A Red Phosphorus-Graphite Anode for K-ion Batteries

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Abstract

Red phosphorus (RP) is a promising anode material for potassium-ion batteries because of its theoretical capacity of 865 mA h g^{-1} delivered at an average potential of 0.5 V vs K^+/K . However, its alloy reaction to form KP entails a volume expansion of 162% resulting in severe stresses that lead to SEI and electrode fracture, loss of electric contact, and ultimately reduced cycle life. Moreover, its low electronic conductivity ($10^{-14} \text{ S cm}^{-1}$) limits rate capability. Here, we report a RP-graphite composite prepared by a two step ball milling procedure to control particle size and optimize carbon coating. Electrodes prepared with the composites achieve high capacity ($723 \text{ mA h g}_\text{P}^{-1}$) at C/20 and retaining 75% at 5C. It also shows very good cycling stability, retaining more than 96% of the capacity after 100 cycles at 1C.

The demand for lithium-ion batteries (LIBs) is expected to increase tenfold by 2030 due to a widespread uptake of electric vehicles (EVs).[1, 2] Concerns have been raised about the availability and cost of lithium in the near-future, because of its geographical concentration.[3] More abundant alkali metals such as sodium and potassium are being considered, due to their higher abundance and lower cost than Li (47 billion tons in the largest deposit available, 7 billion tons and 80 million tons, for soda ash, potash and Li precursors, respectively, resulting in an average cost of 200, 1000, and 8,750 USD tons^{-1}). For the successful uptake of alternative chemistries in most transport applications, they must at least match the energy density of commercial LIBs. [3] [4, 5]. State of the art commercial Li-ion batteries employ a silicon oxide doped graphite anode and a nickel-manganese-cobalt oxide cathode, storing 250 Wh kg^{-1} . [6, 7] To extend the electrification of transport to aviation, heavy goods vehicles and shipping, higher energy densities of about 500 Wh kg^{-1} are required.[8]

Potassium-ion batteries (KIBs) are a promising

alternative to LIBs as K^+ exhibits a low reduction potential similar to that of Li (-2.93 V vs SHE for K, -3.01 V vs SHE for Li). However, the larger size of the ion compared to Li^+ ($1.38 \text{ \AA}$ vs $0.76 \text{ \AA}$) introduces new challenges into the research of suitable electrode materials. Traditional transition metal oxides cathodes, for example, are structurally unstable whilst electrochemically cycling with K^+ ions.[9–11] Notably prussian blue analogues have shown good performance due to their ability to store K^+ ions with minimal structural change.[12] Like Li, K is able to intercalate into graphite forming the phase KC_8 , with a theoretical capacity of 279 mAhg^{-1} at a very low potential (0.25 V vs K^+/K). [13, 14]. Graphite is an appealing negative electrode thanks to its low cost and ease of manufacture, but unfortunately, the energy density of the intercalation of K^+ into graphite is lower than that of Li^+ (279 vs 376 mAhg^{-1}). The development of a potassium anode with high energy density is a crucial step for the energy density of KIBs to be competitive with current and future LIBs.

Red phosphorus (RP) recently earned attention

Figure 1. Schematic of the production process of the electrode material. 1) RP is wet milled in ethylene glycol to reduce its particle-size distribution. 2) The ball milled RP is mixed with graphite using a 7:3 mass ratio via dry milling. 3) The resulting composite is mixed with Super P and the binder to fabricate the electrode. Experimental details are illustrated in the experimental section.

due to its ability to alloy with potassium (KP) to deliver a very high theoretical capacity of $865 \text{ mA h g}_\text{P}^{-1}$. [15, 16] The drawbacks of phosphorous are a very low electronic conductivity ($10^{-14} \text{ S cm}^{-1}$) and a large volume expansion (162%) during the alloying reaction. Although it has been recently demonstrated that the stresses developed as a consequence of the volume expansion do not cause the fracture and failure of the particles - as occurs in crystalline Si with Li - the expansion/contraction process can cause the formation of cracks on the electrode material, followed by delamination and loss of electric contact, reducing its capacity over successive cycles. [17, 18] The preparation of RP-carbon composites has been demonstrated to be an effective way to mitigate these two drawbacks. In particular, ball milling has been proposed as a cheap, easy and scalable method to prepare these composites. [15, 16, 19] In a previous work, we demonstrated that the reduction of the particle size of phosphorus is an effective way to mitigate the stresses on the material and improve its cycle life with Na. [20] In the present work, we show the performance of that material with K. [20]. We prepared a RP-graphite composite where the RP particle size distribution was first reduced by ball milling, then mixed with graphite via another ball milling step to obtain the composite (Figure 1). This material demonstrated cycling performance with K superior to previous works, notably delivering a high first charge capacity ($723 \text{ mA h g}_\text{P}^{-1}$) and retaining most of its capacity even

at high current rates such as 5C.

