**Dynamic reversible evolution of solid electrolyte interface in nonflammable triethyl phosphate (TEP) electrolyte enabling safe and stable potassium-ion batteries**

Shunping Ji, Jielei Li, Junfeng Li, Chunyan Song, Shuo Wang, Kexuan Wang, Kwan San Hui\*, Chenyang Zha, Yunshan Zheng, Duc Anh Dinh, Shi Chen\*, Jintao Zhang, Wenjie Mai, Zikang Tang, Zongping Shao\*, and Kwun Nam Hui\*

S. P. Ji, J. L. Li, J. F. Li, K. X. Wang, S. Wang, C.Y. Zha, Y. S. Zheng, Prof. S. Chen, Prof. Z. K. Tang, Prof. K. N. Hui

Joint Key Laboratory of the Ministry of Education, Institute of Applied Physics and Materials Engineering, University of Macau, Avenida da Universidade, Taipa, Macau SAR, P.R. China

E-mail: [bizhui@um.edu.mo](mailto:bizhui@um.edu.mo); shichen@um.edu.mo

C. Y. Song

Analysis and Testing Center, Shenzhen Technology University, Shenzhen 518118, China

Prof. K. S. Hui

School of Engineering, Faculty of Science, University of East Anglia, Norwich, NR4 7TJ, United Kingdom

E-mail: [k.hui@uea.ac.uk](mailto:k.hui@uea.ac.uk)

Prof. D. A. Dinh

NTT Hi-Tech Institute, Nguyen Tat Thanh University, Ho Chi Minh City 700000, Vietnam

Prof. J. T. Zhang

Key Laboratory for Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

Prof. W. J. Mai

Siyuan Laboratory, Guangdong Provincial Engineering Technology Research Center of Vacuum Coating Technologies and New Energy Materials, Department of Physics, Jinan University, Guangzhou 510632, Guangdong, China

Prof. Z. P. Shao

WA School of Mines: Minerals, Energy and Chemical Engineering (WASM-MECE), Curtin University, Perth, WA 6845, Australia

E-mail: [zongping.shao@curtin.edu.au](mailto:zongping.shao@curtin.edu.au)

**Keywords:** zinc phosphide, triethyl phosphate, solid electrolyte interface, non-flammable electrolyte, potassium-ion batteries

Potassium-ion batteries (PIBs) are a favorable alternative to lithium-ion batteries (LIBs) for the large-scale electrochemical storage of renewable energy because of their cost-effectiveness that stems from the high natural abundance of potassium resources. However, conventional PIB electrodes usually exhibit actual capacities that are considerably lower than their theoretical capacities and poor cyclic stability due to the large radius of potassium ions (1.39 Å). These characteristics seriously inhibit the practical use of PIB electrodes. In addition, the high reactivity and low melting point (63.4 °C) of potassium metal raise serious safety concerns. Here, zinc phosphide composites with high actual specific capacities are rationally designed as new conversion-type PIB anodes for operation in a nonflammable triethyl phosphate (TEP) electrolyte to solve the above-mentioned issues. The optimized zinc phosphide composite with 20 wt% zinc phosphate (ZnP2@ZPO[20]) presented high actual specific capacity (571.1 mA h g−1 at 0.1 A g−1) and excellent cycling performance (484.9 mA h g−1 with the capacity retention of 94.5% after 1000 cycles at 0.5 A g−1) in KFSI-TEP electrolyte. XPS depth profile analysis showed that the improved cycling stability of the composite was closely related to the reversible dynamic evolutions and conversions of the sulfur-containing species in the solid electrolyte interphase (SEI) during the charge/discharge process. This dynamic reversible SEI concept may provide a new strategy for the design of superior electrodes for PIBs.

**Introduction**

Lithium-ion batteries (LIBs) are widely used in many aspects of our daily life. However, their development and application on a larger scale will be inevitably restricted by the scarcity and uneven global distribution of lithium resources.[1] By contrast, sodium and potassium resources are highly abundant and evenly distributed around the world and thus benefit the development of low-cost sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs).[2] In addition, the standard redox potential of the potassium ion is closest to that of the lithium ion (−2.93 V for K+/K vs −3.04 V for Li+/Li) and is lower than that of the sodium ion (−2.70 V), furthermore, K+ has the smaller Stoke radii in aqueous and organic solutions than that of Li+, Na+, and Mg2+, all these features give PIBs higher energy density and faster K-ion diffusion rate in the electrolyte than those of sodium-ion batteries.[3] Graphite is commercially used in LIBs; however, when it is used as a PIB anode, its theoretical capacity is only 279 mA h g−1 after forming the KC8 phase, which is even lower than the theoretical capacity of LIBs (372 mA h g−1).[4] Therefore, exploring high-capacity PIB anodes is crucial for achieving high energy density of PIBs, thus far, numerous noncarbon anodes have been investigated, including metals and alloys[5], transition-metal chalcogenides[6], and organic materials[7]. In comparison, metal phosphides have attracted considerably more attention than other noncarbon anodes because of their high specific capacity and relatively low discharge platforms.[8] Our recent work is the first to provide an experimental report on the application of conversion-type zinc phosphides as PIB anodes with high theoretical capacity (1262 mA h g−1) but large volume expansion/contraction during the charge/discharge process.[9] Metal oxides have been proposed and used as the starting materials for the formation of in situ amorphous metal phosphate matrixes to buffer volume expansion and relieve the massive volume expansion of metal phosphides. Although such a strategy has been proven to be effective, it introduces large amounts of inactive components that inevitably reduce specific capacity. Therefore, controllably adjusting the proportion of inactive components is the key to obtaining high specific capacity while maintaining cycling stability.

