

A Comparative Study of Solid Electrolyte Interphase Evolution in Ether and Ester-Based Electrolytes for Na-ion Batteries

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The solid electrolyte interphase (SEI) largely determines the electrochemical performance of negative electrodes in sodium-ion batteries (SIBs). Ether-based electrolytes, such as diglyme, have been shown to form a more stable and thinner SEI on sodium anodes than traditional commercial ester-based electrolytes. Nonetheless, variations in the detailed evolution of the chemical composition and mechanical strength of the SEIs formed in these two electrolytic solutions during the electrochemical process have rarely been investigated. In this work, we conduct a comparative study of the SEI formed in diglyme-based and carbonate-based electrolytes with $\text{Na}_2\text{Ti}_3\text{O}_7$ (NTO) as a proof-of-concept material, using energy-tuned photoelectron spectroscopy, operando electrochemical atomic force microscopy, and electrochemical techniques. The results show that diglyme forms a thin, homogeneous, and stable SEI with a well-defined inorganic-organic bilayer structure, as opposed to ester-based electrolytes, which form a thicker, nonuniform, and dynamically changing SEI with randomly distributed inorganic-organic structure. Moreover, the less resistive and higher capacitive interfacial processes induced by the diglyme-based electrolyte decrease the overall battery impedance. These advantages enable the NTO anode to exhibit superior specific capacity, cycle stability, and rate capability. This study provides an in-depth view of the factors behind the electrolyte-dependent performance of SIB anodes, which could inform the design and pairing of electrolytes with electrode materials in rechargeable batteries.

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I. INTRODUCTION

Sodium-ion batteries (SIBs) represent an affordable complementary technology to lithium-ion batteries (LIBs) due to the high abundance of Na sources on Earth [1]. The development of high-energy and high-power density electrodes for SIBs has advanced significantly to date [2,3]. However, the intrinsically unstable electrode-electrolyte interphase behavior of SIBs is a major barrier to

their widespread commercialization. Although the anode-electrolyte interphase, also referred to as solid electrolyte interphase (SEI), has been extensively studied and optimized in LIB systems, its role in SIBs is yet unclear, albeit thought to be a major factor in SIB underperformance. The increased solubility of the degradation products caused by the lower Lewis acidity of Na^+ ions [4] and higher redox potential minimizes the reduction of primary products into secondary products, indicating a completely different SEI formed in SIBs compared to LIBs in terms of chemical and physical properties [5].

Aprotic salts dissolved in low-molecular-weight organic solvents are commonly used as electrolytes in SIBs. Examples include NaPF_6 , NaClO_4 , NaCF_3SO_3 , NaBF_4 , NaTFSI , and NaFSI salts in mixtures of ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and propylene carbonate (PC) solvents [6,7]. Both inorganic

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and organic components decompose at the anode surface under a specific potential, and the resulting products determine battery performance, including cycle life, coulombic efficiency, rate capability, working potential, and cell resistance, among other important performance metrics [8–10]. Thus, optimizing SEI properties is a critical step towards providing a predictable and optimal electrochemical activity in battery materials. Several strategies for achieving this goal are being investigated, including the tailoring of electrolyte formulations (e.g., solvent, salt, and concentration) and the use of sacrificial additives [11], which alter the SEI composition and properties, thereby improving mechanical and ion-transport properties.

In terms of electrolyte solvents, ether-based electrolytes first gained significance in SIBs due to their ability to facilitate highly reversible co-intercalation of Na^+ ions in graphite [12], which was otherwise not possible with commercial carbonate-based Na electrolyte systems. Subsequently, the investigation of ether-based electrolytes has been extended to other anode systems, including hard carbon [13], metal oxides [14], metal sulfides [15, 16], and alloy-type anodes [17, 18], which demonstrated superior electrochemical performance when compared to carbonate-based electrolytes. The improvement is strongly correlated with increased electrode wettability, reduced solvent decomposition, and thinner and more ionic conductive SEIs in ether-based electrolytes, which facilitate Na^+ ion diffusion [19]. To date, the consensus indicates that a multilayer-type SEI structure forms in carbonate-based electrolytes, with the outer surface in contact with the electrolyte presumed to be porous and composed of a large portion of organic components (sodium alkyl carbonates, sodium carboxylates, and polyesters) and the inner surface in contact with the anode material consisting of predominantly inorganic compounds such as Na_2CO_3 , NaF , and Na_2O [20–22]. In contrast, studies have shown that ether-based electrolytes can produce a denser and more inorganic-rich SEI with lower Na^+ ion-diffusion activation energies [14]. Despite the importance of understanding the differences in formation, composition, and morphology evolution of the SEI layer formed in different electrolytes during cycling, these aspects have yet to be fully understood [14, 22].

In this study, we present a comparative analysis of the SEI formed in two electrolyte solvents: ester-based EC:DEC (1:1 v/v) and ether-based diglyme (DiG) with a typical NaPF_6 commercial salt, and we correlate the SEI properties with the cycling stability and rate capability of the anode material, $\text{Na}_2\text{Ti}_3\text{O}_7$ (NTO). Despite having a lower energy density than the state-of-the-art hard carbon [1, 23], NTO has a higher average working voltage of ca. 0.3 V vs Na^+/Na , which makes it safer and thus an attractive candidate for practical applications [24–27]. To date, the majority of the literature has focused on optimizing the structural properties of NTO [28, 29],

with only a few alternative electrolytes proposed for use in combination with it [30, 31]. However, there is still a lack of comprehensive understanding of SEI composition and evolution using nondestructive techniques and mechanical properties. In this context, it is critical to use advanced techniques to thoroughly investigate the differences between the SEIs formed in different electrolytes in terms of detailed chemical distribution in the depth direction, mechanical properties, and compositional evolution during an electrochemical process.

In this work, we found that the electrochemical performance of Na/NTO half-cells in DiG outperformed that of cells using the EC:DEC electrolyte solvent in terms of specific capacity, rate capability, and cycling stability. To explain these differences, we conducted a detailed interfacial analysis of the SEI layer and charge-transfer processes using energy-tuned photoelectron spectroscopy (PES), operando electrochemical atomic force microscopy (EC-AFM), and electrochemical impedance spectroscopy (EIS) under various cycling regimes. The results show that the enhancement is due to a thin, homogeneous, and stable SEI with a well-defined double-layered structure. This SEI consists of a rigid, inorganic-rich inner layer and a soft, organic-rich outer layer that effectively shields the NTO anode, thereby reducing electrolyte decomposition. Furthermore, the DiG electrolyte induces less resistive and higher capacitive interfacial processes, lowering the overall battery impedance, which constitutes another important factor for improved performance.

II. METHODS

A. Synthesis and structure characterization of NTO

NTO was synthesized using a solid-state reaction method with a stoichiometric mixture of TiO_2 (Fisher Scientific, 98%) and anhydrous Na_2CO_3 (Sigma Aldrich, 99.9%) in batches of approximately 0.5 g, following previous reports [32]. As-synthesized NTO powders are white and consist of elongated faceted particles of several microns in length and hundreds of nanometers in width, as observed under a scanning electron microscope (FESEM; JEOL JSM–7800F) operated at 5 kV and 5 mA [Fig. S1(a) in the Supplemental Material [33]]. Energy-dispersive X-ray analysis (EDX) at 20 kV revealed a uniform distribution of sodium, titanium, and oxygen atoms, with no apparent phase segregation or presence of elements other than carbon from the adhesive carbon tape [Fig. S1(b) in the Supplemental Material [33]]. For FESEM-EDX analysis, NTO powders were coated by sputtering deposition with a uniform layer of Au/Pd to provide surface conductivity and prevent surface charging.

Powder X-ray diffraction (PXRD) at ambient temperature was used to characterize the structure of NTO. A Smartlab diffractometer (Rigaku Corporation) equipped with a 9 kW Cu rotating anode ($\lambda = 1.54056 \text{ \AA}$) was used

in reflection mode with Bragg-Brentano geometry. Data were collected in the $5\text{--}70^\circ$ 2θ range at a scan speed of $0.02^\circ \text{ s}^{-1}$. The NTO structure was refined against PXRD data using the Rietveld method with the GSAS-EXPGUI software interface [34,35], and the ICSD250000 structure [36] serving as a starting model ($P12_1/m1$ space group). The background was fitted with a Chebyshev polynomial function, and the peak shapes were modeled with a pseudo-Voigt function. The lattice parameters and atomic positions were refined. The atomic displacement parameters (U_{iso} values) for individual Na, Ti, and O atoms were refined isotropically and constrained to be identical for each atom type. The site occupancy for all the atoms was fixed at $n = 1$. Table S1 contains relevant selected crystallographic data, and Fig. S2 in the Supplemental Material [33], including Refs. [36,37], shows a Rietveld refinement plot against PXRD data of NTO. Crystallographic data are consistent with previous reports in the literature [36,38].