To characterize the electrochemical performance of the RP-graphite composite, galvanostatic cycling experiments were performed. The material was tested in a three electrodes setup in a Biologic VMP3, using a EL-cell with K metal as both the counter and the reference electrode. The experiments were done in triplicate. Potassium bis(fluorosulfonyl)imide (KFSI) 1M in EC:DEC 1:1 was used as the electrolyte. The electrodes were cycled in the potential range 0.01 - 2.5 V vs K^+/K at C rates ranging from C/20 to 5C. In this work, we use "discharge" and "charge" to refer to the "potassiation" and "depotassiation" processes, respectively. For the operando Raman measurement, a 2032 coin cell was adapted in order to be used as operando cell. A 4 mm $\varnothing$ hole was drilled through the center of the positive side of the cell and a 7 mm $\varnothing$ sapphire window was glued on the inside of the coin cell part using epoxy, to allow the investigation of the electrode material from outside the cell whilst cycling. The cell was assembled using the standard procedure. In the operando experiments, a current rate of C/20 was applied. Impedance analysis was performed on a three electrode cell with frequencies ranging 200 kHz - 1 Hz, allowing a 1 h rest after every discharge/charge step.

To study the electrochemical performance of this material, galvanostatic cycling at C-rates ranging from C/20 to 5C was performed. In Figure 2, the electrochemical performances of the RP-graphite

Figure 2. Electrochemical performance of RP-C composite. a) shows the galvanostatic profiles of the active material at increasing rates and (b) shows the rate capability of the material. In (c) the differential plots of the cycles shown in (a) are shown. d) Cycling stability of the RP-graphite composite at 1C.

composite are shown. On the first cycle, the galvanostatic profile shows two plateaus. The first one, centered at about 1.2 V vs K^+/K , is mainly related to the formation of the SEI. The second slope, occurring at about 0.3 V vs K^+/K , is likely related to the progressive formation of the KP alloy as the final product of this electrochemical reaction, as Yang et al. predicted (Figure 2a).[21] On the first cycle, the material delivered a discharge capacity of 939 mAh g_P^{-1} and an initial charge capacity (ICC) of 723 mAh g_P^{-1} , with a coulombic efficiency of 77%. The greater-than-theoretical capacity, as well as the low coulombic efficiency on the first discharge is mainly due to the formation of the SEI. The material was then tested at increasing C-rates up to 5C (Figure 2b), showing a good rate capability, delivering 86.3% of the ICC when cycled at 2C and 75.8% of the ICC when cycled at 5C.

The differential capacity plot in Figure 2c shows peaks related to the formation of the alloy and intermediate phases during cycling. Only on the first cycle, we observe a peak in discharge at about 1.2 V vs K^+/K that is lower in the other cycles. As discussed earlier, this is mainly related to the formation of the SEI during the first cycle. We also observe that when increasing currents are used, the hysteresis between the discharge peak at about 0.3 V vs K^+/K and the charge peak at about 0.7 V vs K^+/K increases gradually until 1C and then more abruptly as higher currents (2C and 5C) are used. This change suggests an intrinsic limit of the material due to the slow diffusion of the ions in RP. Moreover, we observed that when a lower current of C/10 is applied again on the same electrode, an increase of capacity of about 3% of the ICC occurs. To understand the reason behind this

Figure 3. a) XRD analysis of RP, SFG6 and RP-graphite composite. b) Raman spectra of RP, SFG6 and RP-graphite composite. c) Particle size distribution of commercial RP and RP ball milled for 60h. d) TEM of RP-graphite composite. The white lines indicate the presence of graphite layers on the surface of the particles. e) SEM image of the cross section of the electrode and (f) reconstructed section of the PXCT scan of electrode material.

behaviour, we cycled the material at C/20 for the first three cycles and then at C/10 for the following cycles while measuring the impedance after every cycle. (Figure S1). We observed that, when a current rate of C/10 is applied, the capacity increases by about 5% after 30 cycles (715 mAh g_P^{-1} from 678 mAh g_P^{-1} , first charge capacity at C/10). (Figure S1a-c) The impedance analysis shows that the charge transfer resistance decreases with the number of cycles (Figure S1d). This can be indicative of an increase of the surface contact between the electrode and the electrolyte, possibly related to the formation of cracks on the electrode caused by the repeated expansion/contraction of RP particles during the alloying reaction, increasing the surface contact. This reduces the path length crossed by the K^+ ions to reach the bulk of the RP particles, increasing the capacity.[22] After 100 cycles, the material was still able to hold 95% of the ICC at C/10 ($648.5 \text{ mAh g}_P^{-1}$).

