Interface and Safety Properties of Phosphorus-based Negative Electrodes in Li-ion Batteries

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Phosphorus is considered as a promising candidate for the replacement of graphite as the active material in Li-ion battery electrodes owing to its six-fold higher theoretical specific charge. Unfortunately, phosphorus-based electrodes suffer from large volume changes upon cycling, leading to poor electrochemical performance. Furthermore, red phosphorus (P_{red}) is known to release phosphine gas (PH_3) once in contact with water (even at the ppm level), and thus, its safety profile need to be asset. In this context, the electrolyte/electrode interface of a P_{red} electrode during the 1st lithiation is fully investigated using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and, on-line electrochemical mass spectroscopy (OEMS). The XPS analyses reveal that at potentials higher than 1 V vs. Li^+/Li , the P_{red} starts to react via the outermost surface layer, which is mainly composed of the native oxide, P_2O_5 to form H_3PO_4 . Once this surface oxide is consumed, the P_{red} reacts with moisture and the electrolyte, resulting in the re-formation of H_3PO_4 and the release of the toxic PH_3 as identified by OEMS. At potential lower than 1 V, a solid electrolyte interphase (SEI) develops on the top of H_3PO_4 as identified by XPS analyses. This SEI prevents further degradation of the P_{red} and inhibits PH_3 release. Following the lithiation, the lithiation process takes place generating particles fracture (identified by SEM) and the transformation of H_3PO_4 into Li_3PO_4 is also notified. Understanding and monitoring the role of the decomposition products and processes within the battery is crucial to further improving battery performance and safety.

Keywords:

Lithium ion battery, phosphorus electrode, phosphine, solid electrolyte interphase, reaction mechanism

1. Introduction

Among the most important features required for the advancement of Li-ion batteries are low cost, high energy, high power, and excellent safety. Significant effort has been dedicated to the development of novel negative electrode materials with higher energy densities that could potentially replace the graphite used as negative electrodes in commercial batteries. Red phosphorus (P_{red}) offers an attractive theoretical specific charge of $2595 \text{ mAh}\cdot\text{g}^{-1}$ when reacting with lithium to form Li_3P ,¹ compared to the $372 \text{ mAh}\cdot\text{g}^{-1}$ obtained from LiC_6 .² However, P_{red} suffers from severe volume changes when reacting with Li, which enhances electrolyte decomposition and leads to particle fracturing and electrical disconnection. Furthermore, P_{red} is known to have very poor electrical conductivity, and thus, to enhance its potential as a negative electrode candidate, research has focused on embedding it in a conductive carbon matrix.^{3,4,5} Recently, many papers focused on the engineering of the electrode materials based on conversion/alloy reactions. It turns out that the binder as well as the particle size distribution are playing an important role in keeping a relatively stable specific charge along multiple cycles. To date, Na-CMC (sodium carboxymethyl cellulose) and PAA (poly(acrylic acid)) binders are the most commonly used with phosphorus based active materials. They demonstrated very good cycling stability along long-term cycling once coupled to nano-particles⁶⁻⁸. However, very good performances were also reported with PVDF (polyvinylidene difluoride) binder despite its early decomposition during cycling.^{9, 10}

Surprisingly, few studies dedicated to the side reactions that can occur at the electrolyte/electrode interface of P_{red} -based electrodes have been conducted, and the impact of these processes on battery performance and safety are not well understood. For these reasons, elucidating the role of the solid electrolyte interphase (SEI) and its role on the safety battery aspect are crucial for the future integration and development of these materials. It is well known from the literature that PH_3 can be generated from P_{red} in aqueous system even if this reaction seems to be rate dependent.^{12, 13} The PH_3 exposure level considered immediately dangerous to life or health (IDLH) is only ca. 50 ppm. The

U.S. National Institute for Occupational Safety and Health (NIOSH) recommends that the short-term respiratory exposure to phosphine gas should not exceed 1 ppm.¹⁴ To the best of our knowledge, and despite the abundant literature on P_{red}-based negative electrodes, there is no report regarding the possibility of PH₃ release during cycling in presence of organic electrolyte containing few ppm of water, which would be a severe safety issue to consider in the development of P_{red}-based electrodes. In this context, we utilized surface characterization techniques scanning electron microscopy (SEM), on-line electrochemical mass spectroscopy (OEMS), and X-ray photoemission spectroscopy (XPS) to probe the electrode/electrolyte interface of P-based electrodes upon the initial lithiation. By this approach, the reactions taking place at the electrolyte/electrode interface were elucidated mechanistically.