B. Electrochemical characterization

Electrode preparation and battery assembly were conducted in an argon-filled glovebox (MBraun; O_2 and $\text{H}_2\text{O} < 0.1$ ppm). Electrodes were prepared by hand mixing and grinding NTO (active material) with conductive carbon black (Super P, 99% Alfa Aesar) and polyvinylidene binder (PVDF Kynar, 99% Alfa Aesar) in a mass ratio of 70:20:10. The powdered mixture was transferred to a vial, and N-methyl-2-pyrrolidone (NMP) (anhydrous, 99% Alfa Aesar) was added to the electrode mixture and stirred in a vial for 12 h to produce a uniform electrode slurry. The electrode slurry was cast onto an aluminum foil (16 μm thickness, 99.45% purity, TOB New Energy) using a doctor blade (MTI Corporation) with a 200 μm aperture. The cast foil was then vacuum dried at 80°C overnight. Electrode discs with active material loading of $1.5\text{--}2 \text{ mg cm}^{-2}$ and 12 mm diameter were cut from the foil with a hydraulic electrode puncher (TOB New Energy) and pressed under 3 tons each using a hydraulic press (Specac).

This study used two electrolyte formulations consisting of the same inorganic salt in the same concentration, i.e., 1 M NaPF_6 (99+ % Alfa Aesar), and two aprotic and polar organic solvents with distinct solvation properties for Na^+ ions: an ester-based solvent mixture of EC:DEC (battery grade, Gotion) (1:1 v/v) and an ether-based diglyme (DiG) (99%, Sigma Aldrich) solvent. Solvents were dried for 2 weeks on activated molecular sieves (0.4 nm pore diameter, Merck) before being mixed with the salt.

The galvanostatic cycling tests used stainless-steel CR2032 coin cells (TOB New Energy) with a stainless-steel conical spring, 10 mm-thick stainless-steel spacer discs, a plastic gasket, and a glass microfiber separator (Whatman). The counter and reference electrode used was

a Na metal disc (Alfa Aesar Merck, 99.5%). Electrochemical measurements were performed on a battery cycler (Neware, current range: 1–10 mA) at low (0.1C) and high (2C) rates in the voltage range of 0.01–2.5 V vs Na^+/Na for 200 cycles and 500 cycles, respectively. Rate performance tests were conducted at 0.1C, 0.2C, 1C, 2C, 5C, 10C, and 0.1C (five cycles per rate) in the voltage range of 0.01–2.5 V vs Na^+/Na . In this work, the C rate is defined in terms of one electron transfer per Ti atom, where $1\text{C} = 177 \text{ mA g}^{-1}$.

Cyclic voltammetry (CV) data were collected in three-electrode Swagelok-type cells, with a Na metal disc (Alfa Aesar Merck, 99.5%) serving as the counter and reference electrode. CV data were collected in the voltage range of 0.01–2.5 V vs Na^+/Na at various sweep rates (0.1, 0.2, 0.4, 0.8, and 1 mV s^{-1}).

EIS was performed in a three-electrode cell (PAT-Cell, EL-CELL) over a frequency range of 0.05 to 10^5 Hz, with an ac amplitude of 10 mV and drift correction. The counter electrode was a Na metal disc, and the reference electrode was a premade Na metal ring (EL-CELL) that was enclosed around the glass microfiber separator. Cells were galvanostatically cycled at 0.1C and then rested for 1 h before collecting EIS data.

The estimated capacitance (C) of the various depressed semicircles shown in Figs. 6(a) and 6(b) was calculated as follows:

$$C = \frac{(\text{CPE} \times R)^{\frac{1}{\alpha}}}{R} \quad (1)$$

where CPE is the constant phase element, R is the resistance, and α is the dispersion coefficient. C values were estimated when $\alpha > 0.75$ [39]. CV and EIS characterization were carried out at ambient temperature using a potentiostat (VMP3, BioLogic). Each electrochemical test was repeated at least 3 times to ensure that the results were consistent.

C. Energy-tuned photoelectron spectroscopy

Energy-tuned photoelectron spectroscopy (PES) was performed using the Surface and Interface Structural Analysis beamline (I09) at Diamond Light Source, UK. For the measurements, coin cells were cycled at 0.1C to specific charge states before being stopped. The cells were then disassembled in the glovebox, and electrodes were removed and dried under vacuum and at ambient temperature in the antechamber of an argon-filled glovebox (MBraun; O_2 and $\text{H}_2\text{O} < 0.1$ ppm). Electrode segments of approximately 10 mm^2 were excised and affixed using carbon tape onto a copper plate. These were then transferred under vacuum in airtight packages to an argon-filled glovebox (MBraun; O_2 and $\text{H}_2\text{O} < 0.1$ ppm) at the synchrotron facilities. At the synchrotron, samples were transferred to the load lock at

the end station of the beamline using an ultrahigh vacuum (UHV) transfer suitcase.

Hard X-ray photoelectron spectroscopy (HAXPES) measurements were performed with an excitation energy of 7050 eV using a Si(111) double-crystal monochromator. For soft X-ray photoelectron spectroscopy (SOXPES), an excitation energy of 1090 eV was used. A plane grating monochromator is used in the soft X-ray branch of the beamline. To minimize radiation damage to samples and the influence of inhomogeneities, a large area was probed with the beam dispersed using defocused settings. The probing spot on the sample is estimated to be approximately $300\ \mu\text{m}$ (L) $\times$ $1\ \text{mm}$ (W). No charge neutralizer was used during the measurements. Spectra were collected using a hemispherical VG Scienta EW4000 analyser set to pass energies of 50 eV for SOXPES and 200 eV for HAXPES measurements. Probing depths [3 times the inelastic mean free path of electrons (IMFP)] were calculated using the TPP-M2 equation as detailed in the NIST database [40] using parameters for polyethylene [41], a low-density material representative of the surface layer studied here. Depths were estimated to be 10 and 50 nm for the excitation energies of 1090 and 7050 eV, respectively. These depths should be regarded as upper limits since they imply that electrons flow in a straight line, which is not the case because electrons can change direction due to scattering events. It should also be noted that smaller probing depths are expected for materials denser than polyethylene in the sample, such as the bulk electrode itself and inorganic species in the SEI.

CasaXPS (Casa Software Ltd.) was used to analyze photoelectron spectroscopy data. The asymmetric Lorentzian line shape LA (1.2, 2.5, 5) was used for the C=C peak, while the Gaussian-Lorentzian line shape GL (30) was used for all other components during the fitting procedures. Energy calibration was performed by setting the binding energy for the graphitic carbon black (C=C) peak in C 1s spectra to 284.5 eV [41].

D. Operando EC-AFM characterization

Operando EC-AFM measurements were performed using a Bruker Multimode AFM with Nanoscope V controller (Bruker) in an argon-filled glovebox (MBraun; O_2 and $\text{H}_2\text{O} < 0.1\ \text{ppm}$). A potentiostat (GAMRY 600+) was used to drive the sodiation of the NTO electrode in EC:DEC and DiG-based electrolytes at a constant current of 0.01 mA, with a custom-made two-electrode cell with Na metal serving as the reference and counter electrode (Fig. S7 in the Supplemental Material [33]). SEI formation was visualized using the peak-force quantitative nanomechanics (QNM) mode, and the spatial distribution of organic-inorganic species within the SEI was investigated by measuring shear force while penetrating the SEI layer with 3D nanorheology microscopy (3D-NRM) [42,43].

The cantilever force constants for QNM (ContGD-G-10, Budget Sensors) and 3D-NRM modes (Multi75GD-G-10, Budget Sensors) are approximately 0.3 and $3.5\ \text{Nm}^{-1}$, respectively, with a resonance frequency of $60\text{--}70\ \text{kHz}$. The QNM mode used a low force ($3\text{--}10\ \text{nN}$) to map the dynamic evolution of the electrode surface morphology, minimizing AFM tip-induced damage to the SEI structure. To investigate the internal SEI structure after the first cycle, the tip was used to penetrate the SEI layer during lateral force spectroscopy measurements. The tip was dithered sinusoidally at $f = 1.5\ \text{kHz}$ with a dithering amplitude $\delta x \approx 2\ \text{nm}$ along the slow scan axis, x , orthogonal to both the tip and cantilever axes, resulting in cantilever torsion. The AFM detected this torsional response, which was quantified by a lock-in amplifier as the tip penetrated the SEI to a depth z . Using the calibration procedure described in detail elsewhere [43], the torsional response can be used to quantify the shear force, F_s , and its dependence on penetration depth, $F_s(z)$. As the tip penetrates, new layers forming the SEI at the depth z corresponding to the tip apex generate additional shear force. Through differentiation of

$$\frac{dF_s(z)}{dz} = \delta F \quad (2)$$

it is possible to calculate the absolute values of shear forces δF acting at this depth. Knowing the amplitude of dithering, δx , and the tip diameter, d , allows for the calculation of shear compliance:

$$G^*(z) = \frac{\delta F}{(\delta x\ d)}. \quad (3)$$

It should be noted that the shear compliance, G^* , has both in-phase (G') and out-of-phase (G'') components in relation to the driving displacement, corresponding to the storage and loss (viscosity) modulus of the SEI. The SEI area probed in this manner is approximately a cylinder with a diameter of the tip cross section of about $20\ \text{nm}$ and a depth equal to the SEI thickness.

