JACS Au
AN OPEN ACCESS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/jacsau
Article

Revisit Electrolyte Chemistry of Hard Carbon in Ether for Na Storage

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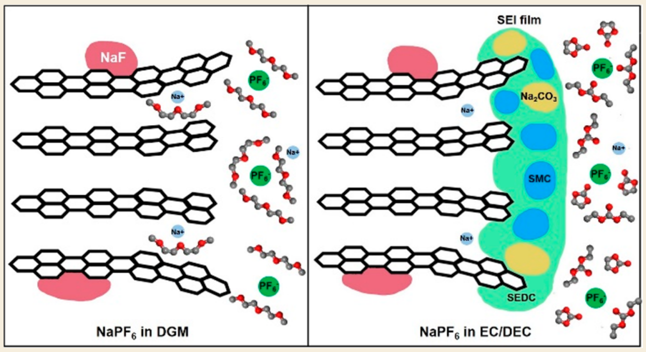
Cite This: *JACS Au* 2021, 1, 1208−1216

ABSTRACT: Hard carbons (HCs) as an anode material in sodium ion batteries present enhanced electrochemical performances in ether-based electrolytes, giving them potential for use in practical applications. However, the underlying mechanism behind the excellent performances is still in question. Here, ex situ nuclear magnetic resonance, gas chromatography−mass spectrometry, and high-resolution transmission electron microscopy were used to clarify the insightful chemistry of ether- and ester-based electrolytes in terms of the solid−electrolyte interphase (SEI) on hard carbons. The results confirm the marked electrolyte decomposition and the formation of a SEI film in EC/DEC but no SEI film in the case of diglyme. In situ electrochemical quartz crystal microbalance and molecular dynamics support that ether molecules have likely been co-intercalated into hard carbons. To our knowledge, these results are reported for the first time. It might be very useful for the rational design of advanced electrode materials based on HCs in the future.



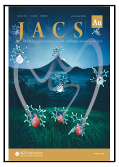
KEYWORDS: *solid−electrolyte interphase, hard carbon, ether electrolyte, anode, sodium ion batteries*

INTRODUCTION

Lithium ion batteries (LIBs) have achieved great success in the past decades, but the limited resources of lithium greatly restrain the applications of LIBs in smart grids, electric vehicles, etc.[1,2] Therefore, replacing lithium with other elements is very necessary. Sodium ion batteries (SIBs) as one of the next-generation batteries address this concern well, due to the abundant reserves of sodium in the earth. Moreover, SIBs share the similar basic fundamentals and fabrication protocols as LIBs.[3−6] However, the heavy mass and large size of Na ions greatly increase the redox overpotential and volume change of electrode materials, resulting in a reduced electrochemical activity and a marked structure instability. Thus, many electrode materials, which have been used in LIBs, do not work in SIBs. Graphite, a typical anode material in LIBs, only stores a small capacity of Na ions in carbonate electrolytes, due to the poor thermodynamic stability of Na-related intercalation compounds in graphite.[7] Using ether rather than carbonate as the electrolyte promotes a reversible capacity to ∼150 mAh g^{-1},[8] where ether is co-intercalated together with Na ions into graphite. However, the cycling stability is still worse than that in LIBs. Hard carbons (HCs), whose structure is featured by numerous structure defects and nanovoids, and random-oriented graphene layers present a large reversible capacity (300−400 mAh g^{-1}) and a low operation voltage (∼0.1 V vs Na^+/Na).[9] Furthermore, this unique structure of HCs also restrains the exfoliation of graphene layers caused by co-intercalation chemistry, benefiting the long-term cycling stability. Therefore, they are considered one of the promising anode materials of SIBs for practical applications.

However, the electrochemical performances of hard carbon are still far from satisfactory use so far. The main obstacles of hard carbons in SIBs come from the poor rate capability, the short cycle life, and the low initial Coulombic efficiency (ICE). In order to address these issues, many strategies have been developed from different aspects, such as structure engineering,[10−16] heteroatom doping,[17−20] and so on. Among them, the exploration of electrolytes has aroused great interest because electrolytes directly dictate the interface reactions on electrode materials and then the reversibility of electrochemical reactions. For ester-based electrolytes, the reducing products of ester molecules always lead to a thick but stable solid−electrolyte interphase (SEI) film,[21−25] thereby offering a reliable protection for hard carbons in SIBs. However, the thick and organic-rich SEI film also lowers the ICEs and rate capability. Different from the case of ester-based electrolytes, ether-based ones form a thin and inorganic-rich SEI film, thus resulting in the improved ICEs and rate capability.[26−32] Using $NaCF_3SO_3$ in diglyme as an electrolyte, reduced graphene oxide (rGO) exhibited a high ICE of 74.5%, an impressive rate

