findings in this paper: (1) Hard carbon materials can obtain CE@1st close to 90%, but such high CEs are negatively affected by the addition of PVdF and conducting carbon additive; (2) We reveal that SEI slowly permeates into the hard carbon electrode along cycling, and is not confined to the surface. This underscores the importance of developing a proper surface coating for the electrode; (3) More importantly, we discover that even extreme capacity losses during long cycling can be recovered through very slow current rates or replacing Na/C cell components. This shows that the fading during long cycling is caused by kinetic problems and not the degradation of the carbon material. Furthermore, it also shows that the "SEI" of hard carbon may not negatively affect its electrochemical properties. (4) We analytically prove that degradation of the electrolyte, along with the passivation of the Na-metal is the root cause for capacity fading of Na/C cells. The degradation greatly affects the sodiation and desodiation processes, causing increased cell polarization, decreased diffusivity values and decreased capacity, especially in the low-voltage plateau region; (5) We found that electrolyte degradation readily happens at the Na-metal surface-even with the absence of electrochemical cycling, where the same type of breakdown products were also found in the cycled electrolyte and on the soaked Na-metal surface, meaning that these SEI products do not stay confined to the surface of the Na-metal and can leach throughout the cell.

It is less likely that it is due to the uniqueness of electrolyte we used in this study that causes the observed electrolyte degradation, as the EC/DEC combination is quite representative among carbonate-based electrolytes employed in LIBs and NIBs. Furthermore, it is quite reasonable to believe that the reactivity of the Na-metal damages the electrolytes, which may not be observed in a full cell setup, where Na-ion containing minerals are used as the cathode.

We hope that the readers will come away with some new insights on the half-cell approach widely used in the literature on anode materials research. It is important to consider the electrode material, the electrolyte and the counter-electrode in an integrated manner. We believe our results are relevant not only just for carbon anodes in NIBs, but other types of NIB anodes/cathode, possibly with other battery chemistries. Furthermore, we also think that such results could be useful for the concept of battery recycling, which is still an under-explored concept in academic settings.

# 5. Experimental Section

A detailed experimental section is provided in the Supporting Information. This includes information on material synthesis, material characterization, electrochemical preparation, and electrochemical testing. Details on the MATLAB code used from the image transfer are available from the corresponding author.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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