2. Experimental Section

Electrochemistry. Electrodes were prepared by mixing 80 wt% P_{red} (Sigma-Aldrich), 10 wt% carbon black (CB, Super C65, Imerys) and 10 wt% polyvinylidene fluoride (PVDF, HSV-900, Arkema) in *N*-methyl-2-pyrrolidone (NMP, Alfa Aesar). The slurry was cast onto copper foil used as a current collector and dried under vacuum at 80°C. Electrodes (13 mm diameter) were punched and dried under dynamic vacuum at 80°C overnight. The active material loading was estimated at ca. 5 mg·cm⁻². Where specified, several electrodes (designated as P_{powder} electrodes) were prepared without binder by mixing 60 wt% P_{red} and 40 wt% CB in a mortar. The mixture was then converted into a pellet by pressing under 3 tons. Electrochemical cells in coin-type cells were assembled in an Ar-filled glove box using a glass fiber separator coupled to a plasticized polypropylene separator (ESPJ137, Lainière de Picardie) and metallic lithium as a counter electrode. A solution of LiClO₄ (1 M) dissolved in 1:1 ethylene carbonate (EC) and dimethyl carbonate (DMC) (i.e., LC30) was used as the electrolyte and the water content was measured at 18 ppm by Karl Fisher Titration. Similar results were obtained from the common LP30 electrolyte (1 M LiPF₆ in 1:1 EC:DMC) as can be seen in Supporting Information (**Figure S1** and **Figure S2**). In the case of the measurement performed with LiPF₆ salt, the XPS phosphorus signals originate from the salt overlap with the signals of the

phosphorus from the active material. Such an overlapping of both signals makes the analysis and interpretation of the phosphorus reaction mechanism very challenging if not impossible. Furthermore, the XPS signal of the fluorine of the PVDF is also overlapping the one of the LiPF_6 salt. Thus, for the rest of the analysis we will use LiClO_4 salt.

The cells were cycled in galvanostatic mode at 25°C between 2.0 V and 5 mV (vs. Li^+/Li) at a C/30 rate (a full charge or discharge in 30 h). For the cells cycled for the SEM and XPS analyses, a potentiostatic step of 8 h was applied at the end of the desired potential. Throughout the manuscript, the potentials are given compared to the Li metal reference, i.e., vs. Li^+/Li .

Measurements were monitored with a computer-controlled battery cycling device (CCCC; Astrol Electronic AG, Switzerland). After cycling, the cells were disassembled in an Ar-filled glove box and the electrodes were gently washed with DMC prior to their transfer to the SEM and XPS using a special air-tight transfer chamber.

Scanning electron microscopy (SEM). SEM measurements were performed with a Carl Zeiss Ultra55 scanning electron microscope, using both the secondary electron and InLens modes. The images were taken at an acceleration voltage of 3kV to ensure that i) we are not damaging the surface (composed of SEI, generally degrading at high acceleration voltage) and, ii) the quality is sufficient enough to avoid too much charging effect.

On-line electrochemical mass spectroscopy (OEMS). The working principle of the OEMS setup and cell has been described elsewhere.¹⁵ Briefly, the setup comprises a quadrupole mass spectrometer (MS, QMS 200, Pfeiffer PrismaTM, Germany) for partial pressure measurements, a pressure transducer (PS, PAA-33X, Keller Druck AG, Switzerland) for cell pressure, temperature, and internal volume determinations, stainless steel gas pipes and Swagelok fittings (3 mm compression tube fittings, Swagelok, OH, US) for OEMS cell attachment, a set of solenoid valves (2-way magnetic valve, Series 99, silver-plated nickel seal, Parker, US), and a scroll pump (nXDS15i, EDWARDS GmbH, Germany) for efficient flushing. The magnetic valves were automatically opened/closed with a solid-state relay module (NI 9485 Measurement System, National Instruments, TX, US) connected