Received: April 8, 2021
Published: July 6, 2021



capability (~196 mAh g^{-1} at 5 A g^{-1}), and an excellent cycling stability (75.2% after 1000 cycles at 1 A g^{-1}).[26] The ICE could be increased to 91.2% by flexible hard carbon papers as a self-supporting anode,[27] but the rate capability was slightly reduced to ~170 mAh g^{-1} at 2 A g^{-1}. Xu et al. tried different methods to realize the merits of ester- and ether-based electrolytes simultaneously for hard carbons, such as a using a SEI film from ester-based electrolytes cycled in ether[28] and the addition of a trace of ester into ether-based electrolytes.[29]

Although using ether-based electrolytes to improve the electrochemical performances of HC has been demonstrated, there are still many doubts about the underlying mechanism. The first one is if there is a SEI film on the surface of HC upon cycling. So far, the related discussions about the SEI film are based on X-ray photoelectron spectra (XPS) of cycled electrodes, in which the signals from organic species, −C−O−C−, −(C═O)−, −(C═O)−O−, etc., could be easily visualized.[26−29] Thus, the formation of a SEI film via electrolyte decomposition is concluded. However, the electrode surface, especially those after cycles, is easily contaminated by adsorbed solvents and highly active air/moisture during the cleaning, storage, and transfer process of the electrodes. Moreover, the XPS signals from organic binders and conductive carbon are not be effectively excluded. Therefore, this conclusion still needs more evidence from other techniques. Moreover, some works on Na storage properties of graphite suggest that the reduced products were soluble in the case of ether-based electrolytes,[33−35] thus no SEI film was detected. Although HC and graphite have completely different structures, they still share the similar element, unique graphene layers, and so on. Thus, it is also possible for HC to exhibit a similar electrochemical feature. The second debate is if there is a co-intercalation chemistry in ether-based electrolytes for HC. Although the SEI film definitely suppresses the co-intercalation reactions, these reactions still possibly occur[36] because a thin SEI film can be broken at some sites due to the volume expansion.

In this work, the intercalation chemistry on HC in SIBs is carefully investigated for Na storage. First of all, it is demonstrated that hard carbon exhibits an electrochemical performances in diglyme (DGM) better than that in ethylene carbonate/diethyl carbonate (EC/DEC), in all the important terms, i.e., Coulombic efficiency, reversible capacity, cycling stability, and rate capability. It can sustain a capacity of 224.4 mAh g^{-1} after 3500 cycles at 1 A g^{-1}. Then, ex situ nuclear magnetic resonance (NMR), gas chromatography−mass spectrometry (GC−MS), and high-resolution transmission electron microscope (HRTEM) were used to clarify the existence or not of a SEI film on HC. These results indicate that there are the marked electrolyte decomposition and the formation of a SEI film in EC/DEC, in line with the previous works. However, what's surprising is no formation of a SEI film in the case of diglyme, which well explains the improved ICE and rate capability. In situ electrochemical quartz crystal microbalance (EQCM) confirms that ether molecules have been co-intercalated into HC likely in terms of $[Na(DGM)]^+$. To our knowledge, these results are reported for the first time on HC. It might be very useful for the rational design of advanced electrode materials based on HC in the future.

■ EXPERIMENTAL SECTION

Hard carbon was bought from Kuraray Co. Ltd

Electrochemical Measurements

Electrochemical performances of hard carbons as the anode material for SIBs were tested in CR2032-type coin cells. First of all, HC, acetylene black (AB), and sodium alginate (SA) were mixed in a weight ratio of 7:2:1. Then, several drops of distilled water were added into the mixture. After being ground for 30 min by hand, the resultant slurry was spread on a copper foil by a doctor blade, followed by drying in vacuum at 60 °C for 12 h. Then, the foil was punched into the discs with a diameter of ~12 mm. In this case, the mass loading of the active materials on the discs was about 1.5−2.5 mg cm^{-2}. The disc was used as the working electrode and assembled with Na metal as the counter electrode and glass fiber (Celgard 2325) as the separator in an Ar-filled groove box (Mikrouna, Super 1220/750/900, $H_2O < 1$ ppm; $O_2 < 1$ ppm). Two different electrolytes, 1.0 M $NaPF_6$ in DGM or in EC/DEC ($H_2O < 20$ ppm), were examined to illustrate their differences. Pouch cells were assembled with homemade $Na_3V_2(PO_4)_3$ as the cathode. Galvanostatic discharge/charge profiles were performed on a battery cycler (LAND CT-2001A, China) at room temperature. Cyclic voltammetry (CV) was conducted on an electrochemical workstation (Chenhua CHI 760E, China) at room temperature. Electrochemical impedance spectra (EIS) were obtained from an electrochemical workstation (Autolab PGSTAT 302N, Switzerland) in a frequency range of 100 kHz to 0.01 Hz.