In addition to capacity, PIBs face the same or even more serious safety problems as LIBs that are based on routine organic carbonate ester or ether electrolyte systems because of the low melting point (63.4 °C) and high reactivity of potassium metal. Many strategies, including aqueous solution systems[10], nonflammable organic electrolytes[11], and all solid-state electrolytes[12], have been extensively implemented and studied to reduce the safety risk of metal-ion batteries. In sharp contrast to reports on all solid-state LIBs, reports on all solid-state PIBs are few in number because the poor solid–solid interface affinity and the large potassium-ion radius (1.39 Å) in PIBs increase interfacial impedance and severely reduce ionic conductivity in the solid electrolyte.[13] In addition, although aqueous solution systems offer low interfacial impedance, high ionic conductivity, and high safety, the low redox potential of aqueous solutions seriously reduces energy density.[14] High concentrations of “water-in-salt” electrolytes can improve the stability of electrodes and expand the electrochemical window but also significantly increase the cost of batteries.[15] Developing nonflammable organic solvents as electrolytes for safe PIBs appears to be a feasible strategy because the solvation effect of potassium ions is weaker than that of lithium and sodium ions. Specifically, a moderately concentrated organic phosphate-based electrolyte has shown excellent cycling stability for the graphite anode of PIBs.[16] Meanwhile, this electrolyte system has also demonstrated good electrochemical stability for a high-voltage potassium-ion cathode (K0.5MnO2).[17] Nonetheless, the research on nonflammable electrolyte for PIBs still remains in its infancy, especially for the system of conversion-type mechanism anodes with high specific capacity and huge volume expansion. An in-depth understanding of the corresponding evolution of the solid electrolyte interphase (SEI) in nonflammable organic solvents is important for designing favorable electrodes for safe PIBs. However, such an understanding remains unclear.

Here, we report the development of superior zinc phosphide composites for operation in triethyl phosphate (TEP)-based nonflammable organic electrolytes that deliver outstanding reversible capacity and superior cycling stability. The reversible evolution of sulfur-containing species in the SEI during the charge/discharge process of the zinc phosphide composites when used as PIB anodes in the nonflammable TEP electrolyte was revealed. This phenomenon helped stabilize the electrode. Thus, excellent cycling stability in the TEP-based electrolyte was achieved. Meanwhile, the balance between high actual capacity and good cycling stability was reached by controlling the mass fraction of zinc phosphate on the basis of the ratios of the Zn, ZnO, and P raw materials. We believe that our present work is beneficial for deepening the understanding of stable SEIs and will advance the study and practical application of high-capacity and safe PIBs.

**2. Results and discussion**

In our recent work, we demonstrated that metal phosphides prepared by using metal oxides exhibit enhanced cycling stability in ethylene carbonate/diethyl carbonate (EC/DEC)-based electrolyte.[9] Zinc phosphate is inactive to K-ion in nature, and pure ZnO, when used as the raw material at the molar ratio of ZnO to P of 2:3, introduced the maximum mass percentage of zinc phosphate of 37.7 wt%, which would reduce the theoretical specific capacities of the zinc phosphide composites. Therefore, we optimized the content of zinc phosphate by controlling the proportion of Zn, ZnO, and P raw materials to keep a balance between the cycling stability and high specific capacity of zinc phosphide. The schematic of the preparation process is shown in the **Figure 1**a. The two reactions involved are:

Zn + 2P = ZnP2 (1)

8ZnO + 12P = 5ZnP2 + Zn3(PO­4)2 (2)

The three zinc phosphide composites with zinc phosphate contents of 10, 20, and 30 wt% were labelled as ZnP2@ZPO(10)without C, ZnP2@ZPO(20)without C, and ZnP2@ZPO(30)without C, respectively, and were designed and prepared via one-step ball milling in accordance with reactions (1) and (2). The calculated mass fractions of zinc phosphate determined through thermogravimetric analysis (TGA) were 21.3, 31.3 and 43.1 wt%, respectively. All the calculated values exceeded the theoretical values because of the volatilization of phosphorus oxide generated by heating ZnP2 during TGA (Figure S1a). The burned product of ZnP2@ZPO(20)without C was analyzed by XRD to confirm this claim, and the Zn2P2O7 phase due to the sublimation of P2O5 was detected (Figure S1b). The pure α-ZnP2 phase (JCPDS no. 72-1626) was detected in all three samples (Figure 1b).[18] Meanwhile, as expected, no diffraction peaks belonging to amorphous zinc phosphate were detected due to the amorphous states. In addition, to enhance the electronic conductivity of zinc phosphide composites for improved battery performance, the zinc phosphide composites ZnP2@ZPO(10), ZnP2@ZPO(20), and ZnP2@ZPO(30) with carbon were prepared by directly adding Super P to the stoichiometric Zn, ZnO and P raw materials, respectively. The addition of carbon was confirmed qualitatively on the basis of Raman spectra (Figure S2) and quantified by TGA (Figure S1c). The calculated mass fractions of carbon for ZnP2@ZPO(10), ZnP2@ZPO(20), and ZnP2@ZPO(30) samples were 31.9, 29.5 and 29.6 wt%, respectively, which all are close to the designed value of 30.0 wt%. The XRD patterns showed that the diffraction peak intensity of zinc phosphide decreased monotonously with the increase of zinc phosphate after the addition of carbon (Figure 1c). These results indicated that the amorphization of zinc phosphide increased with the increase in the proportion of zinc phosphate and carbon and were consistent with our previous findings, which were obtained by using pure ZnO to prepare completely amorphous zinc phosphide.[9] As shown in Figure 1d–i, a high-resolution transmission electron microscope (HRTEM) was also employed to confirm the existence of zinc phosphide. In ZnP2@ZPO(10) (Figure 1d), the measured interplanar spacings of 0.284 and 0.204 nm matched with the (114) and (214) lattice planes of ZnP2 phase, respectively. In the ZnP2@ZPO(20) (Figure 1e) and ZnP2@ZPO(30) (Figure 1f) samples, the interatomic distances of 0.343 nm stand for the (104) facet of ZnP2 phase. All the results were confirmed by their corresponding fast Fourier-transform (FFT) patterns and were consistent with the XRD data. In addition, the presence of a large amount of amorphous components in the ZnP2@ZPO(30) sample was confirmed on the basis of HRTEM images as shown in Figure S3. And the absence of polycrystalline diffraction rings and any diffraction spots in the electron diffraction (ED) pattern verified the amorphous composition of the composite. Although all samples showed an uneven size distribution that ranged from tens of nanometers to tens of micrometers due to the agglomeration of nanoparticles with high specific surface energy (Figure S4), the TEM elemental mappings illustrated that all P, Zn, O, and C elements were evenly distributed in three samples (Figure 1g, 1h and 1i).[19] The presence of amorphous phosphate in three samples was confirmed through Fourier-transform infrared spectroscopy (FTIR) as shown in Figure S5. As for crystalline zinc phosphate (C-Zn3(PO4)2), some obviously split vibration peaks attributed to the phosphate group were found in the range of 900-1300 cm–1, whereas a broad peak without any splitting was observed in this range for amorphous zinc phosphate (A-Zn3(PO4)2).[20] A non-split broad vibration peak that was similar to that for A-Zn3(PO4)2 indicated the existence of amorphous phosphates in the three samples. This result was consistent with the XRD and TEM data of the three samples. The bonding information of all elements, including C, P, O, and Zn, was analyzed by X-ray photoelectron spectroscopy (XPS) as illustrated in Figure 1j. The high resolution C1s spectra showed obvious *sp*2(C=C/C-C, 284.2-284.3 eV) and *sp*3(C-C, 285.1-285.3 eV) peaks belonging to the added Super P in all three samples.[21] The P-Zn (2*p*3/2, 129.7 eV) and P-Zn (2*p*1/2, 130.7 eV) bonds in the P2p spectra confirmed the presence of ZnP2. The PO43– peaks (133.3 eV) assigned to zinc phosphate were also be observed, and correspondingly, O=P/P–O–P (533.2 eV) andP–O− (531.6 eV) bonds were found in the XPS spectra of O1s. Zn2p3/2 (1022.4 eV) and Zn2p1/2 (1045.5 eV) reflected the positive zinc ions in zinc phosphide and zinc phosphate.[22]

