A Strategy to Make High Voltage LiCoO₂ Compatible with Polyethylene Oxide Electrolyte in All-Solid-State Lithium Ion Batteries

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Interface stability between cathode and electrolyte is closely related to the interface resistance and electrochemical performance of all-solid-state lithium ion batteries (LIBs). However, the significant interface issues between cathode and solid-state polymer electrolyte. The thorpy interface issues mainly refer to the inherent space charge layer and detrimental chemical reactions at the electrode and electrolyte interface, which lead to large interface impedance and then deteriorate the fast charging/discharging ability and cycling stability of all-solid-state LIBs.6–9

Polymer electrolyte-based all-solid-state lithium ion batteries (LIBs) with the merits of flexibility, high energy density and high safety have been researched for a long time.10–13 Nevertheless, their applications are still challenged by the interface issues between electrode and solid-state electrolyte. The thorpy interface issues mainly refer to the inherent space charge layer and detrimental chemical reactions at the electrode and electrolyte interface, which lead to large interface impedance and then deteriorate the fast charging/discharging ability and cycling stability of all-solid-state LIBs.6–9

Polyethylene oxide (PEO) electrolyte with high ion conductivity and good interface stability with Li metal has been successfully used in commercial polymer LIBs, in which the cathode material is LiFePO₄ instead of LiCoO₂. The failure application of PEO electrolyte in LiCoO₂-based high energy density LIBs is mainly due to the interface decomposition reactions of PEO at high voltage. Shiro Seki et al. have proposed that the oxidation decomposition of PEO electrolyte takes place from 4.0 V vs. Li/Li⁺, which leads to continuous increasing of LiCoO₂/PEO interfacial resistance and results in poor cycle performance at 4.4 V vs. Li/Li⁺.10 Moreover, during high voltage charging of LiCoO₂, the highly oxidized Co⁴⁺ ions will accelerate the oxidation decomposition of PEO electrolyte.11 It can be concluded that the cathode/polymer electrolyte interface characteristic is quite essential to the electrochemical performance of all-solid-state LIBs, especially for the high voltage cathode LiCoO₂ and PEO electrolyte. However, the interface oxidation decomposition products and reaction mechanism between LiCoO₂ and PEO electrolyte have not been studied clearly. Thus, there is still much work to do to understand and optimize the interface stability between the widely used cathode material LiCoO₂ and PEO electrolyte for high voltage (exceeding 4.4 V vs. Li/Li⁺) applications.

Surface coating of LiCoO₂ powder is a powerful strategy to enhance the interface stability with PEO electrolyte at high working potential. Generally, moderate amount of polymer electrolyte is added into the electrode to guarantee the three dimensional Li⁺ ion conductive pathways in polymer electrolyte-based all-solid-state LIBs. As a result, the LiCoO₂ active material contacts with PEO electrolyte not only on the cathode/electrolyte interface but also in the cathode itself. Some inorganic coating materials, such as Li₁₋ₓAlₓGeₓ(PO₄)₃, Li₅PO₄, and Al₂O₃, acting as an oxidation barrier for PEO electrolyte, have displayed significant improvement to the LiCoO₂/PEO interface at high voltage above 4.4 V vs. Li/Li⁺.10–13 But, element interdiffusion in the inorganic coating materials and LiCoO₂ interface is usually inevitable during high temperature sintering process. Moreover, the reported inorganic coating materials are fickle to remarkably improve the cycling stability of LiCoO₂/PEO/Li all-solid-state batteries. To overcome the above problems, the simple and low-temperature polymer coating seems to be a wise choice. Our group has demonstrated that the uniform and conformal poly(ethyl α-cyanoacrylate) (PECA) polymer coating layer on the surface of 5 V cathode LiNi₀.₅Mn₁.₅O₄ can be prepared by in-situ polymerization of poly(ethyl α-cyanoacrylate) (ECA) monomers in air at room temperature.14 Interestingly, the strong electron withdrawing group of -C≡N in PECA makes the coating layer have excellent properties, including high voltage window (5 V vs. Li/Li⁺), fast Li ion transport, blocking transition metallic ions, buffering electrolyte corrosion and particle cracks, et al. As a result, the PECA-coated LiNi₀.₅Mn₁.₅O₄ possesses significantly enhanced cycling stability in commercial liquid electrolyte. Therefore, the PECA coating layer with the strong electron withdrawing group of -C≡N and high voltage window is expected to suppress the oxidation decomposition of PEO electrolyte when it directly contacts with the high voltage LiCoO₂.