Characterization of SEI film: Ex Situ NMR and GC−MS

The electrodes tested for NMR and MS were discharged/charged for five cycles at 0.05 A g^{-1}. Then, the cells were stabilized at different voltages. After that, the electrodes were taken out from coin cells, placed in centrifuge tubes, and soaked either in DMSO-d_6 for $^1H/^{13}C$ NMR or in D_2O for ^{23}Na NMR. The centrifuge tubes were sealed and sonicated for about 30 min to ensure the organics in the SEI film dissolved as much as possible. Finally, the supernatant was transferred into NMR tubes and sealed air-tightly for NMR. NMR spectra were achieved with an advanced spectrometer (Bruker AVANCE III 500, Germany), using DMSO-d_6 at 2.500 ppm for $^1H/^{13}C$ NMR or NaCl in D_2O at 0 ppm for ^{23}Na NMR. For MS, DMSO-d_6 was replaced with $CDCl_3$ and the other was kept the same. MS was conducted on a gas chromatography−mass spectrometer (TQ8040 NX, Shimadzu, Japan).

Ex Situ Transmission Electron Microscope (TEM) and Scanning Electron Microscopy (SEM) Images

First, the electrodes were discharged/charged for five cycles at 0.05 A g^{-1}. Then, the electrode was discharged to 0.01 V or charged to 1.5 V to identify the surface of HC. The working electrode was taken out from coin cells and washed several times with absolute ethanol. Electrode materials were scraped from the current collector, dispersed in absolute ethanol, and sonicated for tens of minutes. Finally, a small droplet of the suspension was dropped on a porous carbon-coated copper grid for TEM images. TEM images, HRTEM images, high-angle annular dark-field scanning TEM (HAADF-STEM) images, X-ray energy-dispersive spectrum (EDS), and element maps were recorded with an aberration-corrected TEM microscope (FEI Tecnai F20, USA). SEM images were acquired from a field-emission scanning electron microscope (Zeiss Gemini 300, Germany).

In Situ EQCM

EQCM measurements were performed using an electrochemical workstation (Chenghua CHI 760E, China) coupled with a Q-Sense instrument (Baolin Scientific, Sweden). A AT-cut quartz crystal coated with gold (Q-Sense Sensor QSX 338 Gold), a Pt filament, and an aqueous solution of $Ag/AgNO_3$ were used as the working electrode, the counter electrode, and the reference electrode, respectively. The measurement was carried out at a current density of 50 μA in the range of −1.423/−2.923 V vs $Ag/AgNO_3$, using a standard three-electrode configuration. Hard carbon was deposited on the working electrode by a spin coater. The mass change (Δm) of the working electrode followed the Sauerbrey equation.

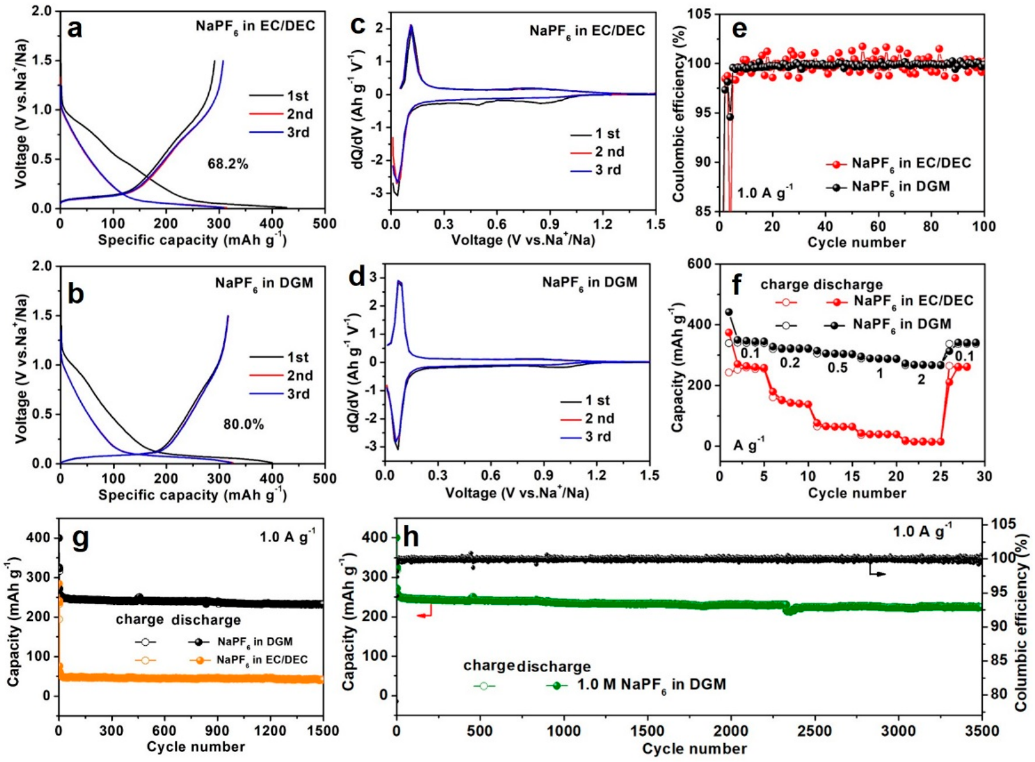


Figure 1. Electrochemical performances of hard carbon in different electrolytes. Galvanostatic discharge/charge curves in EC/DEC (a) and in DGM (b); dQ/dV plots in EC/DEC (c) and in DGM (d); Coulombic efficiency (e), rate performances (f), and cycling performances (g) in EC/DEC and in DGM; long cycling performance of hard carbon in DGM (h).