To test the material at higher rates, we first cycled it in similar conditions for 40 cycles, then we applied a current rate of 1C for 100 cycles. A similar increase in capacity was observed for the first 30 cycles at C/10. At 1C, the material delivered 629 mAh g_P^{-1} and retained 96.3% of the capacity after 100 cycles with a coulombic efficiency for each cycle of 99.4% (Figure 2). The excellent electrochemical properties and cycling stability of this material are likely related to the initial nanosizing of the RP particles and to the homogeneous mixing with a graphite matrix, both contributing to the application of the active material at high currents.

During the synthesis, the particle size distribution, measured using DLS, was greatly reduced after 60 hours of ball milling, resulting in a Dv_{90} (90% of the particles have a size lower than this value) of $0.79 \mu\text{m}$ from the original 12.49 (Figure 3a). This ball milling step did not induce the phase change

Figure 4. a) Schematic of the cell used for the Raman operando experiment. From top to bottom: cap, spring, spacer, K disk, glass fiber separator, copper grid with electrode material, sapphire window, case. b) Raman spectra acquired on the RP-graphite composite at different states of charge. c) Points on the galvanostatic profile of RP-graphite where the Raman spectra were acquired.

from RP to the black allotrope (BP), which has been reported to occur when RP is ball milled in dry conditions. [23] The EG that was added during the milling likely reduced the impact energy during milling, as to avoid the phase conversion. BP peaks were not visible in XRD patterns after the ball milling of RP (Figure 3b). Following the size reduction, RP was mixed for 48h with graphite to obtain the RP-graphite composite. XRD patterns showed the presence of a weak peak from BP[20], and broadened graphite peaks, with reduced intensity, suggesting a reduction in particle size and some amorphization (Figure 3b).

The microstructure of the material was investigated with Raman, TEM, SEM and PXCT. Raman spectra acquired of the composite (Figure 3c) suggest the carbon has coated the RP particles, as the characteristic peaks of RP in the range $300\text{--}500\text{ cm}^{-1}$, [19, 24] while the D and G peak from graphite clearly are visible at 1337 cm^{-1} and 1586 cm^{-1} respectively. The broadening of the graphite peaks agree with the XRD that some amorphization of the graphite occurred during the milling, which is a well reported consequence of this procedure.[25] TEM analysis of the composite showed the presence of a few layers of graphite coating the particles, (Figure 3d), supporting the finding in the Raman that a carbon coating was formed during the milling process. This finding moves beyond our previous work which showed the presence of P-C bonds on the outer layers (16 nm) of RP particles via x-ray photoelectron spectroscopy.[20] In our

previous work, we confirmed that the milling time of RP with graphite heavily affects the cyclability of the resulting material, and that long milling times such as 48h produce a very stable material with long cycle life with sodium.[20] In this work, we further investigated the morphology of the electrode material by SEM and PXCT analysis. Figure 3e,f show a SEM cross section of the electrode and a section of the reconstructed image from the PXCT scan of the electrode material. In (Figure 3f), RP is depicted in red, while graphite is black and Super P is light grey. The brightness of the colours is indicative of the electron density (dark colour = high electron density). As visible in the PXCT, it is possible to distinguish areas that are more P-rich and C-rich. However the resolution does not allow to clearly distinguish between the particles. SEM coupled with EDX, on the other hand, allow us to better define the composition near the RP particles, showing that the elements are more homogeneously distributed in the material, with some regions where the single elements are more abundant (Figure S2).

To investigate the changes of the material while cycling, we performed an operando Raman experiment. A schematic of the operando cell used is shown in Figure 4a. As explained earlier, only the graphite peaks are visible on the Raman. For this reason, we focused our attention to the carbon peaks during the reaction, in particular on the G peak. This peak has been reported to undergo notable changes during potassiation, due to different stages of intercalation of potassium