Here, we investigated the interface reaction and proposed a simple and effective strategy to enhance the interface stability between high voltage LiCoO₂ (4.45 V vs. Li/Li⁺) and solid PEO electrolyte by introducing the PECA buffer layer. We successfully constructed the PECA buffer layer on the LiCoO₂/PEO interface through a simple and low-temperature polymer coating method. The electrochemical performance of LiCoO₂/PEO/Li batteries before and after PECA modification was evaluated carefully. Furthermore, the modification mechanism of PECA buffer layer was proposed based on the comprehensive ex-situ measurements and density function theory (DFT) calculation results.

Experimental

Preparation of PEO electrolyte.—The rigid-flexible coupling cellulose-supported PEO solid-state electrolyte was synthesized by a method reported by our previous work.15 PEO (MW = 300,000, Alfa Aesar Company), lithium difluoro(oxalo)borate (LiDFOB, Alfa Aesar Company), and succinonitrile (SN, Aladdin Company), and acetonitrile (AN, Macklin Company) (10:1:9:120 by weight) were mixed and stirred in a sealed bottle for...
12 hours. Then, the liquid PEO electrolyte was casted onto both sides of cellulose membrane (Nippon Kodoshi Corporation) with doctor-blade and dried at 50°C for 12 hours. The obtained electrolyte was denoted as PEO-LiDFOB in the following text.

**Preparation of PECA-coated LiCoO₂**—First, ethyl cyanoacrylate (ECA, Sinopharm Chemical Reagent Co., Ltd.) was dissolved in acetone (AE, Sinopharm Chemical Reagent Co., Ltd.) solvent in a sealed vial with an inert atmosphere and stirred evenly. The weight ratio of ECA:AE is 1:3. Next, 2.0 g commercial LiCoO₂ (Contemporary Amperex Technology Co., Ltd.) powder was mixed with 0.163 g (2 wt%, relative to LiCoO₂) as-prepared solution and 6.0 g acetone and stirred vigorously under an Argon gas for 3 hours. Then the mixed solution was concentrated by rotary evaporation. Finally, the obtained PECA-coated LiCoO₂ powder was dried in a vacuum oven at 60°C for 3 hours to remove the residual acetone solvent completely.

**Characterizations.**—The X-ray diffraction (XRD) patterns of LiCoO₂ powders before and after PECA coating were obtained by using a Bruker-AXS Micro diffractometer (D8 Advance) with Cu-Kα radiation (λ = 1.5406 Å) from 10° to 80°. Transmission and reflection Fourier transform infrared spectroscopy (FTIR) spectra were carried out using a Bruker IFS 55 FTIR spectrometer in the wavenumber range of 400–4000 cm⁻¹. Raman spectra were recorded by a Renishaw inVia system with excitation from a He-Ne laser at 633 nm at ambient temperature. X-ray photoelectron spectroscopy (XPS) was obtained by using a focused monochromatized Al Kα radiation (1486.6 eV), Cls (284.8 eV) of contaminated carbon in the vacuum chamber was used to calibrate the binding energy. Energy dispersive X-ray spectrometer (EDS) was collected on a HITACHI S-4800 at an accelerating voltage of 15 kV. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images were performed with field emission scanning electron microscopy (FESEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL 2010F), respectively.