The electrode surface for the EC-AFM measurement was prepolished with an Ar^+ low-energy beam using the beam-exit cross-section (BEXP) method [44] to ensure a flat electrode area. Figures S6 and S7 in the Supplemental Material [33] provide details on the EC-AFM setup and sample preparation. Each image was captured over 120 to $480\ \text{s}$.

III. RESULTS AND DISCUSSION

A. Electrochemical behavior of NTO in ester- and ether-based electrolytes

Figure 1(a) shows the charge-discharge voltage profiles of NTO in the voltage range $0.01\text{--}2.5\ \text{V}$ vs Na^+/Na at a 0.1C rate, using two electrolyte solutions: $1\ \text{M NaPF}_6$

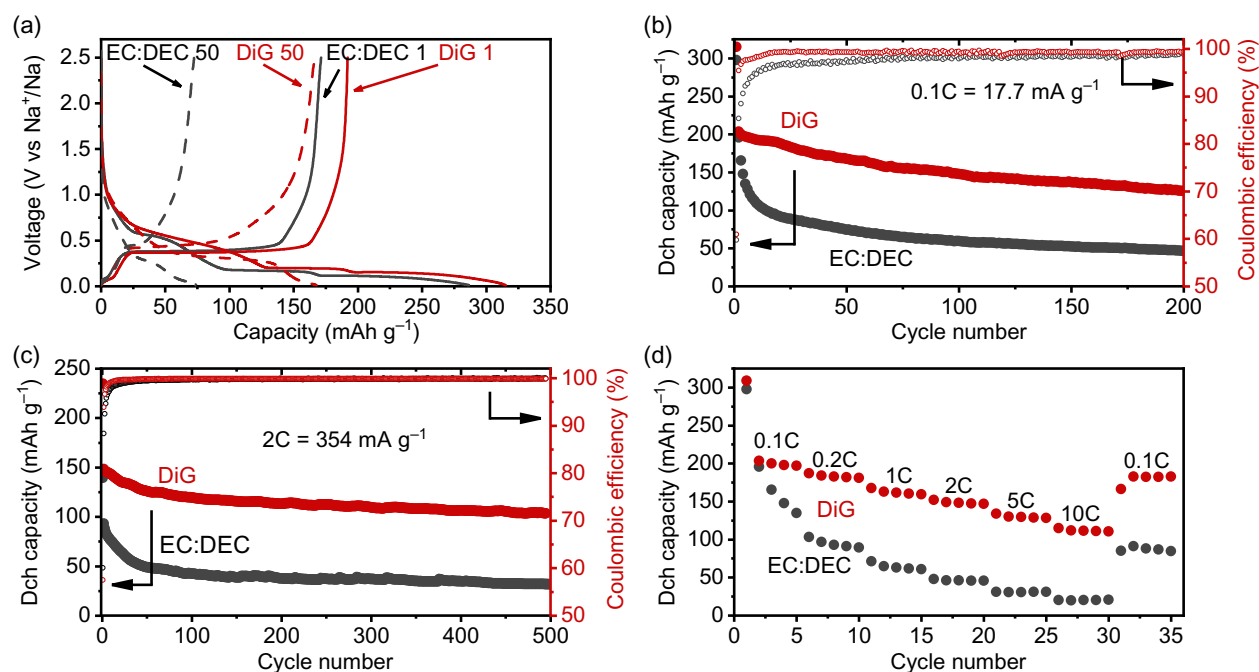


FIG. 1. Electrochemical data of NTO obtained in the voltage range 0.01–2.5 V vs Na⁺/Na, using 1 M NaPF₆ in EC:DEC (black) and DiG (red) electrolytes. (a) Galvanostatic charge-discharge voltage profiles for NTO in cycles 1 and 50. (b) Specific discharge capacity vs cycle plots at 0.1C over 200 cycles, showing coulombic efficiency values. (c) Specific discharge capacity vs cycle number plots of NTO at 2C over 500 cycles, showing coulombic efficiency values. (d) Rate performance tests at varying rates (0.1–10C). Five charge-discharge cycles were performed at each rate.

in EC:DEC (1:1 v/v) and diglyme (DiG) electrolyte solvents. The load curves matched those previously reported in the literature for similar conditions [24,45]. In both cases, the initial discharge process showed a slope between the open-circuit voltage (OCV) and 0.6 V, followed by a plateau, indicating an irreversible reaction of Na⁺ ions with the conducting carbon additive used [24,45,46]. This was followed by two plateaux at 0.2 V attributed to a biphasic reaction involving the insertion of two Na⁺ ions into the NTO structure, followed by partial reduction of Ti⁴⁺ to Ti³⁺ ions [24,45]. During charge, a single plateau at 0.4 V was observed, indicating the extraction of Na⁺ ions from the Na₄Ti₃O₇ structure, demonstrating different reaction mechanisms for Na⁺ ion insertion and removal [24,45]. After 50 cycles, the load curves showed almost no plateaux when using the EC:DEC-based electrolyte, whereas a single plateau during the discharge and charge processes remained when using the DiG solvent.

Using DiG instead of EC:DEC resulted in a decrease in voltage polarization (ΔV) during the second cycle. An increase in voltage during discharging became more pronounced as the C rate increased from 0.1C to 2C (Fig. S3 in the Supplemental Material [33]), possibly due to a lower polarization of the Na metal counter electrode and improved Na⁺ ion-transport kinetics [47]. A more detailed

explanation of this phenomenon will be provided in the EIS section.

Figure 1(b) shows the galvanostatic charge-discharge long-term cycling performance of NTO at 0.1C in both electrolytes. NTO had an initial discharge/charge-specific capacity of 315/192 mAh g⁻¹ in DiG, which was higher than that in EC:DEC (297/177 mAh g⁻¹). This disparity became more apparent when the current rate was increased to 2C, with initial discharge/charge-specific capacities of 235/132 mAh g⁻¹ (DiG) compared to 140/85 mAh g⁻¹ (EC:DEC) [Fig. 1(c)]. The use of diglyme significantly increased the cycle life of NTO, resulting in a specific capacity of 125 mAh g⁻¹ after 200 cycles vs 47 mAh g⁻¹ in EC:DEC at 0.1C [Fig. 1(b)], and a specific capacity of 103 mAh g⁻¹ after 500 cycles vs 32 mAh g⁻¹ in EC:DEC at 2C [Fig. 1(c)]. This electrochemical behavior is similar to that observed in other SIB anode materials when cycled with a DiG-based electrolyte. For instance, at 0.1 A g⁻¹, TiO₂ demonstrated an increase in its initial specific capacity from 165 mAh g⁻¹ (EC:DEC) to 252 mAh g⁻¹ (DiG), and after 500 cycles, the specific capacity was nearly doubled when using the ether-based electrolyte [14].

Both electrolyte systems showed nearly identical initial coulombic efficiency (ICE) values (approximately equal to 60%) at 0.1C and 2C [Figs. 1(b) and 1(c)], indicating that a similar amount of Na⁺ ions may be irreversibly

trapped in the electrode (active material and carbon additive) and SEI during the first discharge process, regardless of the solvent used [22,24,43,45]. This behavior has been found in various titanate materials, such as surface-engineered nano-LTO [46] and other SIB anodes, such as tin-based carbon composite electrodes [47]. Other titanate-based anode materials, such as TiO_2 nanocrystals [14] and hydrogen titanate nanowires [48], have shown higher ICE with ether-based electrolytes compared to ester-based electrolytes. Nonetheless, it is worth noting that at both studied rates (0.1C and 2C), we observed a faster increase and stabilization of the coulombic efficiency (CE) to values of 99% in the DiG solvent. For example, we observed a faster increase in CE from cycle 1 to cycle 2 in DiG (96%) compared to EC:DEC (85%), which increased and stabilized on subsequent cycles to 99% and 98%, respectively, indicating greater Na^+ ion reversibility in DiG due to better SEI layer stabilization.