Potassium-ion half cells were assembled to verify the potassium-ion storage performance for the optimized zinc phosphide composites. **Figure 2**a shows the rate performance and subsequent cyclic stability at 0.1 A g–1 in EC/DEC (v:v =1:1) electrolytes (1.0 M KFSI). The results proved that the capacity and cycling stability of zinc phosphide composites indeed varied with the zinc phosphate content. The specific capacities for all samples were calculated based on the total mass of ZnP2 and zinc phosphate, except for carbon (according to the experimental results, Super P contributes approximately 45 mA h g–1 as shown in Figure S6). As expected, the capacity decreased with the increase in zinc phosphate content, and the ZnP2@ZPO(10), ZnP2@ZPO(20), and ZnP2@ZPO(30) electrodes showed first reversible charge capacities of 595.0, 566.1, and 433.0 mA h g–1 with corresponding initial Coulombic efficiencies (ICEs) of 75, 74, and 71%, respectively, at the current density of 0.05 A g–1 (Figure S7), and delivered the highest capacities of 657.7, 608.9 and 469.3 mA h g–1, respectively, at a current density of 0.1 A g–1 in the EC/DEC-based electrolyte. The cycling performance of the electrodes, especially for ZnP2@ZPO(30) electrode, tended to stabilize with the increase in the amount of zinc phosphate introduced, and their retained capacities were 135.1, 364.4 and 457.6 mA h g–1 after 300 cycles at 0.1 A g–1 (Figure S8). However, the average CEs durinng cycling at 0.1 A g–1 were below 99.5% for all three electrodes in the EC/DEC-based electrolyte. The electrochemical performance of three electrodes were investigated in the TEP-based electrolyte (2.0 M KFSI in TEP) to verify the feasibility of applying the metal phosphide-based materials as the anodes of PIBs coupled with the noninflammable electrolyte. In contrast to common combustible EC and DEC solvents, TEP solvent is naturally noninflammable and could not be ignited even when exposed to an open fire as shown in Figure 2b. This characteristic can indubitably significantly improve battery safety. The rate capability and cycling performance (at 0.1 A g–1) of all the three electrodes in the TEP-based electrolyte are provided in Figure 2c. Similar to those in the EC/DEC-based electrolyte, the average specific capacities of the three electrodes in the TEP-based electrolyte decreased with the increase in inactive zinc phosphate content at different current densities (Figure S9). Among the electrodes, ZnP2@ZPO(10) delivered the highest average reversible discharge capacities of 465.4, 432.8, 402.1, 274.9, 183.6 mA h g–1 at the current densities of 0.05, 0.1, 0.2, 0.5, 1.0 A g–1, respectively. These values were even higher than the average reversible discharge capacities of pure ZnP2. Relatively, the poorer rate performce in the TEP-based electrolyte than that in the EC/DEC-based electrolyte can be attributed to the lower ion conductivity (~ 3.0 mS cm-1) and higher viscosity of 2.0 M KFSI/TEP electrolyte used (Figure S10).[16a] Although the ZnP2@ZPO(10), ZnP2@ZPO(20), and ZnP2@ZPO(30) electrodes presented low first charge/discharge capacities of 479.8/661.1, 450.5/656.1, and 442.0/706.7 mA h g−1, respectively, with the corresponding ICEs of 73%, 69%, and 63%, respectively, at the current density of 0.05 A g−1 (Figure 2d), the reversible discharge capacities of all of the three electrodes recovered to values that were even higher than their initial values at 0.1 A g–1 when the current density was returned to 0.1 A g−1. The ZnP2@ZPO(10), ZnP2@ZPO(20), and ZnP2@ZPO(30) electrodes had maximum specific capacities (Cmax) that reached 640.7, 571.1, and 451.9 mA h g−1, respectively, and the retained capacities of 586.7, 536.1, and 438.4 mA h g–1, respectively, after another 600 cycles at 0.1 A g−1 (Figure S11). In contrast to those in the EC/DEC-based electrolyte, the average CEs of the three electrodes in the TEP-based electrolyte were all above 99.5% after 300 cycles at 0.1 A g–1. These results were suggestive of good cycling stability. The analysis of differential capacity of the ZnP2@ZPO(10) electrode can partly explain the increase in capacity (Figure 2e). With the increase in cycles, potassiation/depotassiation peaks shifted, the two most obvious oxidation peaks (O1 and O2,depotassiation)moved toward the low potential, and the corresponding depotassiation voltages declined from 0.32V (O1), 0.93V (O2) to 0.26 V (O1), 0.71 V (O2), and stabilized after approximately 100 cycles. Similarly, the cyclic voltammetry (CV) curves also showed the same trends wherein the anodic peaks shifted to low potential in the initial cycles (Figure S12). Obviously, all these results indicated the remarkable polarization and activization effect of the electrodes.[23] With the increase in cycles, the utilization rate of the active materials increased due to the activization effect, resulting in the improvement of capacity. The polarization and activation effect of the electrodes appeared to be highly obvious at a high current density as shown in Figure 2f. At 0.5 A g–1, the capacities of the ZnP2@ZPO(10), ZnP2@ZPO(20), and ZnP2@ZPO(30) electrodes increased from initial 267.7, 224.4 and 194.3 mA h g–1 to the Cmax values of 543.6, 513.2 and 379.4 mA h g–1, respectively, and after 1000 cycles, the remaining capacities (C1000th) were 437.9, 484.9, 379.4 mA h g–1 with the capacity retentions of 80.6%, 94.5%, and 100%, respectively, (calculated on the basis of [C1000th/Cmax]\*100%). In particular, the CE of the ZnP2@ZPO(10) electrode declined obviously after over 400 cycles at 0.5 A g–1. By comparison, the ZnP2@ZPO(20) electrode exhibited high capacity and acceptable cycling stability (Figure 2g). Our composites showed higher capacity and cycling stability than the recently reported noncarbon anodes for PIBs (Figure 2h).