**Electrochemical measurements.**—To prepare LiCoO₂ cathode, the LiCoO₂ or PECA-coated LiCoO₂ powder, acetylene black (TIMCAL Ltd.), poly(vinylidene fluoride)-anhydride (PVDF-AD, Solvay Company), and PEO solution were added to a mortar at a ratio of 85:5:7:3 in weight and grinded for 1.5 hours with suitable N-methyl-2-pyrrolidone (NMP, Aladdin Company). Notably, the PEO solution (2 wt% of ECA) as-prepared solution and 6.0 g acetone in the Monkhorst-Pack scheme was sufficient in the energetic relaxation of surface structure. Herein, the Hubbard model corrections were used with an effective single U-J parameter of 4.9 eV for the Co-3d state, according to previously reports. In addition, the fully relaxed structure was considered completed when the magnitude of the force on each atom was smaller than 0.05 eV Å and a total energy convergence within 10⁻⁶ eV per unit cell in all calculation.

**Results and Discussion**

**Preparation of PECA-coated LiCoO₂ powder.**—Figure 1 compared the structure and morphology of LiCoO₂ powders before and after PECA coating by in-situ polymerization method. The XRD results in Figure 1a showed that the crystal structure of LiCoO₂ was retained after PECA coating. Both samples had hexagonal crystal structure and belonged to R-3m space group. In addition, no impurities were detected from the PECA-coated LiCoO₂. The SEM images in Figures 1b and 1c displayed that the PECA-coated LiCoO₂ had the same particle morphology and size with that of LiCoO₂. Their corresponding TEM images in Figures 1d–1g indicated an amorphous layer of about 50 nm coated uniformly on the surface of PECA-coated LiCoO₂. Furthermore, the mapping results in Figure 1h displayed the uniform distribution of Co and N elements on the surface of PECA-coated LiCoO₂, which suggested the successfully uniform coating of PECA on the surface of LiCoO₂.

To confirm the composition of PECA layer on the surface of LiCoO₂ and whether interaction occurred between PECA and LiCoO₂, FTIR, Raman and XPS measurements were conducted. Figures 2a and 2b showed the FTIR and Raman results of LiCoO₂, PECA-coated LiCoO₂ powders, and PECA, respectively. The FTIR peaks of these samples between 400 and 700 cm⁻¹ were attributed to the variations of CoO₆ octahedron, which were consistent with the Raman shifts at 482 cm⁻¹ and 595 cm⁻¹. These results suggested the structure of LiCoO₂ was not changed after PECA coating. In the FTIR spectrum, the sign of ECA monomers polymerized to PECA had disappeared at 3129 and 1615 cm⁻¹, which respectively corresponded to the functional groups of =CH and C≡C in ECA monomers. Here, compared with the FTIR spectrum of ECA monomer (Figure S1), the peaks appearing at 2241 cm⁻¹, 2238 cm⁻¹, and 2238 cm⁻¹ which respectively corresponded to the functional groups of =CH and C≡C in ECA monomers.

Electrochemical impedance spectroscopy (EIS) studies were carried out by applying a sine wave with an amplitude of 5 mV over the frequency range from 1.0 Hz to 4×10⁶ Hz on the Zahner Zennium electrochemical working station. The code Zview was used to fit the impedance spectra to the proposed equivalent circuit. The linear sweep voltammetry experiment of Li/PEO-LiDFOB/stainless steel (SS) coin cell was conducted at a scan rate of 1.0 mVs⁻¹ from the open circuit voltage (OCV) to 6.0 V vs. Li/Li⁺ at 80°C in order to test the stable electrochemical window of PEO-LiDFOB electrolyte. The peak current (AC) impendence method. The SS/PEO-LiDFOB/SS coin cell was tested from 30°C to 80°C with an amplitude of 5.0 mV over the frequency range from 0.1 Hz to 4×10⁶ Hz on the Zahner Zennium electrochemical working station. According to the formula of σ = L/(R · S), where σ (S/cm) was the thickness of electrolyte, L (cm) was the thickness of electrolyte, R (Ω) was the impedance, and S (cm²) was the contact area of electrolyte with the electrode, the ionic conductivity of PEO-LiDFOB electrolyte was calculated.
Figure 1. (a) XRD patterns of LiCoO₂ and PECA-coated LiCoO₂. Typical SEM images of (b) LiCoO₂ and (c) PECA-coated LiCoO₂. Typical TEM images of (d, e) LiCoO₂ and (f, g) PECA-coated LiCoO₂. (h) Typical SEM image and the corresponding Co and N element mapping results of PECA-coated LiCoO₂.