In rate capability tests on NTO, the DiG-based electrolyte outperformed EC:DEC at all rates tested (0.1–10C) [Fig. 1(d)]. After the fifth cycle, the specific capacity values for each rate were 197 (0.1C), 180 (0.2C), 160 (1C), 150 (2C), 130 (5C), and 110 (10C) mAh g^{-1} , as opposed to 135 (0.1C), 90 (0.2C), 61 (1C), 46 (2C), 31 (5C), and 20 (10C) mAh g^{-1} in EC:DEC. When the C rate was reduced from 10C to 0.1C, the discharge capacity increased in both systems. In EC:DEC, NTO delivered a specific capacity of 85 mAh g^{-1} compared to 135 mAh

g^{-1} (cycle 5 at 0.1C), resulting in a capacity retention of 63%. This increase, however, was significantly greater in the DiG solvent, where NTO provided a specific capacity of 182 mAh g^{-1} compared to 197 mAh g^{-1} (cycle 5 at 0.1C), indicating excellent reversibility (92%). These findings showed that by modifying the electrolyte solvent, NTO can exhibit superior or comparable electrochemical behavior to other reported NTO systems in Na half-cells, without the need for complex material design strategies like doping or morphology control in ester-based solutions (Table S2 in the Supplemental Material [33], including Refs. [28,29,45,48–67]).

B. PES-based chemical characterization of the SEI on NTO in ester- and ether-based electrolytes

1. Surface chemistry of the NTO-EC:DEC interphase

High-resolution synchrotron-based energy-tuned PES with two different excitation energies, corresponding to probing depths of approximately 10 nm (1090 eV) and 50 nm (7050 eV), was used to investigate the evolution of the SEI composition in the two electrolytes at different charge states. Figures 2 and S4 (in the Supplemental Material [33]) show high-resolution C 1s, O 1s, and F 1s spectra collected from NTO electrodes at different states of charge.

The C 1s spectra at 1090 and 7050 eV of the NTO electrode extracted from the cell after resting at

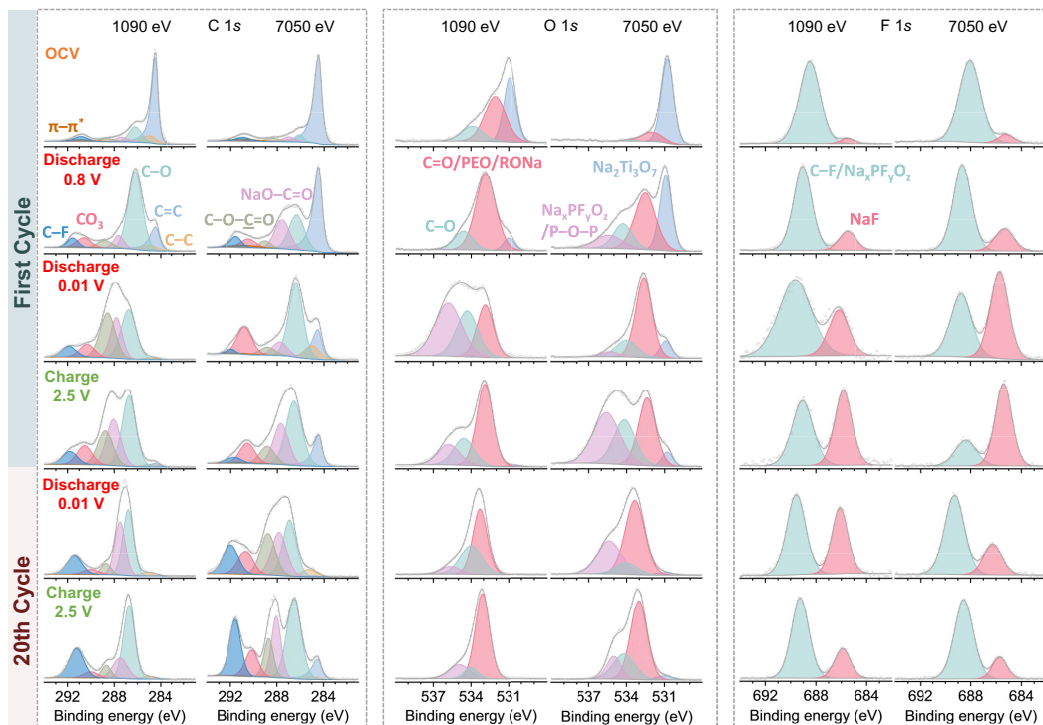


FIG. 2. High-resolution PES spectra (C 1s, O 1s, F 1s) of NTO electrodes cycled in an EC:DEC-based electrolyte at various stages of (de)sodiation during the first and 20th cycles.

the OCV period revealed carbon environments (e.g., C=C, C–C, C–O, and C–F) attributed to the carbon black and PVDF additive species [68]. The presence of NaF (F 1s spectra) may indicate the formation of a spontaneous SEI layer, as supported by the EIS data discussed later. This peak may also be partially attributed to residual electrolyte.

After discharge to 0.8 V, peaks for C–O (at approximately 286 eV), NaO–C=O (at approximately 287.6 eV), C–O–C=O (at approximately 288.8 eV), CO₃ (at approximately 290.5 eV), and C–F (at approximately 291.5 eV) in the C 1s spectra increased in intensity relative to the C=C peak (284.5 eV), particularly in the more surface-sensitive spectrum collected at 1090 eV, indicating the growth of the SEI layer. C–O, NaO–C=O, C–O–C=O, and CO₃ environments can be associated with the formation of semiorganic carbonates (RCH₂OCO₂Na)/organic carbonates (RCH₂OCO₂R)/esters (RCH₂O–C=OR)/poly (ethylene oxide) (–CH₂–CH₂–O–)_n oligomers (PEO)/sodium alkoxides (RONa), carboxylates (RO–C=ONa), esters (RCH₂O–C=OR), and RCH₂OCO₂Na/RCH₂OCO₂R/Na₂CO₃ SEI species, respectively, which are the products of EC and DEC reduction [22,69–73].

The C–O peak is significantly more prominent than the C–O–C=O and CO₃ peaks, suggesting that the C–O peak is primarily assigned to the presence of PEO/RONa species rather than RCH₂OCO₂Na/RCH₂OCO₂R/RCH₂O–C=OR/RO–C=ONa/Na₂CO₃ species and RCH₂OCO₂Na/RCH₂OCO₂R/RCH₂O–C=OR species, respectively. It should be noted that the PEO/RONa species were combined with the C=O peak in the O 1s spectra due to their close binding energies. Therefore, the significantly more intense C=O/PEO/RONa peak compared with the C–O peak at 1090 eV can be attributed to increased PEO/RONa formation, which aligns with the C 1s result.

When the voltage is further reduced to 0.01 V, the SEI layer thickens significantly, attenuating the C=C carbon black peak from the electrode at 1090 eV [22]. The peak intensities for NaO–C=O, C–O–C=O and CO₃ increase, while the relative intensity of the C–O peak decreases when compared to 0.8 V. This indicates a significantly reduced contribution from PEO/RONa to the C–O peak. This is further corroborated by the decreased relative strength of the C=O/PEO/RONa peak compared to the C–O peak in the O 1s spectrum at 1090 eV.

Additionally, a broad peak at higher binding energy, attributed to Na_xPF_yO_z/P–O–P species, was observed in the O 1s spectrum. This peak can be ascribed to the decomposition of the NaPF₆ salt [70]. In the C 1s spectra, the increase in the C–F peak observed during discharge, compared to the OCV state, cannot be attributed to the

CF₂ groups in the PVDF binder. This is due to the SEI, which is starting to bury the electrode and thus the PVDF binder. Therefore, this increase in the C–F peak suggests the formation of organic-fluoride species within the SEI. These species could be present as a result of the PVDF binder decomposing and then incorporating its decomposition species into the forming SEI [22,74]. However, C–F species have also been identified in a carbon anode-based SEI without a PVDF binder [72]. Consequently, the C–F species present in the SEI are most likely related to the reaction between NaPF₆ salt and solvents. At 1090 eV, the C=C (C 1s) peak assigned to carbon black and the NTO (O 1s) peak assigned to the NTO electrode are fully attenuated by the SEI. However, at 7050 eV, the C=C and NTO peaks are clearly visible. This confirms that the formed SEI thickness after the first discharge is greater than the probing depth associated with the 1090 eV spectra but less than the probing depth associated with the 7050 eV spectra, i.e., its thickness is between 10 and 50 nm.

Another major component observed during discharge to 0.8 V is NaF, as evidenced by an increase in the NaF peak in the F 1s spectra when compared to the electrodes at the OCV state. The formation of NaF is most likely caused by the reduction of NaPF₆ salt [58]. The intensity of this peak increases further for the fully discharged electrode, and its relative intensity increases at the higher probing depth, indicating the presence of a buried inorganic SEI layer close to the electrode surface composed of NaF [22,75].