Computational Method

Molecular dynamics simulations based on density functional theory were carried out with the Perdew−Burke−Ernzerhof (PBE) exchange-correlation functional[37] as implemented in the Vienna Ab initio Simulation Package (VASP).[38] The projector-augmented wave potentials[39] were used with plane-wave basis set. The plane-wave cutoff energy was set to be 340 eV. For setting up the supercell, the experimental density of 0.944 g/cm^3 was used. The Γ-point was used to represent the Brillouin zone. The Nosé thermostat[40] was used to regulate the temperature in network virtual terminal (NVT) simulation.

■ RESULTS AND DISCUSSION

Electrochemical Performances of HC in Different Electrolytes

DGM is selected as a model to illustrate the unique feature of Na insertion/extraction in HC. Meanwhile, the conventional solvent, EC/DEC, is also tested under the same conditions as the benchmark. Commercial hard carbon is directly used without further treatment. SEM and TEM images show that they are irregular microparticles with randomly oriented and intermittent lattice fringes (Figure S1).[41,42] A variety of structure defects in the particle offers numerous active sites for Na storage. Figure 1 presents the electrochemical performances of HC in DGM and in EC/DEC at 0.1 A g^{-1}. The differences between them are very obvious, particularly in terms of Coulombic efficiency and rate performances. As shown in Figure 1a,b, hard carbon in DGM exhibits an ICE (~80.0%) higher than that in EC/DEC (~68.2%), indicating the reduced side reactions. To gain more information about these side reactions, dQ/dV is plotted against the cell voltage for two cases. Compared to the redox peaks in CV curves, those in dQ/dV are sharp and easy to distinguish (Figure S2). HC in EC/DEC gives three cathodic peaks at 0.9, 0.5, and 0.1 V in the first cycle (Figure 1c), which could be assigned to the adsorption of Na$^+$ ions on the edge and/or defects of carbon layers, the electrolyte decomposition, and the reduction of Na$^+$ ions within nanovoids.[43−45] In the following cycles, the two cathodic peaks at 0.9 and 0.5 V almost disappear, but that at 0.1 V only slightly decreases. This result indicates that the two reactions happening at high voltages are the essential origin for low ICE. Different from the case of EC/DEC, HC in DGM only has two cathodic peaks at 1.0 and 0.1 V in the first cycle (Figure 1d). The cathodic peak at 0.5 V is invisible in the profile even in the first cycle, suggesting the absence of electrolyte decomposition. This result is quite interesting and has not been reported before to the best of our knowledge. More importantly, the Coulombic efficiency of HC in DGM is more stable in the subsequent cycles (Figure 1e), suggesting the high reaction reversibility. On the other hand, HC in DGM also shows an electrode polarization (~0.08 V) smaller than that in EC/DEC (~0.15 V) for the redox reaction at 0.1 V. It indicates the fast electrochemical reaction kinetics.[46−48] This conclusion is also supported by rate performances (Figure 1f). The capacity difference between DGM and EC/DEC increases as the current density increases. At 2 A g^{-1}, the specific capacity of HC remains ~266 mAh g^{-1} in DGM but only ~15 mAh g^{-1} in EC/DEC. Even in terms of capacity retention, it still comes to the same conclusion, 78% in DGM vs 5.9% in EC/DEC. The improvements in reaction kinetics and reaction reversibility do not come at the expense of cycling stability. HC displays a good cycling stability and a large specific capacity in DGM (Figure 1g). It delivers a capacity of 230 mAh g^{-1} after 1500 cycles at 1 A g^{-1}, much higher than ~40 mAh g^{-1} in EC/

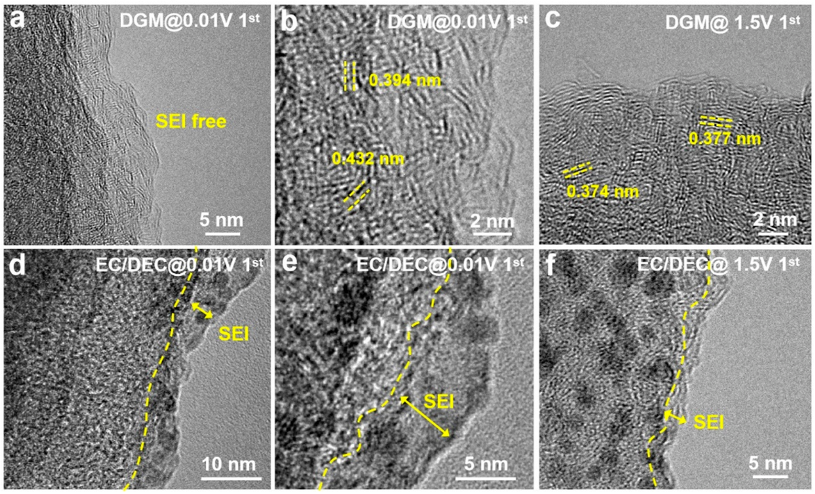


Figure 2. Ex situ HRTEM image characterization. HRTEM images of HC cycled in DGM (a−c) or in EC/DEC (d−f) during the first cycle. (a,b,d,e) 0.01 V; (c,f) 1.5 V.