to a computer with homemade LabVIEW software (NI LabVIEW 2013, National Instruments, TX, US). Linear sweep voltammetry ($40 \mu\text{V}\cdot\text{s}^{-1}$) with the P_{red} -based working electrodes in a potential window of 5 mV to -3.0 V vs. Li^+/Li was performed against a Li metal counter electrode at room temperature using the CCCC device. During the measurements, any gases arising from the electrode/electrolyte interface into the headspace of the OEMS cell were pumped off to the mass spectrometer for analysis. The time delay between the formation of the gases at the electrode surface and their detection at the mass spectrometer was estimated at a maximum of 10 min. The mass signals were recorded as a function of time and cell voltage. Changes in the ion current intensities were monitored by selectively scanning the mass-per-electron signals at $m/z = 2$ (H_2), 28 (C_2H_4), 34 (PH_3), 40 (Ar), and 44 (CO_2). The gas evolution rates of H_2 , C_2H_4 , and CO_2 were accounted for by calibration of the mass spectrometer with gas standards of known concentration. No gas standard was available for PH_3 , which was accounted for semi-quantitatively by employing the same sensitivity factor as for O_2 . This rough estimation is reasonable considering that most sensitivity factors are found in the same order of magnitude.¹⁶

X-ray photoelectron spectroscopy (XPS). XPS measurements were carried out with a VG ESCALAB 220iXL (Thermo Fisher Scientific) spectrometer using focused monochromatized Al $K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). The spectrometer was calibrated using the Ag $3d_{5/2}$ peak at a binding energy of 368.3 eV. The X-ray spot size was about $500 \mu\text{m}^2$ (power: 150 W) and the pressure in the analysis chamber was about 2×10^{-9} mbar. The spectra were recorded in the constant analyzer energy mode at a pass energy of 30 eV in steps of 50 meV with a dwell time of 5 ms. Control spectra were recorded at the beginning and end of each experiment to certify that the sample did not evolve with time or suffer beam damage. The BE scale was calibrated with respect to the C $1s$ component of the CB (C–C bonds), set at 284.4 eV. Peak deconvolution was performed by applying the sum of the Gaussian (70%) and Lorentzian (30%) line shapes after Shirley-type background subtraction. Deconvolutions of the P $2p$ peaks were realized by fixing their spin-orbit splitting and branching ratio to 0.87 eV and 0.5, respectively. In the study, only the P $2p_{3/2}$ component is described for the spectral analysis. No

charge compensation was used for the XPS measurements on P_{red} electrodes mixed with carbon and binder. However, for the P_{red} raw pristine powder, a flood gun was used to compensate the charge due to its very poor electrical conductivity.

3. Results

The galvanostatic curve for the 1st cycle of the P-based electrode is displayed in **Figure 1**. The OCV starts at 3.1 V and decreases almost instantly to reach a short potential plateau at ca. 0.85 V, attributed to SEI formation (region I). Then, the potential drops quickly to 0.35 V, at which the reaction starts, with the formation of the first intermediate LiP phase as indicated in the Material projects website¹⁷,¹⁸. The formation of the Li_3P phase is characterized by the slow decrease of the potential to 5 mV, as has been described in the literature (region II).⁴ As expected from its low conductivity, the theoretical specific charge ($2595 \text{ mAh}\cdot\text{g}^{-1}$) of P_{red} is not reached ($1946 \text{ mAh}\cdot\text{g}^{-1}$), despite the use of a potentiostatic step of 2 h at 5 mV and the addition of the carbon additive. Consequently, part of the P-based electrode does not react properly, because either the particles are disconnected from the carbon network, or only their surfaces react while the phosphorus core remains undisturbed (due to the low conductivity, the kinetics is extremely slow). As expected from the poor lithiation, the delithiation process is extremely rapid (region III) with a coulombic efficiency of ca. 6.5%.⁴

Figure 1. Galvanostatic profile of the 1st cycle of the P_{red} -based electrode.