As NTO was gradually charged back to 2.5 V, the intensity of the C=C carbon black peak in the C 1s spectra increased. Conversely, oxygen-based species shown in the O 1s spectra changed significantly during the charge process, indicating partial dissolution and stripping of the organic SEI components. Furthermore, the NaF peak can still be observed in the F 1s spectra, with a higher relative intensity than in the fully discharged state. This suggests that the organic SEI components are partially stripped after charging.

After 20 cycles, the C=C and NTO peaks are almost completely attenuated by the SEI, even at the highest probing depth, indicating a thicker SEI (>40–50 nm) after continuous cycling. A thick SEI can impede ion diffusion and has been demonstrated to increase impedance (as discussed later in the EIS section), resulting in poor rate capability and rapid capacity decay [Figs. 1(b)–1(d)] [76]. It is worth noting that the relative peak intensity of NaF to C–F/Na_xPF_yO_z (F 1s) is greater at 1090 than at 7050 eV in the fully discharged state, indicating a higher concentration of inorganic NaF distributed in the outer SEI layer. This observation contrasts significantly with the SEI at the first fully discharged state, where NaF is predominantly distributed in the inner SEI. The further decomposition of NaPF₆ salt likely leads to the formation of NaF in the outer SEI layer, resulting in an irregular SEI structure rather

than a well-defined double-layered organic-inorganic structure.

2. Surface chemistry of the NTO-DiG interphase

Figures 3 and S4 (in the Supplemental Material [33]) show high-resolution C 1s, O 1s, F 1s, and Ti 2p spectra for the studied NTO electrodes after different states of charge using DiG. After the OCV process, a slightly higher increase in the intensity of the NaF peak in the F 1s spectra of NTO was observed when compared to the EC:DEC system. This suggests a more prominent spontaneous SEI formation in DiG, which is consistent with the EIS result at OCV (Fig. S5 in the Supplemental Material [33]). Upon discharge to 0.8 V, five major peaks: C–C (at approximately 285 eV), C–O (at approximately 286 eV), NaO–C=O (at approximately 287.5 eV), C–O–C=O (at approximately 288.6 eV), and C–F (at approximately 291.3 eV) are observed in the C 1s spectra, indicating the growth of the SEI layer. At 0.01 V, the SEI thickens, attenuating the C=C carbon black (284.5 eV) and NTO (O 1s) peaks, which is particularly evident at 1090 eV excitation energy. The relative peak intensity of C–O compared to NaO–C=O, C–O–C=O, and CO₃ significantly increased from 0.8 to 0.01 V. This indicates that a greater quantity of PEO/RONa species formed rather than carbonates or carboxylates, in marked contrast to the

EC:DEC electrolyte. This is supported by the increased PEO/RONa to C–O peak intensity in the O 1s spectra when discharged to 0.01 V. These observations suggest that PEO/RONa species are the primary reduction products of the diglyme solvent [14,17,77]. By direct comparison with the F 1s spectra collected for the sample in the EC:DEC electrolyte, we observed a higher relative intensity of the NaF peak with respect to the C–F/Na_xPF_yO_z peak, which we attributed to the formation of a more inorganic (NaF)-rich SEI layer or an SEI with a thinner organic outer layer.

Despite the higher NaF to C–F/Na_xPF_yO_z peak intensity ratio observed in the DiG electrolyte, the NaF peak attenuates faster at 1090 eV when fully discharged than in the EC:DEC electrolyte. This may indicate a more well-defined double-layered SEI structure when using the DiG solvent, with an inorganic-rich inner layer close to the electrode surface and an organic-rich SEI on top. This could be explained by the reduced overlap of reduction voltages between salt and solvent in DiG electrolyte compared to EC:DEC electrolyte, originating from the higher LUMO energy level for ether solvents [19]. The well-defined double-layered SEI in DiG electrolyte may mitigate the passive release of inorganic SEI components into the electrolyte caused by organic species dissolution, a phenomenon that may occur in the less well-defined SEI in EC:DEC electrolyte [78]. In summary, the resulting SEI

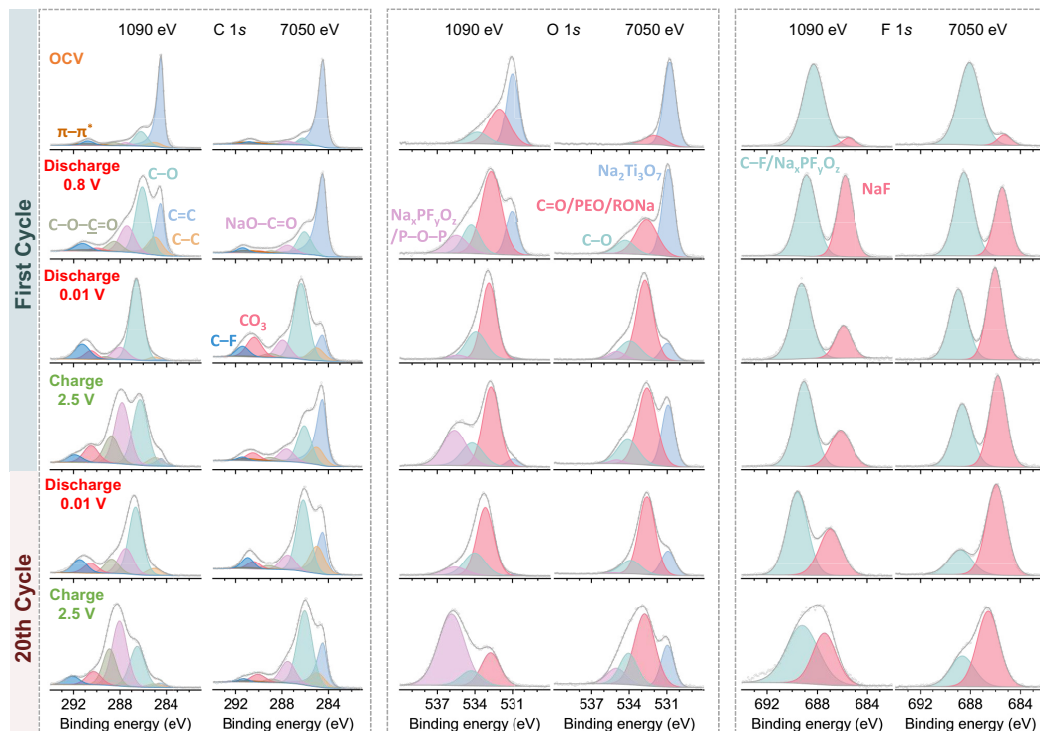


FIG. 3. High-resolution PES spectra (C 1s, O 1s, F 1s) of NTO electrodes cycled in a DiG-based electrolyte at various stages of (de)sodiation during the first and 20th cycles.

manifested as a well-defined layered structure composed of multiple organic and inorganic species at the end of discharge.

When NTO was charged back to 2.5 V, the C=C carbon black peak in the C 1s spectra increased, indicating partial dissolution and stripping of the organic SEI component. The O 1s spectra support these findings, indicating a higher relative intensity for the NTO peak with respect to other oxygen species in the fully charged and discharged states. This difference in the peak intensities of C=C and NTO between the end of charge and discharge is more significant in the DiG solvent than in the EC:DEC solvent, indicating a thinner SEI layer in the former solvent.

After 20 cycles, the C=C and NTO peaks remained visible at 7050 eV excitation energy, with these two peaks even discernible at 1090 eV excitation energy, in contrast to those in the EC:DEC electrolyte. This supports the formation of a thin (<10 nm) and relatively stable SEI layer composed of organic and inorganic species, resulting in excellent rate and cycling stability [Figs. 1(a) and 1(c)]. Comparing the relative intensity of the C–O peak to the NaO–C=O, C–O–C=O, and CO₃ peaks in the C 1s spectra at higher probing depths for different electrolytes reveals that the C–O peak consistently exhibits higher relative intensity in the DiG electrolyte than in the EC:DEC electrolyte. This observation is consistent with a higher fraction of ethers/alkoxides (e.g., PEO/RONa) in the former and a higher fraction of carbonates/esters/carboxylates (e.g., Na₂CO₃/RCH₂OCO₂Na/RCH₂OCO₂R/RCH₂O–C=OR/RO–C–ONa) in the latter.

Additionally, more inorganic species (e.g., NaF) were observed in the DiG electrolyte after 20 cycles, as indicated by the higher NaF to C:F ratio in the F 1s spectra. ROna and NaF species have been reported to exhibit a low-energy barrier for Na⁺ ion diffusion [14], resulting in a less resistive SEI in the DiG electrolyte. Overall, it is determined that the SEI obtained in DiG is thinner and more inorganic-rich than that of EC:DEC.

Furthermore, the SEI in the DiG-based system is more stable in the long term, as its thickness and composition remain relatively constant between the first discharge and 20th discharge, as well as between the discharge and charge states at the 20th cycle. This contrasts with the behavior observed in EC:DEC, where more pronounced compositional changes occur during cycling, and some dissolution and stripping of the SEI persists even after 20 cycles.