Figure 2. (a) FTIR, (b) Raman, and (c) XPS spectra of LiCoO₂, PECA-coated LiCoO₂, and PECA.
After PECA coating on the LiCoO₂ particles, the functional group C≡N (399.6 eV, N1s) displayed a little higher binding energy. However, the functional group C=O-O at about 533.1 eV, O1s) showed remarkably decreased relative intensity. As for LiCoO₂, the binding energy of lattice oxygen in LiCoO₂ (529.6 eV, O1s) shifted slightly to higher binding energy side in the XPS spectrum of PECA-coated LiCoO₂ (529.9 eV, O1s). Furthermore, the Co2p binding energy also increased slightly after PECA coating. The increased O1s and Co2p binding energy of PECA-coated LiCoO₂ further confirmed the decreased electron cloud density due to the interaction between lattice O²⁻ or Co³⁺ ions and the electron withdrawing groups of PECA, such as C≡O-O and C≡N. In addition, the O1s peak at 531.6 eV indicated the existence of Li₂CO₃, which was usually observed on the surface of layer-structured oxides. Li₂CO₃ remained on the surface of LiCoO₂ after PECA coating, as demonstrated by the broad and asymmetric O 1s peak at 532.4 eV.

Due to the above interaction between LiCoO₂ and PECA, the PEO electrolyte would not be oxidized easily by LiCoO₂ when the electron withdrawing buffer layer PECA was introduced. This conclusion was confirmed by the DFT calculation results (Figure S3). The first principles were employed to understand the reduction stability of PECA layer on the surface of LiCoO₂. The relatively stable LiCoO₂ (003) surface was investigated to discuss the LiCoO₂ coated by PECA modeling with 13 Å thick vacuum layers, which is shown in the Figure S2. Firstly, the projected density of states (PDOS) was discussed for evaluating surface property of LiCoO₂ (003). In addition, the corresponding PDOS for bulk LiCoO₂ were also shown. From the Figure S3, it was clear that the introduction of a surface affected the electronic structure of the bulk LiCoO₂ (bandgap 1.87 eV). These results were in agreement with the previously report. For example, the bandgap between the valance and conduction band would decrease in surface region, and it showed the metallic character. In addition, the exposed Li-O groups would easily react with the PEO electrolyte, which may induce the interface reaction during high voltage charging. Therefore, in our work, we established the interface model with the 2 × 2 LiCoO₂ (003) surface supercell and PECA, as shown in the Figure S3a. A relatively small interface supercell was chosen with a reasonable balance of computation cost. We mainly examined the effect of PECA coating layer on the LiCoO₂ surface electronic structure. The total PDOS can be calculated for interface structure (Figure S3b). After coated with PECA, the conduction band part of LiCoO₂ shifted toward higher energy obviously, and the valance band part shifted toward lower energy, which decreased the oxidation stability of LiCoO₂ surface. These results may indirectly suggest that the LiCoO₂ structure coated by PECA would improve the electrochemical stability with the PEO electrolyte.