DEC. Even after 3500 cycles, the capacity is still 224.4 mAh g^{-1}, corresponding to a capacity retention of 88% with a complete structure (Figure 1h and Figure S3). It is almost the best performance for hard carbon (Table S1). The output voltage of the pouch cell is about 3.2 V with homemade $Na_3V_2(PO_4)_3$ in DGM, which indicated the practical application value (Figure S4).

Ex Situ HRTEM Image Characterization of SEI Films

All these data confirm that the electrochemical performances of HC are remarkably improved in DGM, as compared to those in the case in EC/DEC. Usually, these improvements are attributed to the SEI film in different electrolytes.[49−52] However, the cathodic peak related to the electrolyte decomposition is absent in DGM, even in the first cycle (Figure 1c). Therefore, it is likely without a SEI film on HC in DGM. Then, the previous explanation based on the SEI film does not work for HC. So, it is important to clarify if there is a SEI film on HC cycled in DGM. HRTEM is an intuitive tool to visualize the SEI film. As shown in Figure 2a, the surface of hard carbon discharged to 0.01 V is clear without an amorphous layer, thus excluding the formation of a SEI film. The result is in good agreement with that observed in dQ/dV. The intermittent lattice near the surface is a characteristic of HC (Figure 2b). The fringe spacing of about 4.32 Å is larger than that before discharge (∼3.6 Å, Figure S1), probably caused by the intercalation of Na ions. As hard carbon is charged to 1.5 V, the similar surface is also observed (Figure 2c), confirming the non-SEI film again. Meanwhile, the fringe spacing is reduced to ∼3.74 Å (Figure 2c), likely due to Na extraction. The similar surface without a SEI film is also identified after five cycles in DGM (Figures S5a and S6a), suggesting the good surface stability. Further, F 1s spectra were detected at D 0.01 V before and after Ar-ion sputtering. Because the surface always adsorbs a trace of the electrolyte, the signal of $NaPF_6$ is much stronger than that of NaF (Figure S7a). There is no other signal of F. The appearance of NaF could be associated with the hydrolysis of $NaPF_6$, which is almost inevitable in the electrolyte.[28] As the sputtering time is prolonged to 1 min, the signal of $NaPF_6$ markedly weakens, but the signal of NaF enhances significantly (Figure S7b). This result confirms the surface adsorption of $NaPF_6$. It should be pointed out that the existence of NaF does not mean the formation of SEI because NaF is also possibly generated in conductive black or in a binder. In contrast, the surface of HC cycled in EC/DEC is coated by a thin SEI film, as highlighted in Figure 2d−f. The lattice fringes of HC do not show up any more. The contrast differences indicate that the spherical inorganics are randomly dispersed in organic species, resulting in this unique composite.

This result is very consistent with the well-accepted Mosaic model about SEI film.[53,54] Unfortunately, the structure information on spherical inorganics is missed, due to the high-energy electron irradiation. In addition, the surface film is not uniform, which affects the local Na ion flux, increases the stress accumulation, and degrades the electrochemical performances. Therefore, after five cycles, the surface film on hard carbon becomes much thicker (Figures S5b and S6b), but the internal structure remains the same.

Ex Situ ^{1}H NMR and GC−MS Studies on HC

Although HRTEM gives strong evidence to support the absence of a SEI film on hard carbon in DGM, the detection area by HRTEM is always limited. Moreover, the sample preparation for TEM images may interfere with the identification of the SEI film. So, to avoid the possible misleading information by the limitation of TEM, using other techniques to characterize the electrode surface is very necessary. In this context, NMR and GC−MS, which are very good at the detection and characterization of organics, are used.[55,56] Once there is electrolyte decomposition, the formation of organics is inevitable in the SEI film. The electrodes discharged to different voltages are soaked in deuterated dimethyl sulfoxide (DMSO-d_6) overnight. Due to the strong polarity of DMSO, organics are easily dissolved and the solution is subject to NMR. As illustrated in Figure 3a, the ^{1}H NMR spectra are kept exactly the same as the standard spectrum of DGM (Figure S8a) throughout the whole discharge process. This result indicates DGM just adsorbs on the surface of hard carbon. This same result is also obtained in ^{13}C NMR, where both the chemical shift and the relative ratio of the signals remain the same at different voltages (Figure S9). This result excludes the possibility that the polymerization reaction potentially happened to DGM. In contrast, the ^{1}H spectra of hard carbon in EC/DEC become totally different (Figure 3b). The ^{1}H NMR spectrum at OCV is similar to the

