The electrode–electrolyte interfaces play a critical role in influencing the cyclic stability, Coulombic efficiency, and safety of rechargeable batteries. Although there are many recent efforts for investigating the solid electrolyte interface formed on anodes, much less attention has been paid to examine the cathode–electrolyte interface (CEI) established on cathodes. Understanding of the chemistry, morphology, and structure of CEI layers is still illusive requiring further in-depth characterization. The cryogenic electron microscopy is used to reveal a 1.1 nm thick CEI layer formed on a flower-shaped, carbon-coated Na$_3$V$_2$(PO$_4$)$_3$/C (NVP/C) cathode in ether-based electrolyte for Na-ion batteries. The rationally designed NVP/C cathode delivers cyclic stability with a capacity retention of over 88% at 50 mA g$^{-1}$ after 1600 cycles and an excellent high-rate capability at up to 3200 mA g$^{-1}$. These findings may shed new light on the design of CEI layers to achieve high energy and power densities in rechargeable Na-ion/metal batteries.

1. Introduction

Significant research and development efforts have been instigated in the past decade in quest of low-cost rechargeable Na-ion batteries (SIBs) that can deliver high energy and power densities with enhanced cyclic stability and safety.$^{[1-4]}$ Cathodes with high capacities and voltage plateaus as well as long cyclic stability are required to achieve these goals. Among many potential cathode materials, the sodium super ion conductor (NASICON)-structured Na$_3$V$_2$(PO$_4$)$_3$ (NVP)—a typical polyanionic compound with a 3D open framework and a high ionic conductivity—has attracted significant attention because of its high theoretical capacity of $\approx$117.6 mAh g$^{-1}$ with V$^{3+}$/V$^{4+}$ valence change, high thermal stability, and a relatively high voltage plateau of $\approx$3.4 V versus Na/Nax$^{[5,6]}$. Most of previous studies about NVP were focused on improving the electrical conductivity and structural stability based on rational design strategies, such as elemental doping,$^{[7-9]}$ carbon coating$^{[10-14]}$ and structural engineering.$^{[15-17]}$ In addition, more insights into their underlying reaction mechanisms have been obtained taking advantage of advanced in situ/operando characterization techniques.$^{[18-20]}

One largely overlooked aspect of these electrodes is the lack of fundamental understanding of the electrode–electrolyte interfaces that might have a significant implication on electrochemical performance of rechargeable batteries.$^{[21-23]}$ An ideal interfacial film must 1) be thin to minimize the consumption of active alkali ions and thereby reduce the cell impedance, 2) be compact for effective blockage of electrons while preventing the dissolution of active materials, 3) possess a uniform thickness and structure to ensure consistent transport of alkali ions over the whole surface, and 4) be mechanically flexible to endure the volume expansion of active materials.$^{[24]}$ Although some analytical techniques have been used to investigate these interface layers, it is difficult to probe their native structures mainly because they are highly vulnerable to ambient conditions and electron beams which may bring about structural artifacts, relaxation, and/or oxidation, causing misleading results.$^{[25-28]}$ The cryogenic electron microscopy (cryo-EM) and cryogenic electron energy loss spectroscopy (cryo-EELS) have emerged as powerful tools to understand the structure, morphology, and chemical environment of these interfaces while circumventing the aforementioned issues at a cryogenic temperature below $-170\,^{\circ}$C.$^{[29]}$ Despite many recent cryo-EM and cryo-EELS studies of solid electrolyte interface (SEI) layers on various anodes$^{[30-34]}$; however, far less attention has been paid on examining the envisioned cathode–electrolyte interface (CEI) layers on positive electrodes in Li-ion batteries (LIBs) and SIBs. For
example, the chemical species in the CEI layer formed on a LiNiO.5Mn0.3Co0.2O2 cathode in LIBs were identified using the cryo-EELS, whereas the CEI layer formed in a carbonate electrolyte was not well-defined to indicate its uniformity and thickness.\[35\] Another cryo-EM study revealed a uniform CEI of 0.612 nm in thickness formed on LiNiO.5Mn1.5O4 cathode which performed well for up to 1000 cycles in a carbonate-free sulfone-based electrolyte.\[36\] These findings signify the importance of in-depth studies of the structure and formation mechanisms of CEI layers in designing high-performance alkali ion/metal batteries.\[37\]