Potassium metal and the target electrodes (zinc phosphide composites) were analyzed to disclose the source of the activation process and the enhancement in cycling performance. First, as shown in Figure 2i, the symmetric K/K cells were assembled and tested in the TEP electrolyte, at the current density of 0.5 mA cm–2. Similar to those in a previous report, the symmetric K/K cells in this study exhibited excellent long-term stability for potassium metal plating and stripping in TEP electrolyte.[16a] However, during 3000 h of the deposition and dissolution of the potassium metal electrodes, the overpotential decreased from the initial ~0.34 V (10 h) to ~0.14 V. Meanwhile, AC impedance analysis also confirmed the activation of potassium metal electrodes, and the corresponding impedance decreased with plating/stripping cycles (Figure S13). By contrast, such a phenomenon was not obvious in the EC/DEC-based electrolyte, and the corresponding symmetric cell was short-circuited in less than 400 h. The results demonstrated that the potassium metal electrode can also be activated in the TEP electrolyte. The AC impedance analysis of the target ZnP2@ZPO(20) electrode indicated that its charge transfer impedance (Rct) decreased from 1131 Ω (fifth cycle) to 348.6 Ω (100th cycle), and the impedance caused by formed SEI (RSEI) also decreased from 38.5 Ω (fifth cycle) to 12.3 Ω (100th cycle) (Figure 2j and S14). In addition, the potassium-ion diffusion coefficient of ZnP2@ZPO(20) electrode after different cycles (fifth , 35th , and 80th) was analyzed by using galvanostatic intermittent titration technique (GITT) to confirm the activation process of electrode after cycling (Figure S15). The potassium-ion diffusion coefficient of the ZnP2@ZPO(20) electrode was found to have increased with the cycling. When an electrode is activated during cycling, as often occurs on the electrode surface due to the activation of the interface, the activation energy of ion diffusion is reduced and results in a high ion diffusion rate. Obviously, the activation of the electrode results in the increase in the utilization rate of the active materials. This increase is intuitively embodied by the increase in capacity and ion diffusion rate as observed in this work. Therefore, the increased potassium-ion diffusion coefficient of the ZnP2@ZPO(20) electrode with cycles can suggest the activation of the electrode.[4] Therefore, all of the above results verify that the increase in capacity is due to the activation of electrodes during the charging/discharging process.

We focused on the formation and evolution of SEI by charging/discharging ZnP2@ZPO(20) electrodes to different states (**Figure 3**a) and investigated the SEI through etching XPS analysis to understand further the improvement in the cycling performance of electrodes in the TEP-based electrolyte over that in the EC/DEC-based electrolyte. All XPS samples were prepared in a glove box and transferred into a special chamber under an argon atmosphere without exposure to the air to reduce contamination (Figure S16). XPS spectra were collected after different etching time (0, 30, 60s, 120, 360, 600, 1200, and 3600 s). As shown in Figure 3b, the significant changes in the C 1s spectra of the electrode surface after the first discharge (potassiation) from the open-circuit voltage to 0.01 V in the TEP-based electrolyte indicated that some carbon-based species with high oxidation states, including C–O (~286.3 eV), C=O (~288.2 eV), CO32− (~289.8 eV), and C–F (~291.2 eV), were formed likely through the oxidation and decomposition of the electrolyte.[24] During electrode charging, the oxidized carbon-based species on the surface decreased gradually (Figure 3c). Almost the same process of the repeated formation and degradation of the SEI of the carbon-based species was observed during the second discharge/charge process (Figure S17), showing that the SEI of the carbon-based species was unstable as had been confirmed in previous reports.[25] As shown in Figure 3d, the highly obvious CO32– (~289.8 eV) peaks even after 3600 s of etching were indicative of the considerably higher number of oxidized carbon-based species in the EC/DEC-based electrolyte system than in the TEP-based electrolyte system during discharging to 0.01 V. These findings can be ascribed to the more serious decomposition of EC and DEC than that of TEP. The lower LUMO energy levels of EC and DEC than those of the TEP solvent facilitated reduction for SEI formation during discharging.[16a, 24c, 26] Obviously, the excessive consumption of electrolytes was not conducive to the long-term cycle of the battery; this effect can partly explain the poor cycling stability of the half cell and symmetric cells in the EC/DEC electrolyte. In addition to the carbon-based species in the SEI, F1s spectra showed the presence of high amounts of inorganic fluorides (~684.5 eV) that were produced through KFSI decomposition in the EC/DEC and TEP-based electrolytes when discharging to 0.01V (Figure 3e, S18). The inorganic fluorides obviously showed better stability than the carbon-based compounds; moreover, considerable amounts of fluorides were also detected in the SEI of the EC/DEC and TEP-based electrolytes even after charging to 3.0 V (Figure 3f, S19).[25c] In contrast to the other elements detected in the SEI, including K2p, O1s, Zn2p, and P2p (Figure S20–27), which showed little differences in TEP and EC/DEC electrolytes, the S2p spectra presented a significant difference. In the TEP-based electrolyte, several sulfur-containing species with different valence states, including SON– (2p1/2/2p3/2: ~171.9/170.7 eV), SO42– (2p1/2/2p3/2:~170.8/169.6 eV), SO32– (2p1/2/2p3/2: ~168.2/167.0 eV), S0 (2p1/2/2p3/2: ~165.8/164.6 eV), S– (2p1/2/2p3/2: ~163.7/162.5 eV), and S2– (2p1/2/2p3/2: ~161.2/160.0 eV), were detected during discharging, these species were completely generated by the decomposition of KFSI (**Figure 4**a, S28).[16a, 27] These sulfur-containing compounds varied with charging/discharging states and etching depths. In particular, during the first discharging process, S2– species gradually formed and were detected, and then these S2– species decreased until they disappeared completely during charging to 3.0 V due to oxidation. During the second discharge/charge process, the S2– species reappeared and disappeared; these phenomena were accompanied by the variation of S0 and S– species, which have yet to be found and reported.[24c, 28] By contrast, the contents of sulfur-containing compounds in the EC/DEC-based system were obviously much low when first discharging to 0.01V (Figure 4b), whereas much more sulfur-containing compounds can be detected when charging to 3.0V, and these sulfur-containing species reduced again at second discharging to 0.01V. Such changes indicated that some evolving sulfur-containing species in the EC/DEC system were unstable during discharging. Therefore, by comparison, sulfur-containing species showed higher stability in the TEP-based electrolyte than in the EC/DEC system. Moreover, some reversible conversions of sulfur-containing species, especially S0, S– and S2– species, occurred at different charging/discharging states and etching depths in the TEP-based electrolyte (Figure 4c). The reversible transformation of sulfur-containing species in the TEP-based electrolyte is more beneficial to stabilizing SEI and decreasing electrolyte consumption than the repeated formation and degradation processes in the EC/DEC-based electrolyte.[29] The sulfur-containing species in the SEI were detected and analyzed after 1000 cycles (0.5 A g−1) to confirm the stability of the SEI. The results showed that a large number of sulfur-containing species continued to exist (Figure 5a). In addition, relative to the fresh electrode, the electrode that had undergone 1000 cycles exhibited obvious surface coating, which confirmed the existence of SEI (Figure 5b–e). TEM analysis showed that the average thickness of the SEI exceeded 20 nm (Figure 5f), indicating that the thick SEI showed excellent ionic conductivity, and the ED pattern showed that the SEI film was dominated by amorphous components (Figure 5g); these characteristics can partially account for the excellent potassium-ion conductivity of the electrode.[30] Although the sulfur-containing species formed by the TEP-based electrolyte showed conversion or change during charging and discharging as illustrated in Figure 5h, the battery still showed excellent cycling performance; this result differed from the routine viewpoint that an unchangeable SEI should be designed to improve cyclic stability.[31] Our results indicated that a dynamic reversible SEI could also play a critical role in enhancing the cycling performance of an electrode.