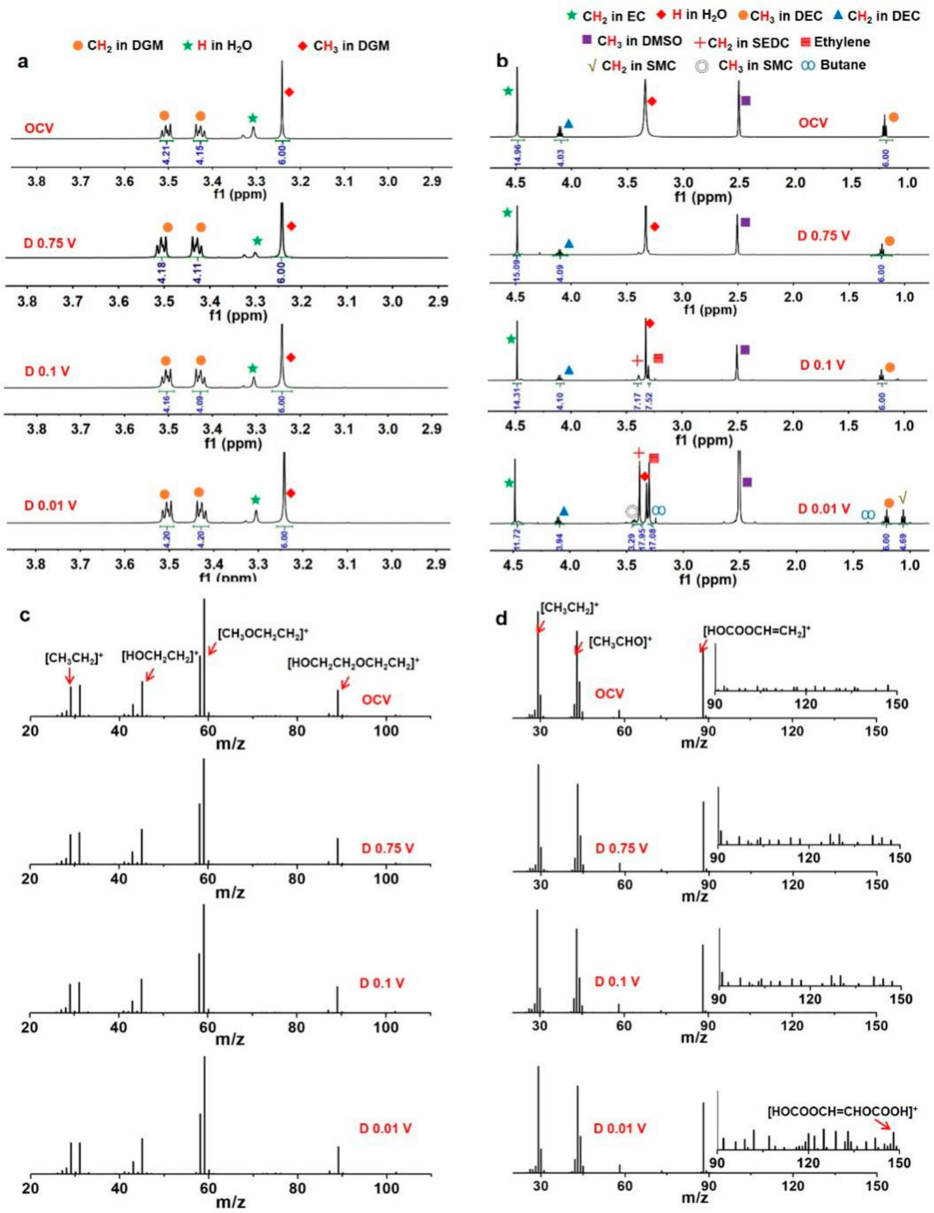


Figure 3. Ex situ ^{1}H NMR and GC−MS studies on hard carbon. In DGM (a,c) and EC/DEC (b,d) at different discharge voltages.

standard spectrum of EC/DEC (Figure S8b). As the voltage decreases to 0.75 V, the weak chemical shift of sodium ethylene dicarbonate (SEDC) at 3.40 ppm appears in the spectrum.[57] The signal intensity greatly increases within 0.1−0.01 V, implying the formation of a large amount of SEDC in this voltage range. In addition to SEDC, the chemical shift from CH$_2$ of ethylene also shows up at 0.1 V and intensifies at 0.01 V. The formation of SEDC and ethylene can be attributed to two-molecule polymerization of ethylene carbonate (Figure S10, eq 1), as supported by their close signal areas. It is noted that the electrolysis products of diethyl carbonate (DEC), i.e., sodium methyl carbonate (SMC) and butane (Figure S10, eq 2), also appear at 0.01 V, despite the low contents. The appearance of these organic species confirms severe electrolyte decomposition in EC/DEC. The similar changes are also identified in the ^{13}C spectra of hard carbon in EC/DEC (Figure S11).