One of the main barriers to practical realization of high energy density Na-ion/metal full cells is the lack of compatibility of Na metal anodes and various cathodes with the electrolyte. For example, Na metal anodes exhibit better performance in ether-based electrolytes than their ester-based counterparts.\[38\] However, most of the latter electrolytes are unstable in upper operation potentials of numerous high-voltage cathodes.\[39,40\] Various additives and more salts were added in these electrolytes to address this issue.\[41\] However, the high concentration of salts means additional costs for battery fabrication.\[42\] Meanwhile, it is also found that a hard carbon paper anode delivered excellent electrochemical performance with a high initial Coulombic efficiency of 91.2% and stable performance for 1000 cycles in ether-based electrolyte, much better than in ester-based counterpart.\[43\] This report raised the demand of cathodes which can perform well in full cells assembled with the former electrolyte. Overall, the basic understanding of the structure and morphology of the perceived CEI layer on NASICON-type cathodes together with their electrochemical performance in ether-based electrolytes is still missing. With foregoing background in mind, this work is dedicated to probing the CEI layer formed on a rationally designed carbon-coated flower-shaped NVP (NVP/C) electrode by employing cryo-EM for the first time for SIBs. Due to the formation of a thin and uniform conformal CEI layer, the NVP/C electrode demonstrates excellent cyclic stability, high-rate capability, and interfacial stability after long cycles.

2. Results and Discussions

2.1. Structure and Morphology

The presence of crystalline NVP phase (PDF: 45-0319) was confirmed by the matching prominent peaks of X-ray diffraction (XRD) pattern of the NVP/C powder,\[14,44\] as shown in Figure 1a. The scanning electron microscopy (SEM) images in Figure 1b,c and Figure S1, Supporting Information, reveal the flower-shaped morphology of the NVP/C powder arising from the self-assembly of NVP/C nanoflakes during the hydrothermal process. Such a structure of electrode material was previously found beneficial for its high wettability with the electrolyte, thus facilitating fast Na⁺ conduction and effective utilization of the active material.\[16,45\] The high-resolution transmission electron microscopy (TEM) image confirmed the presence of carbon coating of \(\approx2–3.5\) nm in thickness, indicated by the red arrows and dotted lines on the NVP nanoflakes,\[46\] as shown in Figure 1d and Figure S2, Supporting Information. In addition, the lattice fringes with a d-spacing of 0.619 nm corresponding to the (012) plane further substantiated the presence of NVP phase in the NVP/C powder.

Figure 1. a) XRD pattern, b,c) SEM images taken at different resolutions, and d) high-resolution TEM image of flower-shaped NVP/C powder.
The SEM energy-dispersive spectroscopy (SEM-EDS) elemental maps confirmed the evenly dispersed Na, V, P, O, and C elements in the NVP/C powder, as shown in Figure 2a–f. The general X-ray photoelectron spectroscopy (XPS) spectrum shown in Figure S3, Supporting Information, presents prominent peaks of Na, V, O, P, and C, whereas their atomic and mass concentrations are summarized in Table S1, Supporting Information. The high-resolution C 1s spectrum was deconvoluted into three peaks which appeared at binding energies of 284.4, 285.6, and 288.3 eV corresponding to the C=C, C–O/C–O–P, and C=O bonds,[47,48] respectively, see Figure 3a. The attachment of oxygenated moieties was also corroborated by the peaks at 531.4 and 532.5 eV representing the C=O and P–O–C bonds[47] in the deconvoluted O 1s spectrum, as shown in Figure 3b. In addition, the additional peaks at 530.4 and 530.9 eV indicate the existence of phosphate moieties in NVP/C.[49] The P–O–C bond in NVP/C was further manifested by a prominent peak at 133.4 eV in the deconvoluted P 2p spectrum,[50,51] see Figure 3c. In addition, two peaks appeared at 132.7 and 134.1 eV represented the P=O and phosphate moieties.[51,52] The high-resolution XPS spectrum of V 2p revealed two peaks at 517 and 524 eV corresponding to the V 2p3/2 and V 2p1/2 transitions,[53] respectively, which were deconvoluted into two pairs of peaks, see Figure 3d. The first pair of peaks, i.e., the V 2p1/2 peak at 524.5 eV and V 2p3/2 peak at 517.3 eV, can be attributed to the V5+ valence state.[54] The second pair of peaks, i.e., the V 2p1/2 peak at 523.3 eV and V 2p3/2 peak at 516.6 eV, indicate the presence of the V4+ valence state in NVP/C powder.[14,55] Figure S4, Supporting Information, shows the high-resolution spectrum of Na 1s comprising a prominent peak at 1071.3 eV, which was deconvoluted into two peaks at 1070.9 and 1071.6 eV, corresponding to the presence of sodium phosphates.[56,57] Overall, the rich surface chemistry of the NVP/C electrode with P–O–C bonds and several phosphate moieties may help