Full cells were then assembled to demonstrate the feasibility of ZnP2@ZPO(20) electrode in practical devices, and organic perylenetetracarboxylic dianhydride (PTCDA) was selected as the cathode, as shown in **Figure 6**a. PTCDA was commercially purchased, and its XRD pattern and electrochemical performance in the PIB half cell were analyzed before it was used in the full cell (Figure S29). The PTCDA without any pre-treatment showed a good cycling stability in the PIB half cells in the TEP-based electrolyte and delivered the reversible specific capacity of 73.6 mA h g−1 (100 mA g−1) after 200 cycles (Figure S29d).[7b, 32] The activated ZnP2@ZPO(20) electrodes were used to assemble full cells with fresh PTCDA electrodes. The galvanostatic discharge–charge curves of the half cell and full cell are compared in Figure 6b, which showed an average discharge platform of ~1.5 V for the full cell. In addition, the specific capacity of the full cell was controlled and calculated on the basis of the PTCDA. The CV curves of the full cell showed multiple cathodic and anodic peaks within the voltage range of 0.5–3.2 V at the scan rate of 0.2 mV s−1, which reflected the different potassiation depths of PTCDA (Figure 6c). Figure 6d shows the rate performance of the full cell, which delivered the average discharge capacities of 124.8, 84.6, 61.1, 49.9 mA h g−1 at the current densities of 20, 50, 100, 200 mA g−1, respectively. In addition, the full cell presented good cycling stability, specifically, it retained a discharge capacity of 65.6 mA h g−1 after 200 cycles (0.1 mA g−1) (Figure 6e). The full cell can power an electric fan (1.0 W) (Figure 6f). This results confirmed the practicability of the ZnP2 composite in nonflammable TEP electrolytes.

**Conclusion**

Zinc phosphide composites with high capacity and good cycling stability were optimized and prepared by controlling the ratio of the Zn, ZnO and P raw materials and used in noninflammable TEP-based electrolyte. All the zinc phosphide composites showed better electrochemical performance in the noninflammable TEP-based electrolyte than the conventional EC/DEC-based electrolyte. In particular, the ZnP2@ZPO(20) composite demonstrated high actual specific capacity (571.1 mA h g−1 at 0.1 A g−1) and excellent cycling stability (capacity retention of 94.5% after 1000 cycles at 0.5 A g−1). Investigating the SEI through XPS depth profile analysis revealed a large number of sulfur-containing species in the SEI that were due to the decomposition of KFSI. These sulfur-containing species evolved and transformed reversibly in the TEP-based electrolyte with the charge/discharge process instead of undergoing repeated formation and degradation in the EC/DEC-based electrolyte. Such a reversible SEI contributed to the improved cyclic stability of the electrode. Our results provide an experimental reference for understanding and designing a next generation SEI or solid electrolyte with dynamic stability that can broaden our horizons for finding a reliable SEI or solid-state electrolyte.

**Supporting Information**

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

**Acknowledgements**

S. J. and J. L. contributed equally to this work. This work was funded by the Science and Technology Development Fund, Macau SAR (File no. 0191/2017/A3, 0041/2019/A1, 0046/2019/AFJ, 0021/2019/AIR), University of Macau (File no. MYRG2017-00216-FST, MYRG2018-00192-IAPME, MYRG2020-00187-IAPME) and the UEA funding.

**Conflict of Interest**

The authors declare no conflict of interest.

**References**

[1] a) A. Battistel, M. S. Palagonia, D. Brogioli, F. La Mantia, R. Trocoli, *Adv. Mater.* **2020**, DOI: 10.1002/adma.2019054401905440; b) B. Dunn, H. Kamath, J. M. Tarascon, *Science* **2011**, 334, 928.

[2] T. Hosaka, K. Kubota, A. S. Hameed, S. Komaba, *Chem. Rev.* **2020**, 120, 6358.

[3] M. Okoshi, Y. Yamada, S. Komaba, A. Yamada, H. Nakai, *J. Electrochem. Soc.* **2017**, 164, A54.

[4] L. Fan, R. Ma, Q. Zhang, X. Jia, B. Lu, *Angew. Chem. Int. Ed.* **2019**, 58, 10500.