Figure 2 shows the morphological changes of the electrode with cycling. In the pristine electrode (Figure 2a & 2b), micron-sized phosphorous particles are embedded in the CB/PVDF matrix. However, as lithiation proceeds, the particle morphology markedly changes; at 0.95 V (Figure 2c & 2d), the surface appears smoother and/or covered by a polymer layer (most probable the organic SEI layer). Upon reaching 0.65 V (Figure 2e & 2f), several filaments appear in the SEM images, which may be attributed to the SEI due to their charging effect and their decomposition under microscopy beam (melting observed in the images after several seconds of exposure). For all the samples cycled below 0.65 V, a charging effect indicating the formation of a thick polymeric insulating SEI layer is observed. As the lithiation proceeds, significant fractures in the phosphorous particles can be noted at 150 mV (see Supporting Information, **Figure S3**), indicating a substantial volume change due to the reaction Li-P (Figure 2g & 2h). At full lithiation (5 mV, Figure 2i & 2j), the particles are pulverized due to the large volume change (full lithiation to Li_3P causes a volume change of 216%), and only particles smaller than 2 μm are visible.

Figure 2. SEM images (two magnifications) of the pristine and post-mortem cycled P_{red} electrodes: a,b) pristine; and after cycling at c,d) 0.95 V; e,f) 0.65 V; g,h) 150 mV; and i,j) 5 mV.

The OEMS analysis of the P-based electrode is displayed in **Figure 3**. The P_{red} -based electrode cycled using linear sweep voltammetry, displays cycling behavior similar to that reported in Figure 1, with

two main cathodic peaks near 0.8 and 0.35 V. A signal for H_2 ($m/z = 2$) appears at an early cycling stage (i.e., 2.2 V), which is attributed to the reduction of protons in the electrolyte. This signal evolves constantly during the discharge, with three separate maxima at 1.8, 0.9, and 0.4 V. Surprisingly, PH_3 ($m/z = 34$) is released from the P_{red} -based electrode at relatively high voltages (> 1.5 V) at which only surface reactions can occur, since the Li-P reaction starts below 1 V. The maximum for PH_3 evolution is reached at ca. 1.6 V (still far removed from the Li/P reaction potential); then, the evolution rate decreases slightly, reaching a second maximum at ca. 1.1 V. However, below 1.1 V, after the onsets of the Li-P reaction and SEI formation, no additional PH_3 is detected. Unfortunately, these results indicate that a P_{red} -based electrode in a Li-ion battery would be toxic in the event of casing failure, and its use as replacement for graphite in Li-ion batteries should, accordingly, be of concern. At ca. 1 V, as would be expected from SEI formation, ethylene gas ($m/z = 28$), a well-known decomposition product of ethylene carbonate (EC), is formed.¹⁹ After full lithiation, a second small release of C_2H_4 is observed, which can be attributed to the development of an SEI on the fractured particle surfaces. Indeed, at the end of lithiation, the largest volume change in the particles (largest amount of Li_3P) is observed. As discussed for Figure 1, the theoretical capacity of the P_{red} -based electrodes is clearly not attained; thus, a core-shell process, in which only the surfaces of the P particles react and the cores remain as P, is suggested to occur. When the large particles start to fracture, they release fresh P-based surfaces (Figure 2 g–j), and the opportunity for additional SEI formation.

Figure 3. Potential (black), current response (red), and C₂H₄ (green), H₂ (violet), as well as PH₃ (pink) gas evolution profiles for OEMS cells containing P_{red} based electrodes.

The OEMS measurements show two distinguishable regions, one higher than 1 V that is attributed to surface reactions with the release of PH₃, and the other lower than 1 V that is attributed to SEI formation and the Li-P reaction. To understand the origins of these different, mostly surface, reactions, we followed the first lithiation by XPS post-mortem analyses.

The XPS measurements of the C 1s and P 2p core levels acquired on the pristine electrode and at the open circuit potential (OCP) are displayed in **Figure 4** whereas the F 1s and Cl 2p core spectra are reported in the Supporting Information, **Figure S4 and S5**. Three main components are visible in the C 1s core level at 284.5, 286.8, and 291.2 eV, ascribed to CB (C–C), CH₂, and CF₂ from the PVDF, respectively.^{19,20} Smaller contributions are attributed as follows: 285.6, 287, and 288.6 eV associated with C–H (hydrocarbon), C=O, and O–C=O species, respectively.²¹

At the OCP, the C 1s core level spectrum shows slight changes compared to the pristine sample, a small increase of the hydrocarbon component is observed, which is believed to be associated to adsorbed species from the DMC and EC. A slight shift to higher BE was also observed for the two PVDF components CF₂ and CH₂ respect to the carbon black components, which is probably linked to the spontaneous decomposition of the PVDF binder caused by the electrolyte, leading to LiF peak (**Figure S4**, Supporting Information). The Cl 2p and O 1s core spectra recorded at OCP can be found in Supporting Information (**Figure S5**).