The conclusion on the basis of GC−MS is similar to that from NMR. Different from the electrode processing for NMR, the electrode for GC−MS was treated by CDCl$_3$ instead of DMSO. The difference of CHCl$_3$ and DMSO in polarity allows them to dissolve different organics, thereby providing another perspective to validate the conclusion. The electrode cycled in DGM exhibits the same fragmentation pattern as that of DGM (Figure S12), where the ions at m/z 29, 45, 59, and 89 can be assigned to the fragments of DGM caused by electron ionization (EI) (Figure 3c), i.e., [CH$_3$CH$_2$]$^+$, [HOCH$_2$CH$_2$]$^+$, [CH$_3$OCH$_2$CH$_2$]$^+$, and [HOCH$_2$CH$_2$OCH$_2$CH$_2$]$^+$. This result indicates that there are some DGM molecules adsorbed on the electrode surface, which cannot be removed by simple washing. As expected, the fragment pattern remains almost identical at the different voltages, indicating the good stability of the electrolytes and the absence of SEI film on the surface. The same result is even observed in the electrode discharged to 0.01 V after three cycles (Figure S13). On the contrary, the electrode cycled in EC/DEC exhibits the different fragmentation patterns, as the discharging occurs. A batch of new fragment ions at m/z > 90 appears in the fully discharged

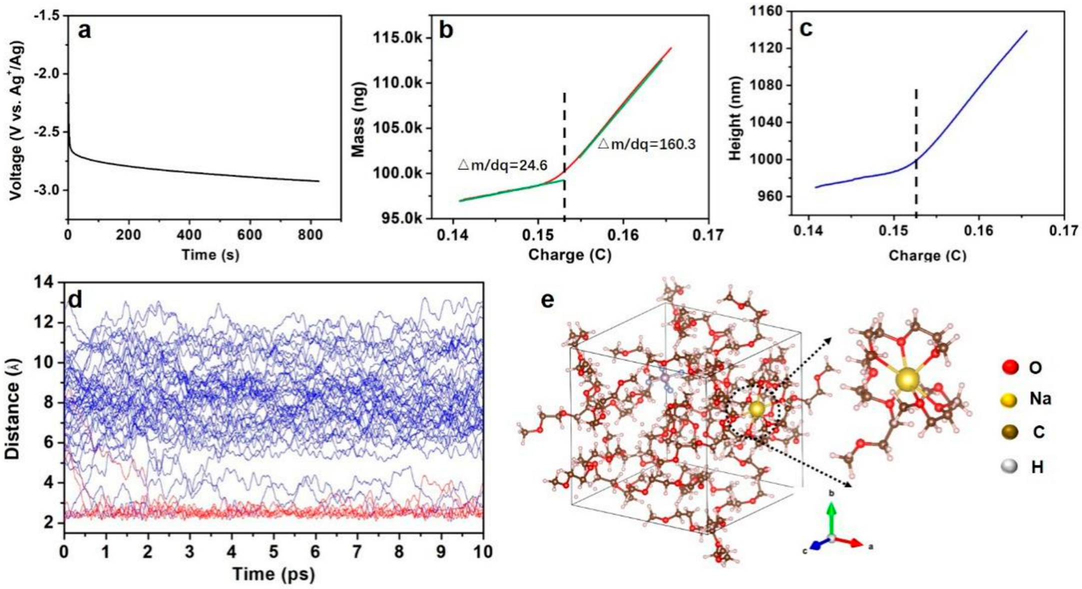


Figure 4. In situ quantitative characterization of live formation and chemistry of hard carbon in DGM. (a) Discharge curves. (b,c) Matched mass and height change during the discharge process. (d) Distance between each the O atom and Na ion during the 40,000-step molecular dynamics simulation. (e) Interaction between DGM solvent and Na^+ ions.

electrode (Figure 3d), indicating the formation of new organics (e.g., SEDC at m/z 148) in the electrode. This result can be attributed to the electrolyte decomposition at a low voltage, which is also in good agreement with what was observed in NMR.