[5] a) H. Yang, R. Xu, Y. Yao, S. Ye, X. Zhou, Y. Yu, *Adv. Funct. Mater.* **2019**, 29, 1809195; b) K. Cao, H. Liu, Y. Jia, Z. Zhang, Y. Jiang, X. Liu, K. J. Huang, L. Jiao, *Adv. Mater. Technol.* **2020**, 5, 2000199; c) L. Zhou, Z. Cao, J. Zhang, H. Cheng, G. Liu, G. T. Park, L. Cavallo, L. Wang, H. N. Alshareef, Y. K. Sun, J. Ming, *Adv. Mater.* **2021**, 33, 2005993; d) Y. Zhang, C. Liu, Z. Wu, D. Manaig, D. J. Freschi, Z. Wang, J. Liu, *ACS Appl. Mater. Interfaces* **2021**, 13, 16345.

[6] a) J. H. Chu, W. Wang, Q. Y. Yu, C. Y. Lao, L. Zhang, K. Xi, K. Han, L. D. Xing, L. Song, M. Wang, Y. P. Bao, *J. Mater. Chem. A* **2020**, 8, 779; b) Z. Yu, Y. Xie, B. Xie, C. Cao, Z. Zhang, H. Huo, Z. Jiang, Q. Pan, G. Yin, J. Wang, *Energy Storage Mater.* **2020**, 25, 416; c) Y. Liu, Z. Sun, X. Sun, Y. Lin, K. Tan, J. Sun, L. Liang, L. Hou, C. Yuan, *Angew. Chem. Int. Ed.* **2020**, 59, 2473; d) Q. Peng, S. Zhang, H. Yang, B. Sheng, R. Xu, Q. Wang, Y. Yu, *ACS nano* **2020**, 14, 6024; e) H. N. Fan, X. Y. Wang, H. B. Yu, Q. F. Gu, S. L. Chen, Z. Liu, X. H. Chen, W. B. Luo, H. K. Liu, *Adv. Energy Mater.* **2020**, 10, 1904162.

[7] a) S. Liu, M. Xiong, W. Tang, Y. Hu, Y. Yan, L. Xu, C. Fan, *ACS Appl. Mater. Interfaces* **2021**, 13, 38315; b) Y. Chen, W. Luo, M. Carter, L. Zhou, J. Dai, K. Fu, S. Lacey, T. Li, J. Wan, X. Han, Y. Bao, L. Hu, *Nano Energy* **2015**, 18, 205.

[8] a) J. H. Zhou, X. Y. Lian, Y. Z. You, Q. T. Shi, Y. Liu, X. Q. Yang, L. J. Liu, D. Wang, J. H. Choi, J. Y. Sun, R. Z. Yang, M. H. Rummeli, *Adv. Funct. Mater.* **2021**, 31, 2102047; b) W. Zhang, J. Mao, S. Li, Z. Chen, Z. Guo, *J. Am. Chem. Soc.* **2017**, 139, 3316; c) B. Li, Z. He, J. Zhao, W. Liu, Y. Feng, J. Song, *Small* **2020**, 16, 1906595; d) W. Zhang, W. K. Pang, V. Sencadas, Z. Guo, *Joule* **2018**, 2, 1534.

[9] S. Ji, C. Song, J. Li, K. S. Hui, W. Deng, S. Wang, H. Li, D. A. Dinh, X. Fan, S. Wu, J. Zhang, F. Chen, Z. Shao, K. N. Hui, *Adv. Energy Mater.* **2021**, 11, 2101413.

[10] a) H. Kim, J. Hong, K. Y. Park, H. Kim, S. W. Kim, K. Kang, *Chem. Rev.* **2014**, 114, 11788; b) Z. Liu, Y. Huang, Y. Huang, Q. Yang, X. Li, Z. Huang, C. Zhi, *Chem. Soc. Rev.* **2020**, 49, 180.

[11] a) Z. Zeng, V. Murugesan, K. S. Han, X. Jiang, Y. Cao, L. Xiao, X. Ai, H. Yang, J.-G. Zhang, M. L. Sushko, J. Liu, *Nat. Energy* **2018**, 3, 674; b) J. Wang, Y. Yamada, K. Sodeyama, E. Watanabe, K. Takada, Y. Tateyama, A. Yamada, *Nat. Energy* **2017**, 3, 22.

[12] a) S. Randau, D. A. Weber, O. Kötz, R. Koerver, P. Braun, A. Weber, E. Ivers-Tiffée, T. Adermann, J. Kulisch, W. G. Zeier, F. H. Richter, J. Janek, *Nature Energy* **2020**, 5, 259; b) A. Banerjee, X. Wang, C. Fang, E. A. Wu, Y. S. Meng, *Chem. Rev.* **2020**, 120, 6878.

[13] a) H. Yuan, H. Li, T. Zhang, G. Li, T. He, F. Du, S. Feng, *J. Mater. Chem. A* **2018**, 6, 8413; b) H. Fei, Y. Liu, Y. An, X. Xu, G. Zeng, Y. Tian, L. Ci, B. Xi, S. Xiong, J. Feng, *J. Power Sources* **2018**, 399, 294; c) A. Haffner, A. K. Hatz, O. E. O. Zeman, C. Hoch, B. V. Lotsch, D. Johrendt, *Angew. Chem. Int. Ed.* **2021**, 60, 13641; d) J. Zheng, H. Fang, L. Fan, Y. Ren, P. Jena, Y. Wu, *J. Phys. Chem. Lett.* **2021**, 12, 7120.

[14] a) T. Liu, K.-T. Liu, J. Wang, X. Ji, P. Lan, Z. Mu, Y. Pan, S. Cheng, M. Liu, *Energy Storage Mater.* **2021**, 41, 133; b) Y. Li, W. Deng, Z. Zhou, C. Li, M. Zhang, X. Yuan, J. Hu, H. Chen, R. Li, *J. Mater. Chem. A* **2021**, 9, 2822.

[15] a) C. Yang, J. Chen, X. Ji, T. P. Pollard, X. Lu, C. J. Sun, S. Hou, Q. Liu, C. Liu, T. Qing, Y. Wang, O. Borodin, Y. Ren, K. Xu, C. Wang, *Nature* **2019**, 569, 245; b) L. Jiang, Y. Lu, C. Zhao, L. Liu, J. Zhang, Q. Zhang, X. Shen, J. Zhao, X. Yu, H. Li, X. Huang, L. Chen, Y.-S. Hu, *Nat. Energy* **2019**, 4, 495; c) L. Jiang, L. Liu, J. Yue, Q. Zhang, A. Zhou, O. Borodin, L. Suo, H. Li, L. Chen, K. Xu, Y. S. Hu, *Adv. Mater.* **2020**, 32, 1904427.