**Figure 2.** a) Reference SEM image, and EDS elemental maps of b) Na, c) V, d) P, e) O, and f) C in NVP/C powder.
maintain its structural integrity and fast charge transfer for long cycles.

### 2.2. Cryogenic Electron Microscopy

The cryo-EM samples were prepared following the below procedure to minimize their exposure to ambient environment. First, the desodiated electrodes were recovered after disassembly of the precycled cells inside an Ar-filled glove box and washing with 200 μL of diethylene glycol dimethyl ether (DEGDME) solvent to remove any salt precipitated on the electrode. A clean, fine-tip tweezer was used to scratch the electrode particles from the carbon-coated Al current collector which were transferred to a vial filled with DEGDME solvent. The vial was then gently shaken to form a turbid solution, and a few drops of the solution were applied on a Cu grid coated with a holey carbon film. The Cu grid with a sample was stored and dried in a cryo-grid box which was sealed inside the Ar-filled glove box. The Cu grid box was transferred to the liquid nitrogen immediately after removing the grid box and opened inside the liquid nitrogen container of the cryogenic TEM (cryo-TEM) holder. Finally, the grid was transferred to the cryo-TEM holder and the shutter was closed before topping up the liquid nitrogen and transferring it to the TEM column. Once the temperature of the cryo-TEM holder reached −175 °C, the electron beam with a low intensity was shed on the Cu grid to examine the CEI layer on the NVP/C electrode. A conformal CEI layer consistently matching the contour of the underlying NVP/C particle was revealed at a magnification of 200 000×, as shown in Figure 4a. Upon further magnification at 300 000×, it was possible to measure the thickness of the conformal CEI layer at ≈1.1 nm, as shown in Figure 4b. This finding is illustrated in a schematic shown in Figure 4c. The CEI layer was much thinner than reported SEI layers on several anodes,[33,58] which made it rather difficult to probe its atomically resolved structure even using the cryo-EM without an aberration corrector. Therefore, we were not able to get deeper insights into the atomic structure of the CEI layer even after using a higher magnification up to 500 000×, as shown in Figure S5a,b, Supporting Information.

### 2.3. Electrochemical Performance

To investigate the redox behavior of the NVP/C electrode, the cyclic voltammetry (CV) curves of first five cycles were obtained at a scan rate of 0.2 mV s⁻¹, as shown in Figure 5a. The peaks at 3.43 and 3.28 V can be assigned to the sodiation and desodiation of the NVP/C electrode, respectively.[45] The preserved CV curves of subsequent cycles revealed enhanced structural stability of the electrodes. Although the CV is a powerful and popular electrochemical technique commonly used to investigate the reduction and oxidation reactions occurring at the electrode–electrolyte interfaces,[39,60] the technique is not advanced enough to measure the thickness of CEI layer. The galvanostatic charge discharge