In Situ EQCM of HC in DGM

In situ EQCM allows us to accurately monitor the tiny weight change of the electrodes as a function of the applied voltages. Therefore, it can provide useful information about the formation of the SEI film and the intercalation of Na^+ into the electrodes because both of them involve the mass gain or loss in the electrodes.[58] In a typical experiment, the electrodes are discharged either in DGM or in EC/DEC at a constant current density in a specially designed cell, using Na as the reference electrode. As shown in Figure 4a, the voltage quickly falls to −2.65 V (vs Ag^+/Ag) and then gradually approaches −2.8 V (vs Ag^+/Ag) during discharging, which indicates the adsorption and insertion of Na^+ into hard carbon. Figure 4b shows the plot of mass vs charge, where two stages can be clearly seen. During the first stage, the mass change per electron, $\Delta m/dq$, is 24.6 g mol^{-1}, which is close to the ionic mass of Na^+ (23 g mol^{-1}), indicating the adsorption of Na^+ ions on hard carbon, probably at the edges or structure defects of carbon layers. During the second stage, $\Delta m/dq$ increases to 160.3 g mol^{-1} until the end of the discharging. This result is consistent with the mass/charge ratio of $[Na(DGM)]^+$ (157 g mol^{-1}), implying that the solvent molecules are intercalated into hard carbon together with Na^+ ions. Interestingly, the carbon layers are not exfoliated upon the intercalation of the organic molecules because graphite domains in hard carbon are randomly oriented and intermittent in conjunction with amorphous carbon. Here, the domains of amorphous carbon prevent the graphite layer from being easily peeled off. As a result, hard carbon exhibits a stable cycling over 3500 cycles, as demonstrated in Figure 1h. Moreover, the mass/charge ratios related to the SEI components, such as polyDGMs, sodium alkyl alcohol (RCONa), etc. are not observed. It excludes the formation of a SEI film on hard carbon again, consistent with the results from NMR, MS, and HRTEM. To our knowledge, these results, especially the identification of solvent molecules in hard carbon, are reported for the first time. The height change with charge, as shown in Figure 4c, is consistent with the weight change in Figure 4b, indicating that the adsorption and the intercalation of Na-related species make the electrode expand accordingly.

Molecular Dynamics Simulations

To further understand the co-intercalation of DGM with Na^+ into hard carbons, the solvated structures of $NaPF_6$ in DGM are simulated by molecular dynamics (MD) based on first-principles theory.[59−61] As illustrated in Figure 4e, a supercell contains 16 DGM molecules, one Na^+ ion, and one PF_6^- ion, keeping in line with a low concentration of $NaPF_6$ in DGM. The cell is then heated to 1000 and 2000 K in turn. At each temperature, MD simulations are conducted for 1 ps with a time step of 0.25 fs to identify the thermodynamically stable configuration. Then, the cell is cooled to room temperature by velocity scaling. After that, the cell is treated by NVT simulation at 300 K for 10 ps. Then, it is noted that each Na ion is surrounded by six O atoms (Figure 4d). Three of them come from the same DGM molecule, while the other three originate from three different DGM molecules. In this context, the three molecules are easy to dissociate from Na ions because they are only a monodentate ligand. The DGM molecule binding to Na ions with three O atoms is co-intercalated together into hard carbon. This configuration is quite stable in DGM, as supported by the trajectories of all O atoms in the cells. This result provides the solid basis for the co-intercalation of DGM with Na ions into hard carbon. The same conclusion could be also obtained in the cases of graphite and soft carbon. As shown in HRTEM images (Figure S14), all of the particle surfaces after five cycles exhibit clear lattice fringes without a sign of a SEI film. These results strongly confirm the absence of a SEI film. However, on other electrode materials, the unsaturated surface atoms, especially transitional metal species, probably activate DGM molecules and promote the decomposition, resulting in the formation of a SEI film.[62]

CONCLUSIONS

In conclusion, intercalation chemistry of hard carbon in ether-based electrolytes is carefully investigated for Na storage using ester-based electrolytes as the benchmark. It is noted that hard carbon exhibits electrochemical performances in ether better than those in ester, in all the important terms, i.e., Coulombic efficiency, reversible capacity, cycling stability, and rate capability. It can sustain a capacity of 224.4 mAh g^{-1} after 3500 cycles at 1 A g^{-1}. More exciting, ex situ NMR, MS, and HRTEM support the absence of a SEI film on the surface of hard carbon. In contrast, there is the severe decomposition of electrolyte and the formation of a SEI film in ester. ECQM reveals that the intercalation of Na^+ into hard carbon is accompanied by one molecule of ether, $[Na(DGM)]^+$. The incomplete dissociation of ether from solvated Na^+ lowers the energy barrier and facilitates the fast intercalation/deintercalation. The absence of a SEI film increases the Coulombic efficiency and rate capability. The absence of a SEI film can be attributed to the high stability of solvated Na^+ ions, as indicated by DFT calculations. Finally, the similar phenomenon is also observed in graphite and soft carbon.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00158.

NMR and MS spectrum, SEM, TEM, and HRTEM images, charge/discharge profiles, CV curves, EIS data (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the financial support from the National Key R&D Program of China (2016YFB0901600), the National Nature Science Foundation of China (21971146), Taishan Scholarship in Shandong Provinces (ts201511004), Science & Technology Commission of Shanghai Municipality (18QA1404600), and Super Post Doctoral Fellow Program of Shanghai (E01SCB17). We also acknowledge the assistance of Shandong University Structural Constituent and Physical Property Research Facilities. We thank Dr. Jiong Jia for his support with nuclear magnetic resonance (500 M) and thank Dr. Heliang Yao for help with the transmission electron microscope observations.

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