[16] a) S. Liu, J. Mao, Q. Zhang, Z. Wang, W. K. Pang, L. Zhang, A. Du, V. Sencadas, W. Zhang, Z. Guo, *Angew. Chem. Int. Ed.* **2020**, 59, 3638; b) S. Liu, J. Mao, L. Zhang, W. K. Pang, A. Du, Z. Guo, *Adv. Mater.* **2021**, 33, e2006313.

[17] L. Deng, T. Wang, Y. Hong, M. Feng, R. Wang, J. Zhang, Q. Zhang, J. Wang, L. Zeng, Y. Zhu, L. Guo, *ACS Energy Lett.* **2020**, 5, 1916.

[18] a) W. Li, J. Yu, J. Wen, J. Liao, Z. Ye, B. Zhao, X. Li, H. Zhang, M. Liu, Z. Guo, *J. Mater. Chem. A* **2019**, 7, 16785; b) K. H. Nam, Y. Hwa, C. M. Park, *ACS Appl. Mater. Interfaces* **2020**, 12, 15053.

[19] S. Fadda, A. Cincotti, A. Concas, M. Pisu, G. Cao, *Powder Technol.* **2009**, 194, 207.

[20] S. Bach, V. R. Celinski, M. Dietzsch, M. Panthofer, R. Bienert, F. Emmerling, J. Schmedt auf der Gunne, W. Tremel, *J. Am. Chem. Soc.* **2015**, 137, 2285.

[21] J. Sun, G. Zheng, H. W. Lee, N. Liu, H. Wang, H. Yao, W. Yang, Y. Cui, *Nano Lett.* **2014**, 14, 4573.

[22] Q. Huang, L. Liu, Z. Wu, S. Ji, H. Wu, P. Chen, Z. Ma, Z. Wu, R. K. Y. Fu, H. Lin, X. Tian, F. Pan, P. K. Chu, *Surf. Coat. Technol.* **2020**, 384, 125321.

[23] a) J. Zheng, J. Lu, K. Amine, F. Pan, *Nano Energy* **2017**, 33, 497; b) Z. Wu, S. Ji, J. Zheng, Z. Hu, S. Xiao, Y. Wei, Z. Zhuo, Y. Lin, W. Yang, K. Xu, K. Amine, F. Pan, *Nano Lett.* **2015**, 15, 5590.

[24] a) S. Liu, Q. Zhang, X. Wang, M. Xu, W. Li, B. L. Lucht, *ACS Appl. Mater. Interfaces* **2020**, 12, 33719; b) H. W. Wang, D. Y. Zhai, F. Y. Kang, *Energy Environ. Sci.* **2020**, 13, 4583; c) M. Zhou, P. Bai, X. Ji, J. Yang, C. Wang, Y. Xu, *Adv. Mater.* **2021**, 33, 2003741; d) Q. Zhang, J. Mao, W. K. Pang, T. Zheng, V. Sencadas, Y. Chen, Y. Liu, Z. Guo, *Adv. Energy Mater.* **2018**, 8, 1703288; e) Q. Liu, A. M. Rao, X. Han, B. Lu, *Adv. Sci.* **2021**, 8, 2003639.

[25] a) A. J. Naylor, M. Carboni, M. Valvo, R. Younesi, *ACS Appl. Mater. Interfaces* **2019**, 11, 45636; b) H. Wang, H. Wang, S. Chen, B. Zhang, G. Yang, P. Gao, J. Liu, X. Fan, Y. Huang, J. Lin, Z. Shen, *ACS Appl. Energy Mater.* **2019**, 2, 7942; c) L. Deng, Y. Zhang, R. Wang, M. Feng, X. Niu, L. Tan, Y. Zhu, *ACS Appl. Mater. Interfaces* **2019**, 11, 22449.

[26] B. Li, J. Zhao, Z. Zhang, C. Zhao, P. Sun, P. Bai, J. Yang, Z. Zhou, Y. Xu, *Adv. Funct. Mater.* **2019**, 20, 1807137.

[27] B. Tong, Z. Song, H. Wan, W. Feng, M. Armand, J. Liu, H. Zhang, Z. Zhou, *InfoMat* **2021**, 3, 1364.

[28] W. Liu, P. C. Liu, D. Mitlin, *Adv. Energy Mater.* **2020**, 10, 2002297.

[29] a) D. Zhao, P. Wang, X. Cui, L. Mao, C. Li, S. Li, *Electrochim. Acta* **2018**, 260, 536; b) Z. Wu, S. Li, Y. Zheng, Z. Zhang, E. Umesh, B. Zheng, X. Zheng, Y. Yang, *J. Electrochem. Soc.* **2018**, 165, A2792; c) L. Lin, K. Yang, R. Tan, M. Li, S. Fu, T. Liu, H. Chen, F. Pan, *J. Mater. Chem. A* **2017**, 5, 19364; d) M. Zhu, Y. Zhang, F. Yu, Z. Huang, Y. Zhang, L. Li, G. Wang, L. Wen, H. K. Liu, S. X. Dou, C. Wu, *Nano Lett.* **2021**, 21, 619.

[30] a) K. Sun, S. J. Dillon, *Electrochem. Commun.* **2011**, 13, 200; b) B. Kang, G. Ceder, *Nature* **2009**, 458, 190.

[31] a) L. Fan, S. Wei, S. Li, Q. Li, Y. Lu, *Adv. Energy Mater.* **2018**, 8, 1702657; b) D. H. S. Tan, Y. T. Chen, H. Yang, W. Bao, B. Sreenarayanan, J. M. Doux, W. Li, B. Lu, S. Y. Ham, B. Sayahpour, J. Scharf, E. A. Wu, G. Deysher, H. E. Han, H. J. Hah, H. Jeong, J. B. Lee, Z. Chen, Y. S. Meng, *Science* **2021**, 373, 1494.

[32] L. Fan, R. Ma, J. Wang, H. Yang, B. Lu, *Adv. Mater.* **2018**, 30, 1805486.