The spectrum of the P 2p core level of the pristine electrode presents three main components (P 2p_{3/2}) at 129.5, 130.2, and 134.6 eV. The component at 130.2 eV is attributed to P–C species,^{5,22,23} whereas the one at 129.5 eV is related to P_{red} with a zero-oxidation state (P⁰). To ensure the proper assignment of the phosphorus components, we compared P 2p core level spectra acquired on P_{powder} (with and without the addition of carbon) to that for the standard electrode, P_{red}/C/PVDF. The results, displayed in the supplementary information (see **Figure S6**, Supporting Information), show that P–C and P₂O₅

components evolve strongly in the presence of the conductive carbon. This observation highlights the reactivity of the phosphorus surface with carbon and traces of moisture. The P–C species are also visible in the C 1s core level spectrum, as a component at 283.5 eV. The third component in the P 2p core level spectrum at 134.6 eV is related to the native phosphorous oxide (the pentoxide, P₄O₁₀ (P⁵⁺)) that develops at the surface of the P_{red.}^{3,24} An additional minor contribution at 131.7 eV is assigned to P₄O₂.²⁵ Unlike the C 1s core level, a shift of the pentoxide component to lower binding energy (BE), from 134.6 to 133.8 eV, is observed (Figure 4-b) at the OCP, due to the spontaneous reaction that occurs between the native P₂O₅ and the electrolyte. Similar behavior is noticed in the P 2p core level of the soaked P_{powder}-electrode, confirming that a chemical reaction occurs with the electrolyte (see **Figure S7**, Supporting Information). As P₂O₅ is known to be a drying agent for solvents, we believe it reacts with the traces of water (ca. 20 ppm) to form H₃PO₄ (Equation 1). Therefore, the component at 133.8 eV is assigned to H_{3-x}PO₄^{3-x}, which will be further discussed below.²⁶

Figure 4. C 1s and P 2p XPS core level spectra acquired on a) pristine P_{red} electrode and b) electrode at the OCP.

The electrode/electrolyte interactions were further investigated by measuring different key potentials from 2.0 V to 5 mV. The spectra for the C 1s and P 2p core levels are presented in **Figure 5**, while the one of F1s core level and Cl2p core level are displayed in the **Figure S8 and S9**. At 2 V (Figure 5-a), the H₃PO₄ component in the P 2p spectrum slightly shifts to higher BE at 134.2 eV, whereas no change appears in the C 1s core level. Due to its strongly acidic nature, H₃PO₄ is unstable toward residual water and other ions in the electrolyte, leading to proton-deficient phosphoric acid species (H_{3-x}PO₄^{3-x}). In the literature, Horowitz et al.²⁷ showed that the addition of one proton to the PO₄³⁻ ion induced a 1 eV shift to higher BE. Therefore, the loss of a small number of protons should result in a shift to lower BE. This assumption is further confirmed by the oscillation of the BE position of the H₃PO₄ component between 134.3 and 134.6 eV in the P 2p core levels recorded at different potentials (Figure 5-b-g). Moreover, by comparing the P 2p core level acquired at 2.0 V (Figure 5-a) to the one recorded at the OCP (Figure 4-b), increasing intensities of the P–C/P⁰ components can be observed, revealing that the H₃PO₄ layer is thinner (i.e., it has undergone slight dissolution as it is a strong acid, thus dissolves directly in the electrolyte) at 2 V. According to the OEMS data, PH₃ gas begins to evolve at a similar potential, and the changes seen in the core level could reflect the beginning of this reaction process. At 1.5 V, the C 1s core level spectrum is starting to show some signs of the SEI formation such as CO₃ and CO peak, directly linked to SEI carbonate products. The P 2p core level spectrum (Figure 5-b) reveals a strong increase in the H₃PO₄ component as well as decreases in the P⁰ and C–P components. These phenomena are interpreted as an increase in the thickness of the H₃PO₄ “layer” at the outermost surface of the phosphorus particles, which could be caused by an electrochemical reaction inside the cell (Equation 2) followed by a chemical reaction (Equation 3).