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**Figure 3.** Deconvoluted XPS spectra of a) C 1s, b) O 1s, c) P 2p, and d) V 2p of NVP/C powder.
(GCD) profiles at 50 mA g\(^{-1}\) demonstrated an ultralow polarization of 0.05 V in the second cycle and well-preserved shapes for up to 1500 cycles, as shown in Figure 5b. The NVP/C electrodes delivered excellent cyclic stability with over 88% capacity retention at 50 mA g\(^{-1}\) after 1600 cycles, as shown in Figure 5c. The high-rate capability of the electrodes was equally impressive with reversible capacities of 99, 83, 69, 55, 43, 33, and 23 mA h g\(^{-1}\) at 50, 100, 200, 400, 800, 1600, and 3200 mA g\(^{-1}\), respectively, see Figure 5d. Upon returning to 100 and 50 mA g\(^{-1}\), the electrodes displayed capacity recovery rates of 97.6% and 90.9%, respectively. The high initial capacity of the NVP/C electrodes can be ascribed to their activation and irreversible decomposition of the electrolyte to form a CEI layer in the first cycle. To verify the formation of a robust CEI layer on the NVP/C cathode, the ex situ electrochemical impedance spectroscopy (EIS) analysis was conducted after 50th and 1600th cycles upon discharging to the same voltage of 2.5 V, as shown in Figure 5e. A typical model circuit was used to fit the EIS data,[16] as shown in Figure S6, Supporting Information, and the corresponding impedance parameters are summarized in Table S2, Supporting Information. The cell demonstrated excellent interfacial stability with very low values for all impedance parameters. Notably, there was a large reduction in charge transfer resistance, \(R_{ct}\), from 26.5 to 15 \(\Omega\) during the prolonged cycles from 50 to 1600 cycles. In summary, it can be said that the excellent electrochemical performance can be attributed to the robust 3D flower-shaped structure of the NVP/C cathode with 1) a short Na\(^+\) ion diffusion distance, 2) an increased electrical conductivity because of the carbon coating, 3) large open space among nano flakes that can accommodate the strains arising from the V\(^{3+}/V^{4+}\) redox reaction,[14] and 4) excellent interfacial properties in the ether-based electrolyte with a thin CEI layer and a small charge transfer resistance.[46]

In view of the fact that there is thus far no relevant report on CEI visualization and thickness measurements for SIB cathodes, we were only able to compile the CEI thickness data for LIB cathodes probed by cryo- or conventional EM and the information of corresponding electrochemical performance in different electrolytes available from the literature, as shown in Table S3, Supporting Information.[35,36,61–70] The comparison indicates that the CEI thicknesses on LIB cathodes ranged between sub-nanometer and 27 nm, with the majority showing 5–10 nm. The CEI thickness of the NVP/C SIB cathode reported in this study is clearly among the thinnest. It should be noted, however, that the CEI thicknesses measured using conventional TEM may not be accurate because of possible oxidation of CEI and artifacts generated in CEI by the electron beam.[35] It is also cautiously assumed that the electrochemical performance of the electrodes with a thin CEI[36] tends to be marginally better than those with a relatively thick CEI.[35,67,69] A thinner CEI would reduce the cell impedance and facilitate fast transport of Na ions, which are essential for enhanced cyclic stability of the cathodes.[44] However, more research effort is required to verify this hypothesis by establishing firmer understanding of the formation.

Figure 4. High-resolution cryogenic TEM images of the NVP/C cathode taken at magnifications of a) 200 000\(^{\times}\) and b) 300 000\(^{\times}\) while maintaining the temperature at around \(-170^\circ\)C; c) schematic illustration of the formed conformal CEI layer on cycled NVP/C cathode.
mechanisms, nanostructures, and dimensions of CEI layers that are specific to different battery components and battery operating conditions. Because of the absence of CEI studies for SIBs, no general conclusion or assumption can be drawn regarding the relative CEI thicknesses between LIBs and SIBs. Depending on the type of batteries, many factors may affect the CEI layers, notably 1) electrolyte solvent, salt, and additives; 2) electrode materials; and 3) service temperature.