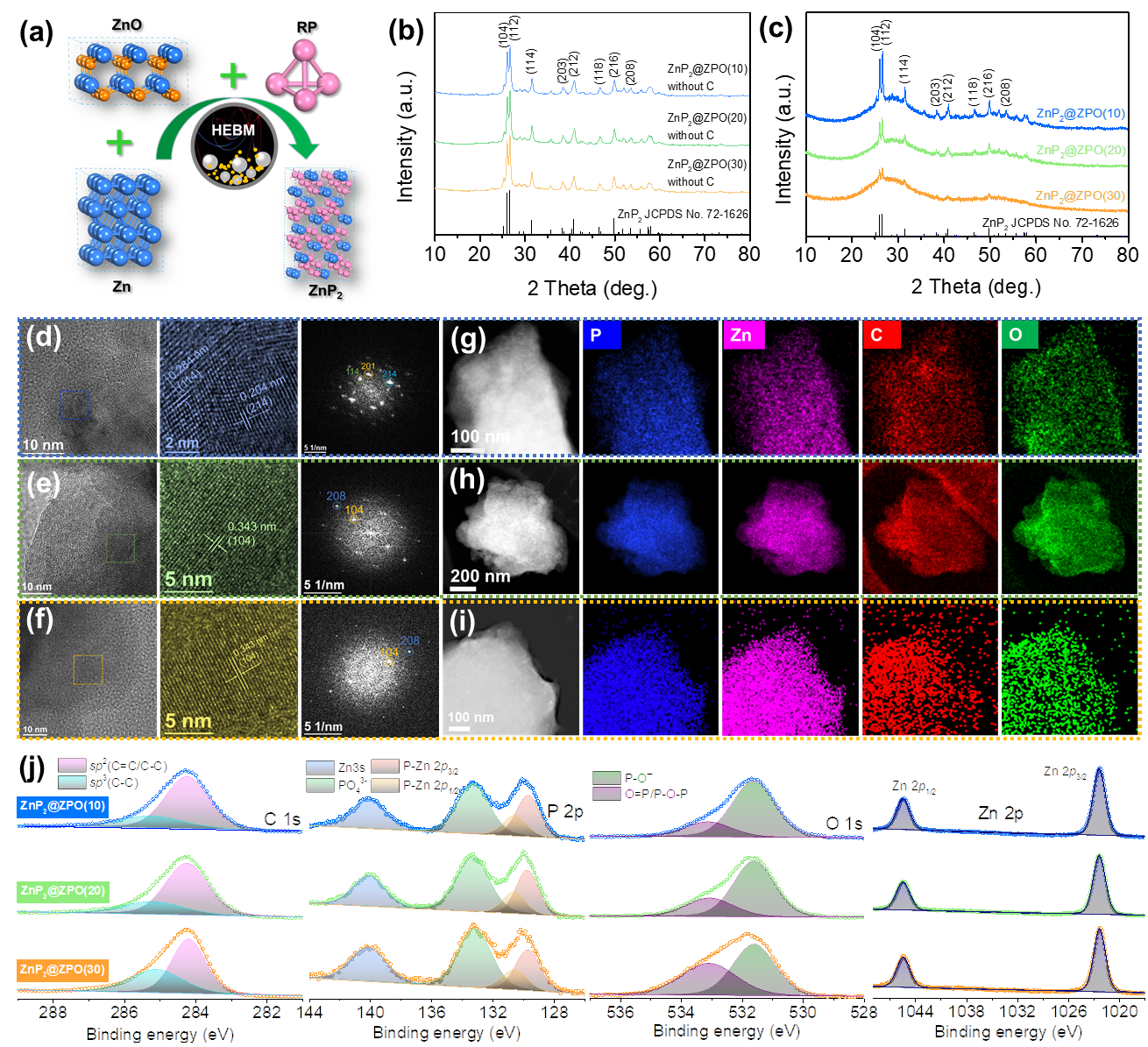


Figure 1. a) Synthesis of optimized ZnP2 composites with different mass fractions of zinc phosphate obtained by controlling the ratio of raw materials. b, c) XRD patterns of ZnP2 composites without and with carbon. TEM images, HRTEM, FFT and corresponding EDS element mappings of (d, g) ZnP2@ZPO(10), (e, h) ZnP2@ZPO(20), and (f, i) ZnP2@ZPO(30). j) High-resolution XPS spectra of ZnP2@ZPO(10), ZnP2@ZPO(20), and ZnP2@ZPO(30).



Figure 2. a) Rate capabilities and cycling performance at 0.1 A g−1 in KFSI-EC/DEC electrolytes. b) Digital photos of igniting glass fiber separators soaked with EC/DEC and TEP solvents. c) Rate and cycling performance at 0.1 A g−1 in KFSI-TEP electrolytes. d) First discharge-charge curves of the three electrodes at 0.05 A g−1 in KFSI-TEP electrolyte. e) Differential capacity (dQ/dV vs V) curves of ZnP2@ZPO(10) at different cycles. The inset shows the first cycle. f) Long-term cycle performances in KFSI-TEP electrolyte at 0.5 A g−1. g) Analysis of retained capacity and capacity retention after 600 and 1000 cycles at the current densities of 0.1 and 0.5 A g−1, respectively. h) Comparison with reported metal phosphides and other noncarbon anodes for PIBs in terms of cycling performances and capacity retention. i) Voltage-Time curves of symmetric K/K cells in EC/DEC and TEP-based electrolytes at the current density of 0.5 mA cm−2. Insets are the enlargements of the indicated area. j) Nyquist plots of ZnP2@ZPO(20) electrode after different cycles. The inset is an enlargement.



Figure 3. a) First two galvanostatic profiles of the ZnP2@ZPO(20) electrode for XPS analysis. b, c) High-resolution C1s XPS spectra at different etching times after first discharging and charging to different states in TEP-based electrolyte. d) High-resolution C1s XPS spectra at different etching time after first discharging and charging to different states in EC/DEC-based electrolyte. e, f) High-resolution F1s XPS spectra.



Figure 4. High-resolution S2p XPS spectra at different etching times after discharging and charging to different states in TEP-based electrolyte (a) and in EC/DEC-based electrolyte (b). c) Area percentage variation of various sulfur-containing species with etch time and charge/discharge states in TEP-based electrolyte.



Figure 5. a) S2p XPS spectra of the ZnP2@ZPO(20) electrode at 1.0 V after 1000 cycles. b-e) SEM images of the ZnP2@ZPO(20) electrode when fresh and after 1000 cycles. f, g) TEM image and corresponding ED pattern of ZnP2@ZPO(20) electrode after 1000 cycles. h) Illustration of the distribution of sulfur-containing species in the SEI with charge/discharge states.



Figure 6. a) Schematic of the PTCDA//ZnP2@ZPO(20) full cell in KFSI-TEP electrode. b) Galvanostatic discharge–charge curves of the half cell and full cell. c) First five cycles of CV measurements of the full cell. d) Rate capabilities of the full cell. e) Cycle performance of the full cell at the current density of 100 mA g–1. f) Optical photos of the full cell powering an electric fan.