Equation 2 describes the reduction of H_3PO_4 into P^0 , which is theoretically expected at ca. 2.6 V.²⁸ A similar mechanism was previously proposed by Vogel et al.²⁹ in a highly concentrated H_3PO_4 electrolyte, where H_3PO_4 was reduced on the surface of platinum to form Pt–P bonds. In this case, we believe that the phosphorus reacts with itself, generating “P–P” bonds. Regarding the shift in the reaction potential, it is likely related to the poor conductivity of the phosphorus particles: as they are not all homogeneously coated with carbon, it may be that the higher resistance inside the cell results in a higher polarization.

The chemical reaction given by Equation 3 consists of the re-oxidization of P^0 to form H_3PO_4 , PH_3 , and H_2 . Indeed, the newly formed P–P species will be directly exposed to the H_2O generated through the electrochemical reaction given in Equation 2 and instantaneously consumed. Therefore, a cyclic process is generated between the two reactions (Equation 1 and 2).

In the 1.5–0.6 V potential range (Figure 5-b-e), the C 1s peaks show a continuous decrease in the CB (C–C) component. Increases are observed in the four components located at 286.1 (C–H), 288 (C–O), 290 (O–C=O), and 291.6 eV (carbonate/dicarbonate species),^[20] belonging to the SEI layer. To achieve reliable deconvolution of the SEI components, PVDF-free P_{red} electrodes were also analyzed (**Figure S10**, Supporting Information). All the contributions are shifted to higher BE by about 1 eV compared to the literature,³⁰ which is most probably related to a local charging effect³¹ often observed with the decomposition of EC and DMC.²⁰

From 1 to 0.6 V (Figure 5c-e), the absolute intensity of the H_3PO_4 component progressively decreases, indicating that this component starts to be covered by an additional layer, i.e., the SEI that grows on the surface of the phosphorus particles. These results are in accordance with the OEMS data in which the formation of ethylene gas due the decomposition of EC was observed in the same potential range (Figure 3). Additionally, we can noticed the decomposition of the PVDF binder occurring mostly below 1 V as seeing with the presence of LiF component detected at ~ 686.5 eV

(Supporting Information, **Figure S8**). The same observation can be drawn for the electrolyte salt LiClO_4 where LiCl contribution appears below 1 V (Supporting Information, **Figure S9**).

With continued lithiation between 0.6 and 0.4 V (Figure 5e-f), the SEI does not appear to significantly evolve, as confirmed by the unchanged intensity of the CB (C–C) component. At 0.4 V, slight increases in the P 2*p* core levels of the P^0 and C–P components are observed (Figure 5f). Such behavior is explained by the presence of particle fractures caused by the Li–P reaction, as seen in the SEM images (Figure 2-i-j).

At 5 mV (i.e., full lithiation) (Figure 5g), the SEI reaches its maximum thickness, since the CB (C–C) signal is in the noise level. For the P 2*p* core level, the increases in the P^0 and C–P components become even more pronounced (Figure 5g). By deconvoluting the peak, we are able to detect the presence of two Li_xP components located at 126.6 and 128.6 eV (most likely, LiP and Li_3P , respectively), and a lithiated H_3PO_4 component located at 132.7 eV, which is associated with Li_3PO_4 . The presence of Li_3PO_4 is the result of the ionic exchange between protons and Li ions, and therefore, protons in the electrolyte would be expected, explaining the evolution of H_2 at the end of the lithiation. However, we cannot fully exclude the participation of the formed PH_3 in the phenomena observed at the end of discharge.^{32,33,34}

Figure 5. Spectra of the C 1s and P 2p XPS core levels acquired on P_{red} electrodes cycled at a) 2.0 V, b) 1.5 V, c) 1.0 V, d) 0.8 V, e) 0.6 V, f) 0.4 V and, g) 5 mV.