C. Operando EC-AFM of the SEI on NTO in ester- and ether-based electrolytes

Operando EC-AFM measurements on NTO revealed real-time SEI formation at the nanoscale during discharge [Figs. 4(a) and S6 in the Supplemental Material [33]]. NTO

electrodes were nanopolished to create a flat section prior to the sodiation process [Fig. S7(a) in the Supplemental Material [33]]. Figures 4(b) and S7(b) (in the Supplemental Material [33]) show SEM images of the as-prepared micro-electrode section surface for EC-AFM measurements. The electrode surface consisted of NTO grains (bright areas) embedded in a carbon black and PVDF binder matrix (darker areas). Fig. S7(c) in the Supplemental Material [33] shows a representative AFM topography image of the electrode and its corresponding nanomechanical AFM mapping [Fig. S7(d) in the Supplemental Material [33]], which enabled the identification of the polished electrode surface consisting of stiff NTO grains embedded in soft carbon and binder. EDX mapping of the polished electrode revealed a uniform compositional distribution across the sample, indicating that no other impurities were introduced during the nanopolishing process (Fig. S8 in the Supplemental Material [33]).

The discharge profiles of NTO using the microcell cycled in DiG and EC:DEC (Fig. S9 in the Supplemental Material [33]) are comparable to those observed in galvanostatic data in coin cells [Fig. 1(a)], indicating that the AFM microcell used can provide representative information about the initial SEI formation. However, the absence of pressure between components inevitably leads to an increase in voltage polarization in the electrochemical data. The EC-AFM tip mapped the electrode surface during galvanostatic discharge at selected voltages in EC:DEC, and the EC-AFM images obtained during the first discharge are shown in Figs. 4(c)–4(f).

At the OCV state, we observed that the electrode, which had been soaked in electrolyte for approximately 10 min, had a clean and smooth surface [Figs. 4(c) and 4(c')]. When the voltage was reduced to ca. 0.35 V vs Na⁺/Na, significant changes were detected in the topographical images in sample regions where a dominant presence of carbon black and/or PVDF was expected (as shown in the stiffness maps in Fig. S7 in the Supplemental Material [33]). Figure 4(d) shows these locations as dashed yellow circles. These results are attributed to SEI formation on these components, as well as the sodiation of carbon black [22,46,79].

At ca. 0.18 V [Figs. 4(e) and 4(e')], we observed fine and well-distributed nanoparticles (<20 nm in diameter) on the surface of NTO, which we attributed to further electrolyte decomposition and SEI formation. These findings were supported by nanomechanical mapping, which allowed for higher resolution of these products due to their distinct contrast (Fig. S10 in the Supplemental Material [33]). Furthermore, an increase in electrolyte decomposition products was observed in regions containing carbon black and PVDF [as shown by the white dashed line circled area in Fig. 4(e')], indicating the formation of a thickened SEI. This SEI thickened further at ca. 0.10 V, as shown in Fig. 4(f), eventually covering the entire electrode

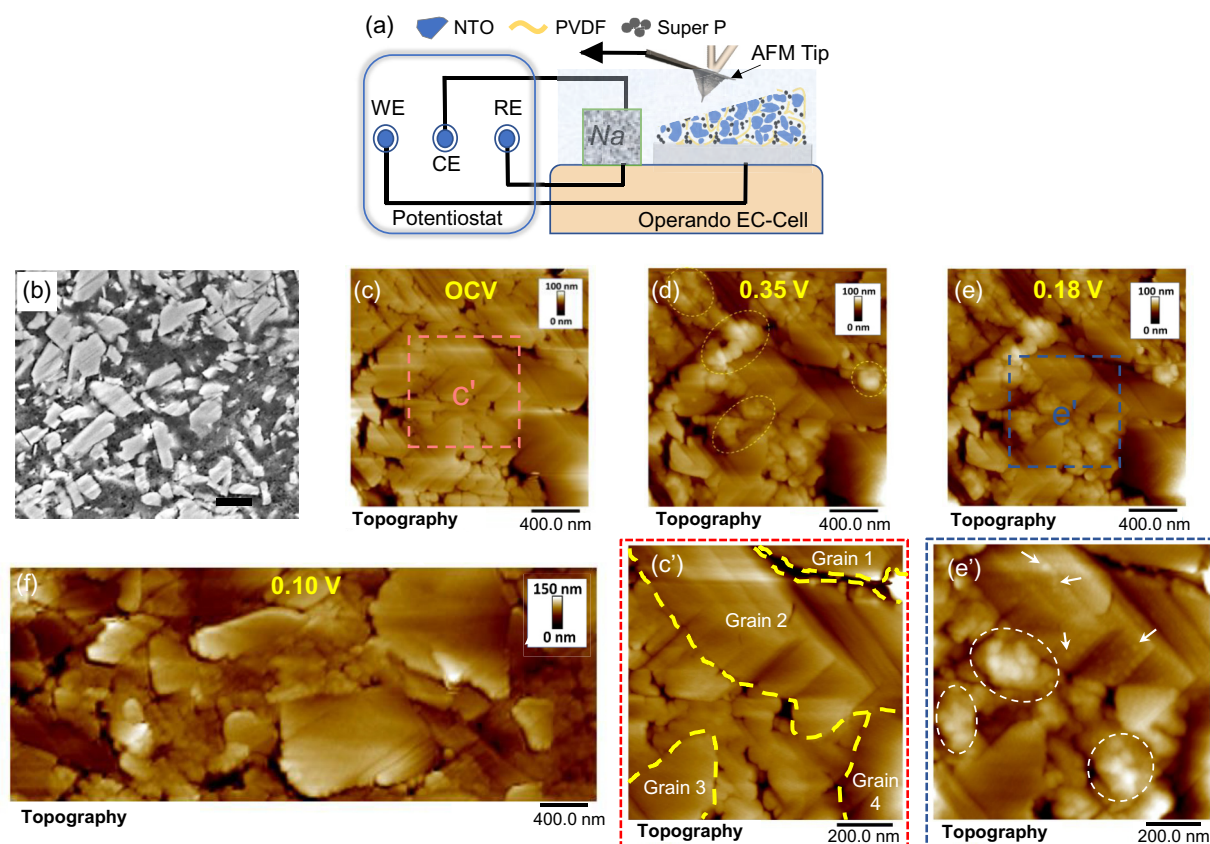


FIG. 4. (a) Schematic of the EC-AFM setup for measuring the as-prepared electrode section area. (b) SEM image of the nanopolished area for EC-AFM measurement. The scale bar represents 1 μm . (c)–(f) Operando EC-AFM images of the NTO electrode surface during the first discharge process in EC:DEC at selected discharge voltages. (c'), (e') correspond to higher magnification images of the squared areas in (c), (e), respectively.

surface and presenting a rough morphology. These results are consistent with the low α value obtained from the EIS data (Table S3 in the Supplemental Material [33]), which implies a rough SEI in EC:DEC [80,81], and the low ICE observed (ca. 60%) in the galvanostatic data [Fig. 1(a)]. When NTO was cycled in DiG, however, different topographical features were found, with fewer SEI products detected during the first discharge [Figs. 5(a)–5(c)].

Figures 5(d) and 5(e) show the distribution of organic and inorganic components in the SEI layer formed in DiG and EC:DEC electrolyte solutions, respectively. Force curves recorded the AFM tip deflection signal as it approached and indented into the electrode surface [82]. Following the initial discharge procedure in the DiG-based electrolyte [Fig. 5(d)], the tip deflection curves showed distinct slope regions near the electrode surface of up to ca. 10 nm, corresponding to the various SEI components with differing mechanical moduli [83]. Specifically, the inorganic-rich inner SEI had a higher modulus than the organic-rich outer layer. This observation is consistent with the PES results, which showed a well-defined double-layered SEI formed in the DiG electrolyte (Fig. 3).

In contrast, the tip deflection curves for the EC:DEC electrolyte showed less steep components near the electrode surface up to ca. 20 nm, indicating a thicker SEI with a lower average modulus. This observation was consistent with PES results (Fig. 2). Figures 5(f) and 5(g) show statistical results of the absolute value of the average SEI modulus $|G^*|$ vs depth in the SEI layer, z , in the two electrolytes using the 3D-NMR technique (see Methods) [43]. The SEI formed in the DiG solvent has a narrower distribution of thickness and effective modulus than the SEI formed in the EC:DEC solvent, indicating the formation of a more homogeneous SEI.