**Preparation and evaluation of PEO-LiDFOB electrolyte.—** The cellulose-supported PEO-LiDFOB solid-state electrolyte was prepared by the method reported by our group previously. The morphology, electrochemical window, and ionic conductivity of the obtained cellulose-supported PEO-LiDFOB electrolyte were characterized and displayed in Figure 4. The SEM images showed that the PEO-LiDFOB electrolyte had smooth surface and a thickness of about 30 µm. The PEO electrolyte filled uniformly in the porous structure of cellulose, which formed the three dimensional-connected pathways for Li⁺ ions diffusion. The linear sweep voltammetry curve of Li/PEO-LiDFOB/SS coin cell under a scan rate of 1.0 mV/s at 80 °C indicated that the stable electrochemical window of PEO-LiDFOB electrolyte was about 4.2 V vs. Li/Li⁺. However, when the cutoff voltage was limited at 4.45 V vs. Li/Li⁺, almost identical FTIR spectra (Figure S4) of this solid-state polymer electrolyte before and after linear sweep voltammetry measurement was obtained. This may be due to the very little electrolyte decomposition during the linear sweep voltammetry measurement. The ionic conductivity of PEO-LiDFOB electrolyte from 30 °C to 80 °C was calculated based on the EIS measurement results (Figure S5). The linear temperature dependence of ionic conductivity for PEO-LiDFOB electrolyte was observed in the range of 30–80 °C. The ionic conductivity for PEO-LiDFOB electrolyte at 30 °C was 1.03 × 10⁻³ S/cm. When the temperature rose to 80 °C, the ionic conductivity increased to 8.95 × 10⁻² S/cm, which was similar to the reported PEO-based electrolytes. The interface compatibility between PEO-LiDFOB electrolyte and Li metal anode was also evaluated by the constant current polarization measurement in symmetric Li/PEO-LiDFOB/Li cell at 80 °C, as shown in Figure 4e. After charging and discharging sequentially under a constant current of 0.2 mA/cm² for 100 hours, the cell voltage remained nearly constant between 0.5 V and ~0.5 V vs. Li/Li⁺. No short circuit or remarkable polarization was observed. Furthermore, the SEM image of the Li metal anode after the constant current polarization measurement displayed uniform distribution of Li particles without Li dendrite formation. Therefore, the high ionic conductivity and high interface stability with Li metal anode made the prepared PEO-LiDFOB electrolyte competent to the following battery measurement between 2.5 V and 4.45 V vs. Li/Li⁺.

**Electrochemical measurements.—** The commercial LiCoO₂ powder as cathode material had stable cycling performance in liquid electrolyte (1M LiPF₆ in EC:DMC = 1:1 (v/v)) between 2.5 V and 4.45 V.
V vs. Li/Li$^+$, as shown in Figure S6. When the same LiCoO$_2$ cathode material was used in PEO-based all-solid-state LIBs, the electrochemical results indicated that the PECA-coated LiCoO$_2$ had higher discharge capacity, higher coulombic efficiency, and lower polarization than that of uncoated LiCoO$_2$ (Figure 5a). The initial discharge capacity for PECA-coated LiCoO$_2$ was 172.8 mAh/g, while that for bared LiCoO$_2$ was 144.5 mAh/g. Moreover, the capacity retention of PECA-coated LiCoO$_2$/PEO/Li cell was much better than the corresponding uncoated-LiCoO$_2$ cell (Figure 5b). To explore the reason of capacity fading in LiCoO$_2$/PEO-LiDFOB/Li cell and how PECA coating layer improved its electrochemical performance from the aspect of cathode/electrolyte interface, EIS of LiCoO$_2$/PEO-LiDFOB/Li and PECA-coated LiCoO$_2$/PEO-LiDFOB/Li cells at different cycle states were carried out. The results in Figures 5c–5d as well as Figure S7 and Table S1 showed the cycle number dependence of the impedance spectra for LiCoO$_2$/PEO-LiDFOB/Li and PECA-coated LiCoO$_2$/PEO-LiDFOB/Li cells, respectively. All the obtained plots were well fitted using the electric equivalent circuit shown in the inset of Figures 5c–5d. From the OCV state to the 20th discharge state, the bulk resistance ($R_b$) and interphase resistance ($R_i$) of LiCoO$_2$/PEO-LiDFOB/Li cell increased continuously. In a sharp contrast, the PECA-coated LiCoO$_2$/PEO-LiDFOB/Li cell showed less bulk and interphase resistance increase than that of LiCoO$_2$/PEO/Li cell from the OCV state to the 2nd discharge state. No obvious impedance increase was observed from the 2nd to the 20th discharge state. It indicated that the interface impedance of PECA-coated LiCoO$_2$/PEO-LiDFOB/Li cell was constant after two cycles charging and discharging. Furthermore, the $R_b$ remained less than 10 $\Omega$ during cycling. Therefore, it can be concluded that the enhanced electrochemical performance of PECA-coated LiCoO$_2$/PEO-LiDFOB/Li in high voltage range was
beneficial from the PECA coating layer on the surface of LiCoO$_2$, which can obviously suppress the interface impedance increase during cycling.