3. Conclusion

This work is aimed at probing the CEI layer formed on a carbon-coated flower-shaped NVP/C cathode—a NASICON-structured polyanion compound—for the first time for SIBs using the cryo-EM. A conformal CEI layer of ≈1.1 nm in thickness was revealed on the NVP/C cathode in ether-based electrolyte. In addition, the NVP/C cathode delivered excellent cyclic stability with capacity retention of over 88% at 50 mA g⁻¹ and a large reduction in charge transfer resistance after 1600 cycles. The comparison with the reported data on CEI layers for LIBs indicates that the electrochemical performance of the electrodes with a thin CEI tends to be marginally better than those with thicker CEI layers although further in-depth studies are required to confirm this preliminary observation. Overall, the understanding of electrode–electrolyte interfaces is of prime importance for rational design of advanced electrodes and electrolytes in rechargeable batteries. In particular, the direct visualization of these nanoscale interfaces in their native states can provide information related to the interfacial chemistries and nanostructures crucial to realizing the evolution of electrodes during reactions and their failure mechanisms.
4. Experimental Section

Synthesis of Na3V2(PO4)3 Powder: The NVP/C cathode was prepared using the hydrothermal method[46] with a modified inert environment for annealing from argon to nitrogen to reduce the overall cost. Specifically, 360 mg of vanadium pentoxide and 760 mg of oxalic acid were dissolved in 20 mL of deionized water and stirred vigorously at 70 °C for 1 h. A 940 mg of sodium phosphate dihydrate and 200 mg of glucose were added in the aforementioned mixture and stirred for 5 min. A 50 mL of n-propanol was added in the aforementioned solution under continuous stirring for 15 min followed by drying at 70 °C to obtain the NVP precursor. Finally, the precursor was preheated at 400 °C for 4 h followed by annealing at 750 °C for 8 h in nitrogen atmosphere at a temperature ramp of 5 °C min⁻¹ to obtain flower-shaped NVP/C powder.

Material Characterization: A powder X-ray diffractometer (XRD, PANalytical, X’pert Pro) with Cu Kα (λ = 1.54059 Å) radiation source was used to identify the phase structures. The structure and morphology of the NVP/C particles were examined on a scanning electron microscope (SEM, JEOL-6390) and a transmission electron microscope (TEM, JEM-2100F, JEOL). The energy-dispersive spectrometer (EDS, Bruker) was integrated with the aforementioned SEM for elemental mapping. The XPS was conducted on a PHI 5600 equipment (Physical Electronics) to probe the surface chemistry of NVP/C particles.

Electrochemical Characterization: The slurry of cathode was obtained by stirring of the mixture of NVP/C, Ketjen black (KB) carbon, and polypyrrolidene difluoride (PPyDF) binder at a mass ratio of 80:10:10 with N-methyl-2-pyrrolidone (NMP) solvent overnight, which was then cast on a carbon-coated Al foil using a doctor blade. The solvent was removed from the slurry after drying at 70 °C in a vacuum oven for 10 h and the electrodes were obtained by punching them into circular discs of 11 mm in diameter. The electrochemical performance of the electrodes was evaluated on a battery tester (LAND CT2001) using CR2032-type coin cells. The metallic Na discs were used as counter and reference electrodes. The polypropylene film (Celgard 2400) and 1 M NaCF2SO3 dissolved in DEGDMDE were used as separator and electrolyte, respectively. The GCD profiles of the assembled cells were acquired in a voltage window ranging 2.5–3.8 V (vs. Na/Na⁺) to maintain small polarization and reasonable stability of ether-based electrolytes.[42] The mass of NVP/C in the cathode was used to determine the capacities of the cells. The electrochemical workstation (CHI 660c, Shanghai ChenHua Instrument Co.) was used to acquire the CV curves of the cells at a scan rate of 0.2 mV s⁻¹ and the EIS spectra in the frequency range from 0.01 Hz to 100 kHz.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

cathode-electrolyte interface, cryogenic electron microscopy, sodium ion batteries, sodium metal batteries, sodium super ionic conductors

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