4. Discussion

Based on the foregoing results, we can mechanistically elucidate the reactions that occur during the first lithiation of the P_{red} -based electrode. The scheme presented in **Figure 6** summarizes the overall mechanism, which is subdivided into several steps. Based on the detailed XPS analyses, we identified that in the first step (Step 1), P_2O_5 reacts chemically with traces of water in the electrolyte, leading to the formation of H_3PO_4 . The second step (Step 2), with an onset at ca. 3 V, consists of the slight dissolution of H_3PO_4 in the electrolyte, which could be facilitated by the presence of residual water. From ca. 2 to 0.6 V (Step 3), the reduction of H_3PO_4 occurs at the outermost surface of the P_{red} particles, leading to the formation of reduced phosphorus P^0 (Step 3). The freshly formed P^0 specie, which is in direct contact with the traces of water generated by the reduction of H_3PO_4 , will react instantaneously to produce PH_3 , H_2 , and H_3PO_4 . Because H_3PO_4 is regenerated, the reactions are cyclical and the P_{red} -based electrode continues to decompose.

The formation of the SEI (Step 4) is the key to buffering the decomposition of the P_{red} -based electrode. At 0.6 V, we can correlate the release of ethylene (by OEMS) with SEI formation (by XPS) and the binder decomposition, leading to the inhibition of PH_3 gas evolution. The surface analyses (XPS combined to SEM) demonstrate that an SEI layer thickness in the range of 4–5 nm is sufficient to chemically passivate the phosphorus particles and indirectly stop PH_3 production. Due to the low electronic conductivity of the SEI, the reduction of H_3PO_4 is probably prevented, and then, PH_3 cannot be released.

Below 0.4 V, the P_{red} particles begin to fracture due to the reaction with Li (SEM analyses); this is correlated with a slight increase in the P^0 and C–P components, despite the thick SEI layer. Such behavior is possible due to the crack formation in the phosphorus particles and the emergence of fresh surface area that is not yet covered by the SEI due to the insulating nature of P_{red} .

Our work evidences a severe safety issue with the formation of toxic PH_3 that must be considered, especially if nanoparticles with high surface area in contact with the electrolyte are to be used as anode for Li-ion batteries. For the micrometer-sized P_{red} active material aggregates of low surface

area employed in our electrodes about 1.1 mg PH_3 per g of phosphorus is estimated to be formed on the first discharge, which could be a potential safety hazard if large-scale cells with several hundred grams of phosphorus suffer from gas leakage.

Figure 6. Mechanistic scheme for the reactions occurring at the electrode/electrolyte interface on the P_{red} -based electrode during the first lithiation.

5. Conclusion

By combining three complementary surface characterization techniques (SEM, OEMS, and XPS), we elucidated the interfacial reaction mechanisms for P_{red} -based electrodes during the first lithiation. We observed three main phenomena: i) the release of phosphine gas (PH_3) caused by multiple surface reactions; ii) electrolyte reduction; and iii) surface layer passivation (i.e., the formation of an SEI). We demonstrated that the native surface layer composed of P_2O_5 reacts with water traces (present in the organic electrolyte) to form a highly reactive layer of H_3PO_4 . Once this process is initiated, it will

generate an electrochemical reduction leading to P_{red} and water which will then react further to regenerate H_3PO_4 . This process will continue until reaching potential below 1 V where the SEI starts to be formed. The thickness and insulating character of the SEI inhibit PH_3 gas release. Combining different surface sensitive techniques lead to understand the changes in the electrode/electrolyte interface during cycling in order to properly engineer and stabilize this interface and prevent gas releases that would raise concerns over battery safety.

Supporting Information

XPS core levels for C1s and P2p acquired on pristine electrodes cycled with LP30 electrolyte, OEMS data of P_{red} based electrodes cycled with LP30 electrolyte, SEM images of the pristine and post-mortem cycled P_{red} electrodes, XPS F1s, O1s, Cl2p core levels acquired on P_{red} pristine and OCP electrodes, P2p XPS core levels acquired on different pristine sample, P2p XPS core levels acquired on Ppowder -electrode soaked in the electrolyte (LC30), F1s and Cl2p XPS core levels acquired on P_{red} electrodes along lithiation, C1s XPS core level acquired on a pristine Ppowder -electrode and a Ppowder -electrode cycled at 1 V. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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TOC

Lithium ion battery, phosphorus electrode, phosphine, solid electrolyte interphase, reaction mechanism

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