**Investigation on the interface reaction.**—To further explain the origin of the increased interphase impedance for LiCoO$_2$/PEO-LiDFOB/Li during cycling and the suppression effect of PECA coating layer on it, reflective FTIR spectra of LiCoO$_2$ cathode and PEO-LiDFOB electrolyte before and after 20 cycles were measured (Figure 6). Before FTIR measurement, the LiCoO$_2$ cathode and PEO-LiDFOB electrolyte were separated from each other manually. In the FTIR spectra of LiCoO$_2$ electrode and PEO-LiDFOB electrolyte withdrawn from the cycled LiCoO$_2$/PEO-LiDFOB/Li cell, the absorption peaks at 1794 and 1761 cm$^{-1}$ disappeared, while the peak at 1721 cm$^{-1}$ strengthened. According to the analyses of FTIR peak assignment in Figure S8 and Table S2, this result indicated the ring-opening reaction of DFOB$^-$ anion at high voltage. Moreover, the absorption peaks between 1000 cm$^{-1}$ and 1200 cm$^{-1}$ split obviously in the cycled LiCoO$_2$/PEO-LiDFOB/Li cell, suggesting the weaken interaction between PEO and LiDFOB after battery cycling, which may be caused by the decomposition of LiDFOB. On the contrary, the FTIR results of LiCoO$_2$ and PEO in the cycled PECA-coated LiCoO$_2$/PEO-LiDFOB/Li cell showed no obvious differences from that of the pristine PEO electrolyte. It means that the PECA coating...
can effectively suppress the ring-opening reaction of DFOB$^-$ anion at high voltage and guarantee the strong interaction between PEO and LiDFOB.

The decomposition of LiDFOB in LiCoO$_2$/PEO-LiDFOB/Li cell was also identified by the XPS results (Figure 7 and Figure S9). For the pristine PEO-LiDFOB electrolyte, the B1s peak at 192.0 eV, as well as the B1s peak at 193.4 eV and F1s peak at 686.1 eV, corresponded to B-O and B-F of LiDFOB, respectively. After 20 cycles charging and discharging, the relative intensity of B-O peak increased remarkably, but the F1s (B-F) peak changed barely. Xu et al. have reported that the ring opening process could reduce the symmetry and the coordinated number of B center and make the B1s peak shift to a lower binding energy. Thus, the increased relative intensity of B-O peak in PEO electrolyte from cycled LiCoO$_2$/PEO-LiDFOB/Li cell might be attributed to the ring opening process of LiDFOB. As for PEO electrolyte from the PECA-coated LiCoO$_2$/PEO-LiDFOB/Li cell, the relative intensity of B-F decreased while that of the B-O peak heightened much more than that of the uncoated sample. It can be attributed to the LiF (F1s, 685.4 eV) and F-C (F1s, 688.3 eV) species on the surface of PEO electrolyte. Moreover, a new B1s peak emerged at 192.8 eV, which was associated with the decomposition products of LiDFOB, such as Li$_x$BO$_y$F$_z$ species. Compared with the XPS results of PEO electrolyte from the LiCoO$_2$/PEO-LiDFOB/Li cell, these new species may be resulted from the interface reaction between LiDFOB and PECA.