into the graphite layers.[26] As a standard, we performed the experiment on an electrode containing only graphite (Figure S3). We observed that, during potassiation, the peak visible as a shoulder of the G peak at 1616cm^{-1} increases in intensity while the intensity of the G peak decreases. This behaviour has been reported by Chacon-Torres et al., who demonstrated that the relative intensity of the two peaks is indicative of the different potassiation stages of graphite.[27] When graphite is fully potassiated, both peaks disappear and a large asymmetric band appears at about 1550cm^{-1} . This is related to the interaction between the metallic nature of the potassiated graphite and phonon processes as described by Share et al.[28] The experiment performed on the composite, however, shows a different behaviour. In this case, we observed a constant shift of the G peak to lower Raman shift during potassiation and to higher Raman shift during depotassiation (Figure 4b,c). This finding suggests that this behaviour is not entirely related to the reaction between graphite and potassium (which occurs at 0.25 V). Ni et al. described that changes in the position of the G peak can occur with strain of the graphite layers.[29] In particular, they demonstrated that, when the layers are stretched, the position of the G peak moves to lower Raman shift. We speculate that this phenomenon is what is causing the reversible shift of the G peak in our composite. In our case, the graphite layers that make the carbon coating on the particles can be stretched during the potassiation of RP and its volume expansion, resulting in about 5% strain of the layers (calculated from [29]) that could be the cause of the shift of the G peak. As previously mentioned, the shift is reversible, and the G peak moves to its original position when RP is fully depotassiated.

In Figure 5a and Table S1 the performance of the RP-C composite described here are compared to some of the most promising K-ion anodes reported in the literature. For ease of comparison, the capacity is normalised by the total electrode mass (including carbon, additives and binder). The materials selected for comparison are other P/C composites prepared by ball milling, carbonaceous anodes such as graphite and hard carbon, and Sn_4P_3 , with an electrode mass loading in the range of $1.11\text{-}1.88\text{mg cm}^{-2}$ and a first cycle coulombic efficiency between 50-68% for P-based electrodes, around 80% for carbonaceous electrodes and about 66% for Sn_4P_3 based electrode (Figure 5b). Compared to previous works, our

material is one of the best performing, especially at high rates. The capacity delivered by the electrode is $403\text{mAh g}_{\text{electrode}}^{-1}$ for a current of $24\text{mA g}_{\text{electrode}}^{-1}$. For a current one hundred times greater, the material is still able to deliver 75.8% of the capacity, showing its superior performance and capacity retention, similar to graphite and hard carbon. Moreover, the first cycle coulombic efficiency is also very high, second only to carbonaceous materials that, however, deliver a lower capacity. This demonstrates that the nanosizing of RP particles, with a simple and scalable method such as ball milling, prior to mixing with carbon additive is an effective way to obtain high performing electrodes.

In summary, we synthesized a RP-graphite composite using ball milling to reduce the particle size of RP in a first step and then to mix RP with a decreased particle size with graphite in a second step. The resulting material showed excellent performance with high rate capability up to 5C and long cycle life at 1C. A maximum capacity of 723mAh g^{-1} was achieved at C/20 and 75.8% of the capacity was retained when currents as high as 5C was applied. At 1C the material was able to retain 96.3% of the capacity after 100 cycles. Analysis on the morphology with SEM-EDX revealed that P and C are homogeneously distributed in the electrode. TEM showed that a carbon coating is present on the particles, which could cause the superior performance of the material. Operando Raman analysis showed that the G peak related to the graphite layers reversibly shifts to lower frequency during the RP alloying and moves back to the origin during dealloying. This could be related to the stretching of the graphene layers caused by the volume expansion of the RP particles. This material achieved better performance compared to previous anode materials previously reported, posing as an ideal candidate for application in KIBs.

Experimental section

Material and composite preparation

The RP-graphite composite was prepared using a procedure previously reported.[20] 3.4 g of commercial RP (Sigma Aldrich) was ball milled for 60 h (FRITSH Pulverisette 7) in a 45 ml zirconia jar with the addition of 10 ml of ethylene glycol (EG) and 180 balls ($\varnothing$ 5 mm) at 500 rpm. The EG serves the purpose to reduce the impact energy of

Figure 5. a) Comparison between the performance of the material presented in this work with other anode materials previously reported in literature. b) Comparison of the first cycle coulombic efficiency of the materials. Full details of the electrode materials are shown in table S1.[15, 16, 19, 30–32]

the balls, thus preventing the phase conversion of RP to black phosphorus.[20, 23] Its high viscosity and low boiling point improves the safety of the procedure by reducing the risk of overpressure. The ball milled RP was then mixed with graphite (SFG6, TIMCAL) (7/3 phosphorus-to-carbon mass ratio) for 48h in a PM100 ball mill using a 12ml stainless steel jar with 5 balls ($\varnothing$ 1cm, total mass about 20g) at 500rpm to ensure a homogeneous mixture of the two components. The resulting RP-graphite composite was mixed with Super P carbon (TIMCAL) and polyacrylic acid binder (PAA, 450 kDa, Sigma Aldrich) in a 8:1:1 mass ratio respectively, using NMP as the solvent in a glovebox with low O₂ and H₂O content (< 1ppm). The obtained slurry was cast on a copper foil 35 μ m thick and let dry overnight in a fume hood. Afterwards, the casting was heated up to 100 °C under vacuum to remove further residues of solvent. The resulting mass loading was about 1 mgp cm² with an average thickness of 15 μ m. The porosity of the casting was visually evaluated via SEM cross sectional analysis and resulted to be about 0.1. 1 cm $\varnothing$ disks were cut from the casting to be used as electrodes for the electrochemical tests. For the operando Raman experiments, a copper grid was used instead of a foil, to allow the sampling of the electrode material. The casting procedure used is the same as the one previously described. The graphite electrode