Figure 5(h) shows a schematic comparison of the initial SEI formation process in DiG and EC:DEC electrolytes, based on PES and EC-AFM data. Initially, in the voltage range from OCV to ca. 0.35 V, carbon black sodiation and PVDF swelling occur, followed by an initial electrolyte reduction to create an inorganic-dominated SEI (DiG) and organic-inorganic hybrid SEI (EC:DEC) species. The SEI gradually thickens as the voltage drops due to ongoing electrolyte decomposition until it reaches full discharge. However, the first produced compact, inorganic-rich SEI,

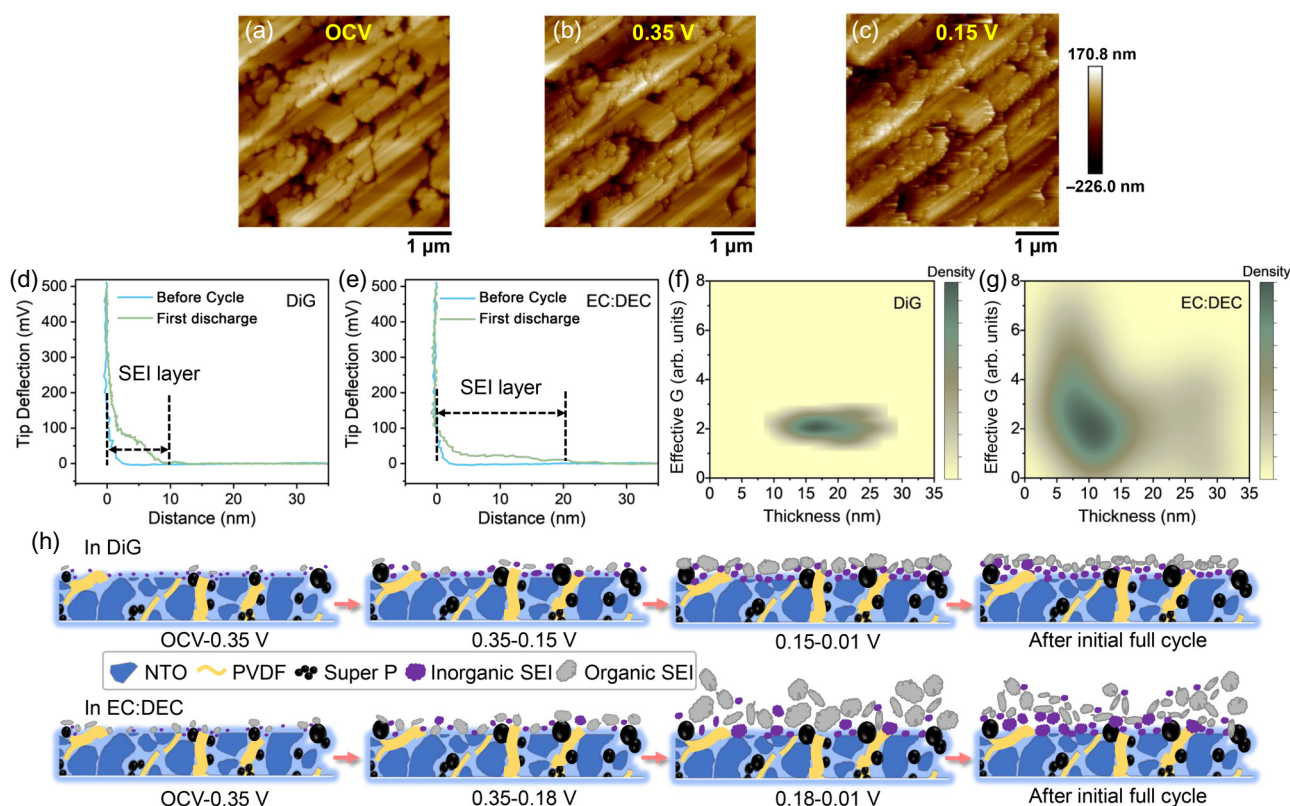


FIG. 5. Operando EC-AFM images of the NTO electrode surface during the first discharge process in DiG at selected discharge voltages of OCV (a), 0.35 V (b), and 0.15 V (c) vs Na^+/Na . AFM force curves of SEI formed in DiG (d) and EC:DEC (e) electrolytes. Statistic results of SEI thickness and effective modulus obtained using 3D-NMR (see Methods) in DiG (f) and EC:DEC (g) electrolytes after the end of the first discharge. (h) Proposed SEI formation models for NTO electrode cycling in EC:DEC and DiG electrolytes.

which is essentially the result of salt reduction in DiG, effectively shields the anode surface from contact with the electrolyte, reducing further solvent reduction [19]. As a result, a thinner and more well-defined SEI forms in DiG. In contrast, the competitive reduction of both salt and solvent in EC:DEC, attributed to the partial overlap of LUMO energy levels between salt and solvent, produces a relatively heterogeneous and loose SEI with randomly distributed larger-sized species, causing intensive electrolyte reduction and thick SEI formation [19]. During the desodiation process of the NTO anode, the SEI in both electrolytes partially dissolves, primarily the organic components. This phenomenon is more pronounced in EC:DEC due to its higher organic content, resulting in a rough and loose SEI morphology at the end of the cycle.

D. Three-electrode EIS analysis of NTO in ester- and ether-based electrolytes

EIS data were collected during the discharge processes in cycles 1, 2, and 20 [Figs. 6(a) and 6(b)] to better understand the sodiation kinetics and SEI behavior of NTO in the two electrolyte solvents used. The data were fitted

to equivalent circuits based on the observed features in the Nyquist plots. Table S3 in the Supplemental Material [33] shows the key fitting parameters extracted from the EIS data. In both electrolytes, the Nyquist plots obtained during cycle 1 showed an almost negligible arc in the high-frequency region ($R_{\text{SEI}} \parallel \text{CPE}_{\text{SEI}}$), which is typically attributed to Na^+ ion migration through the SEI layer [Figs. 6(a) and 6(b), insets] [14]. This semicircle appeared less pronounced in the EC:DEC solvent than in the DiG solvent, resembling a shoulder, most likely due to overlap with a second semicircle at medium frequencies. This response was observed in both cases at the OCV state (Fig. S5 in the Supplemental Material [33]), indicating the formation of a spontaneous SEI layer immediately after the cells were assembled, as confirmed by the PES results (Figs. 2 and 3). The spontaneous formation of the SEI layer is probably due to the dehydrofluorination reaction of the poly(vinylidene fluoride) (PVDF) binder used and the deposition of the products from the spontaneous reaction between Na metal and electrolyte [22,84]. A second semicircle attributed to charge-transfer processes at the electrode-electrolyte interphase ($R_{\text{CT}} \parallel \text{CPE}_{\text{CT}}$), followed by an additional third semicircle at low frequencies, was also observed in the Nyquist plots. The

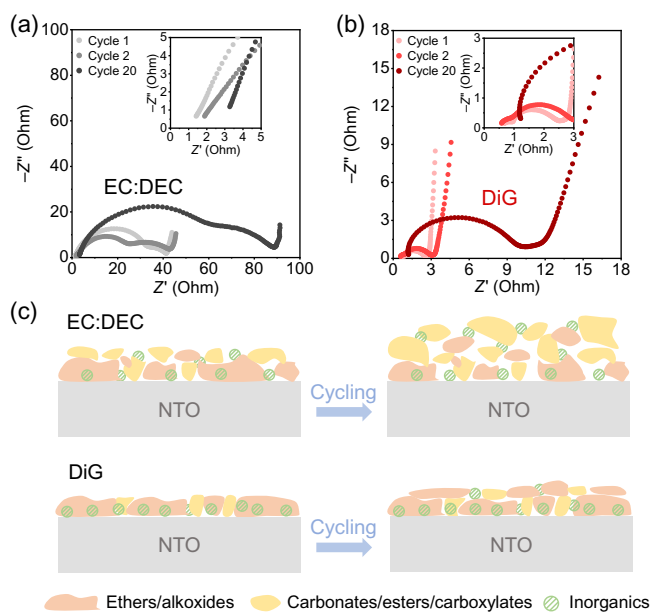


FIG. 6. EIS data during discharge on cycles 1, 2, and 20 in (a) EC:DEC and (b) DiG-based electrolytes. (c) Schematic illustration showing key structural differences between the SEIs formed in EC:DEC and DiG-based electrolytes and their evolution with extended cycling.

estimated capacitance for the third semicircle was in the range of 10^{-3} – 10^{-4} F, indicating that an electrochemical reaction contributes to the impedance during Na^+ ion insertion into NTO ($R_{\text{echem}} \parallel \text{CPE}_{\text{echem}}$) [85]. In the low-frequency domain, we observed a tail associated with a combination of a Warburg diffusion element (Z_w) and an intercalation capacity (CPE), which explains the diffusion and accumulation of Na^+ ions in the electrode [86].