According to the above analysis on FTIR and XPS results as well as the EIS results, it can be concluded that the compatibility between PEO-LiDFOB electrolyte and high voltage LiCoO$_2$ cathode was mainly influenced by the stability of Li salt LiDFOB instead of the PEO polymer. The PECA coating layer played an important role in enhancing the LiCoO$_2$/PEO-LiDFOB electrolyte interface stability. According to previous reports, LiDFOB was a general electrolyte additive in high voltage LIBs. Its DFOB$^-$ anions could oxidize to F$_2$BOC●O radical at 4.4 V vs. Li/Li$^+$, in which the boron strongly interacted with oxygen atoms in other molecules, such as carbonyl oxygen, ethers, and even bridging and nonbridging oxygens on the metal oxide surfaces. As a result, DFOB$^-$ anions formed oxidation-resistant (CO$_2$BF$_2$)$_2$ dimers on the cathode surface, which was believed to suppress the decomposition of liquid electrolyte catalyzed by transition metals. However, in all-solid-state LiCoO$_2$/PEO/Li batteries, the ring-opening reaction of DFOB$^-$ anions by breaking B-F bond was observed, suggesting the oxidation decomposition products of LiDFOB in all-solid-state electrolyte were different from that in liquid electrolyte. Furthermore, the XPS results demonstrated that the LiCoO$_2$/PEO-LiDFOB electrolyte interface reactions were different from that of PECA-coated LiCoO$_2$/PEO-LiDFOB electrolyte. Therefore, the increased interface impedance in LiCoO$_2$/PEO/Li cell may be related with the interface decomposition of LiDFOB. The ring-opening reaction products of DFOB$^-$ anions at high voltage decreased the interaction between Li salt and PEO, which may lead to decreased Li$^+$ conductivity and increased the interface impedance. During battery cycling, the decomposition products of DFOB$^-$ anions seemed to be instable and then resulted in continually increased interface impedance. When PECA coating layer separated the LiCoO$_2$ and PEO electrolyte, only trace amounts of DFOB$^-$ anions decomposed into LiF and F-C compound in the first several cycles. As PECA was a Li$^+$ conductor, Li$^+$ transfer between LiCoO$_2$ and PEO electrolyte was fluently. Therefore, the PECA coating was an effective way to suppress the interface impedance augment of LiCoO$_2$/PEO/Li cell by avoiding the continuous decomposition of LiDFOB and retaining the interaction between PEO and LiDFOB during high voltage cycling.

**Conclusions**

In conclusion, the interface stability between LiCoO$_2$ and PEO-LiDFOB electrolyte was challenged by high oxidation ability of LiCoO$_2$, the decomposition of LiDFOB, and the weak interaction between PEO and LiDFOB. As a result, the LiCoO$_2$/PEO-LiDFOB/Li cell showed continuous interface impedance increase and poor cycle performance. PECA coating on the surface of LiCoO$_2$ was an effective method to improve the interface stability between high voltage LiCoO$_2$ and PEO-LiDFOB electrolyte. The FTIR, XPS, and
electrochemical measurement results as well as the DFT calculation results indicated that the PECA coating decreased the oxidation ability of LiCoO$_2$, suppressed the decomposition of LiDFOB, and remained the interaction between PEO and LiDFOB during high voltage cycling. Thus, compared with the LiCoO$_2$/PEO-LiDFOB/Li cell, the PECA-coated LiCoO$_2$/PEO-LiDFOB/Li cell displayed decreased inhibition in energy conversion. The authors declare no competing financial interest.

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