prepared as standard for the Raman operando was made by mixing pristine SFG6 and PAA binder in a mass ratio 9:1 using NMP as the solvent. The slurry was cast on a copper grid and dried as previously described for the composite.

Physio-chemical characterization

The RP-graphite composite was characterized using a Rigaku Smartlab 9kW x-ray diffractometer with a Cu K α source to interrogate the presence of crystalline impurities. The particle size distribution of RP was measured using dynamic light scattering (DLS) using a Malvern Mastersizer 2000 analyzer. The lasers used for the analysis were a He/Ne (633 nm) and a diode laser (466 nm). The morphology of the RP and the composite was investigated using a Zeiss Merlin scanning electron microscope with a built-in Oxford Instruments X-Max 150 energy-dispersive Xray (EDX) and a JEOL 3000F field emission gun transmission electron microscope, operated at 300kV. Cross sections of the electrodes were prepared using a precision etching and coating system II (PECS) Gatan, with an argon ion beam. Operando Raman spectroscopy experiments were performed on a Renishaw InVia Raman microscope using a 512 nm diode laser. The operando cell used in this experiment is described in the next section. The Raman spectrum of the electrode was acquired

while the cell was cycling. Ex situ ptychographic X-ray computed tomography (PXCT) was conducted on the I13 beamline at Diamond Light Source in the United Kingdom. The phosphorus anode samples were extracted from the electrode then loaded into a borosilicate glass capillary (diameter of capillary = 100 μm). The end of capillary was sealed by polymer clay and cyanoacrylate adhesive. The capillary was prepared in an Ar-filled glovebox to prevent air exposure of the sample. A monochromatic beam of 15 keV was selected with a fixed sample-detector distance of 9.5 m, the spatial resolution of each pixel was 55 nm. For each ptychographic tomography scan of phosphorus sample, 900 projections were taken equiangularly from -90° to 90° . For each projection, a region of $26 \mu\text{m}^2 \times 26 \mu\text{m}^2$ was scanned with a step size of $1.5 \mu\text{m}^2 \times 1.5 \mu\text{m}^2$, with an exposure time of 0.05 s. The obtained projections were processed using the software Blender.

Electrochemical characterization

To characterize the electrochemical performance of the RP-graphite composite, galvanostatic cycling experiments were performed. The material was tested in a three electrodes setup in a Biologic VMP3, using a EL-cell with K metal as both the counter and the reference electrode. The experiments were done in triplicate. Potassium bis(fluorosulfonyl)imide (KFSI) 1M in EC:DEC 1:1 was used as the electrolyte. The electrodes were cycled in the potential range 0.01 - 2.5 V vs K^+/K at C rates ranging from C/20 to 5C. In this work, we use "discharge" and "charge" to refer to the "potassiation" and "depotassiation" processes, respectively. For the operando Raman measurement, a 2032 coin cell was adapted in order to be used as operando cell. A 4 mm $\varnothing$ hole was drilled through the center of the positive side of the cell and a 7 mm $\varnothing$ sapphire window was glued on the inside of the coin cell part using epoxy, to allow the investigation of the electrode material from outside the cell whilst cycling. The cell was assembled using the standard procedure. In the operando experiments, a current rate of C/20 was applied. Impedance analysis was performed on a three electrode cell with frequencies ranging 200 kHz - 1 Hz, allowing a 1 h rest after every discharge/charge step.

Data availability

The authors declare that all data supporting the findings of this study are included within the paper and its Supplementary Information files. Source data are available from the corresponding author upon reasonable request.

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Competing Interests

The authors declare no competing interests.

Author contributions

I.C and M.P conceived and designed the experiments. I.C. prepared the samples and performed electrochemical tests and Raman, XRD, SEM, EDX and DLS analysis. A.W.X performed the TEM analysis. J.I. wrote the proposal for the PXCT experiment at Diamond Light Source and gave advice for the sample preparation. H.J.L performed the PXCT analysis at Diamond Light Source. J.A contributed to the final manuscript.

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