Comparing the EIS datasets for the two electrolyte solutions across cycles 1, 2, and 20 revealed that the DiG solvent facilitated all processes more effectively, as evidenced by the lower resistance values in the EIS data (Table S3 in the Supplemental Material [33]). Furthermore, cycling in DiG (with a maximum of 20 cycles studied) resulted in minimal increases in R_{SEI} , R_{CT} , and R_{echem} values compared to EC:DEC. Equation (1) yielded capacitance values for charge-transfer processes in discharged cycles 1 and 2 that were approximately 15 and 5 times higher in DiG ($C_{\text{CTcycle1}} = 180 \mu\text{F}$ and $C_{\text{CTcycle2}} = 90.2 \mu\text{F}$) than in EC:DEC ($C_{\text{CTcycle1}} = 11.3 \mu\text{F}$ and $C_{\text{CTcycle2}} = 15.3 \mu\text{F}$). These differences may explain the lower polarization and higher rate capability observed in the galvanostatic data [Fig. S3 in the Supplemental Material [33] and Figs. 1(c) and 1(d)]. These findings also point to improved wettability of the diglyme solvent, which leads to increased charge accumulation at the electrode-electrolyte interphase [87]. Contact angle measurements have confirmed the superior wettability of diglyme in comparison to ester-based solvents [18].

The dispersion parameter (α) in Eq. (1) provides insight into the homogeneity and roughness of a surface layer, where $\alpha < 1$ indicates a heterogeneous and/or rough surface, while $\alpha = 1$ indicates a homogeneous and smooth layer [80,81]. Higher estimated α values for SEI formation (α_{SEI}) in DiG indicate a more compact and homogeneous SEI in the ether solvent (Table S3 in the Supplemental Material [33]) [80]. In DiG, the α parameter showed little change between charge and discharge processes during the two initial cycles, indicating the formation of a relatively stable SEI layer. Using the EC:DEC solvent resulted in a significant increase in the α parameter, likely due to the partial dissolution of species in the SEI during cycling. Thus, the data show that the SEI exhibited was more dynamic in EC:DEC than in DiG, reforming as cycling progressed [80]. This trend is consistent with the PES data (Figs. 2 and 3) and could explain the faster capacity decay observed in long-term cycling data with the ester-based solvent in Na half-cells [Figs. 1(b)–1(d)].

In summary, EIS data showed that the diglyme-based electrolyte resulted in more stable, less resistive, and higher capacitive interfacial processes, lowering the overall impedance of the system. As a result, using this electrolytic solution results in lower polarization as well as improved cycling stability and rate performance in NTO.

Based on the data obtained from PES, EC-AFM, and EIS, a schematic illustration highlighting the key differences in the initially formed SEI and its evolution during extended cycling is presented in Fig. 6(c). The initial SEI formed in DiG is thinner (<10 nm) and exhibits a well-defined double-layered structure, consisting of a NaF-rich inner layer and an ether/alkoxide-rich (e.g., PEO/RONa) outer layer. In contrast, the initial SEI formed in EC:DEC is thicker (10–50 nm) and displays a more irregular structure, where ether/alkoxide species (e.g., PEO/RONa) are covered by carbonates, esters, and carboxylates (e.g., $\text{Na}_2\text{CO}_3/\text{RCH}_2\text{OCO}_2\text{Na}/\text{RCH}_2\text{OCO}_2\text{R}$, $\text{RCH}_2\text{O}-\text{C}=\text{OR}$, and $\text{RO}-\text{C}=\text{ONa}$), with NaF particles randomly embedded within the matrix. The SEI is dynamic and thickens with prolonged cycling, accompanied by partial dissolution into the electrolyte. The evolution is more pronounced in EC:DEC, where a much thicker (>40 – 50 nm), organic-dominated SEI—primarily composed of carbonates, esters, and carboxylates—was observed. This can be attributed to the loosely packed SEI structure in EC:DEC, which fails to effectively isolate the anode from the electrolyte, leading to continuous electrolyte decomposition. In contrast, the compact NaF-rich inner SEI layer and the higher reductive stability of the diglyme solvent in DiG mitigate electrolyte decomposition, resulting in a more stable SEI with only minor changes in thickness, composition, and resistance during cycling.

Although diglyme demonstrates promising interfacial compatibility with the NTO anode, its broader commercial viability in SIB technology needs to be considered. Generally, ether solvents show lower oxidation stability than ester solvents due to their higher highest occupied molecular orbital (HOMO) levels, making them more susceptible to oxidation on the cathode side [19]. However, some studies have shown that diglyme-based electrolytes are compatible with 4 V-class cathodes, including layered oxide cathodes such as $\text{Na}_{0.66}\text{Ni}_{0.26}\text{Zn}_{0.07}\text{Mn}_{0.67}\text{O}_2$ (NZM) with an upper cut-off voltage of 4.1 V [88], and polyanionic cathodes such as $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ (NVOPF) and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) [89,90], with upper cut-off voltages of 4.3 and 4.5 V, respectively [3]. NZM, NVOPF, and NVPF half-cells perform even better in diglyme-based electrolytes than in ester-based ones [88–90]. Moreover, diglyme electrolytes have demonstrated good cycle stability in NZM-carbon, NVOPF-NTO, and NVPF-NTO full-cells, suggesting high compatibility with full-cell configurations [2–4]. Notably, the NVOPF-NTO full-cell delivers a higher capacity and significantly improved cycle stability at 20C for over 4200 cycles in diglyme electrolyte (1 M NaPF_6 in diglyme) than in ester electrolyte (1 M NaClO_4 in PC/EC/FEC) [89]. Furthermore, the weakly solvated Na^+ -diglyme complex in the diglyme electrolyte (0.5 M NaPF_6 in diglyme), which facilitates Na^+ ion diffusion and lowers interfacial charge-transfer energy, enables the NVPF-NTO full-cell to exhibit superior low-temperature performance at -20°C (5C) compared to the ester electrolyte (0.5 M NaPF_6 in PC/EC) [90]. It should be noted that although diglyme electrolytes have been found to have poorer cycling stability or rate capability than ester-based electrolytes in some studies [47,91]—possibly due to compatibility issues with specific cathode or anode materials—diglyme electrolytes remain a promising alternative for sodium full-cells.

However, practical applications require considerations beyond oxidation stability, including cost, toxicity, and flammability [92–95]. Diglyme is more expensive than ester solvents like DMC due to its complex synthesis and regulatory restrictions [93,94]. In terms of toxicity, diglyme presents greater risks, including reproductive and developmental toxicity, as well as potential carcinogenicity linked to its metabolite, 2-methoxyethoxyacetic acid [95]. Furthermore, diglyme is flammable, while some ester solvents like EC and PC are nonflammable. However, the combination of EC or PC with low-flash-point solvents such as DEC or DMC makes the resulting electrolytes flammable as well.

Although ether-based electrolytes are often considered unsuitable for high-voltage systems, diglyme has been shown to exhibit sufficient oxidative stability for application with 4V-class cathodes in full-cell configurations, a valuable trait that expands its applicability to high-energy-density SIBs. Nevertheless, as mentioned

earlier, the primary limitations of diglyme lie in its higher cost and toxicity, which may hinder its commercial viability. These challenges could potentially be mitigated through protective handling strategies, appropriate formulation strategies and safety engineering, as well as improved synthetic routes to reduce production costs, positioning diglyme-based electrolytes as a strong contender for next-generation battery technologies.

IV. CONCLUSIONS

In conclusion, switching from an ester-based to an ether-based electrolyte significantly improves the electrochemical performance of the NTO anode in half-cells, including specific capacity, cycle stability, and rate capability, which are comparable to or even exceed those of other reported NTO systems that use complex material design strategies. When cycled in diglyme-based electrolyte, the NTO anode has an initial reversible specific capacity of 192 mAh g^{-1} and a specific capacity of 125 mAh g^{-1} after 200 cycles at 0.1C and 103 mAh g^{-1} after nearly 500 cycles at 2C. EIS data show that the diglyme-based electrolyte promotes less resistive and enhanced capacitive interfacial processes, decreasing the overall battery impedance. This explains the improved cycling stability and rate performance. Furthermore, we use energy-tuned PES and operando EC-AFM to compare the formation, composition, and morphological evolution of SEI layers in both electrolytes. The combined results indicate a more stable and thinner SEI in the diglyme-based electrolyte. This SEI has a well-defined structure, with a stiff, inorganic-rich inner layer and a soft, organic-rich outer layer. This combination can effectively protect the NTO anode while reducing electrolyte decomposition, extending the cycle life of NTO-based batteries. The findings of this study provide a comprehensive framework for understanding the underlying factors responsible for the performance improvements reported in ether-based electrolytes for SIB anodes. These findings offer valuable guidance for future design and matching between electrolytes and electrode materials in rechargeable batteries.

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The authors declare that they have no competing interests.

DATA AVAILABILITY

The data that support the findings of this article are openly available [96].

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