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Potassium-ion Battery Anode Materials Operating Through the Alloying–Dealloying Reaction Mechanism

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Anode materials that operate via the alloying–dealloying reaction mechanism are well known in established and maturing battery systems such as lithium- and sodium-ion batteries. Recently, a new type of metal-ion battery that utilizes K^+ ions in its operating principle has attracted significant attention due to a possibility of building high voltage cells using an abundant potassium ionic shuttle. Establishing promising electrode materials is of paramount importance for this new type of battery. This feature article summarizes available early results on the alloying–dealloying anode materials in potassium electrochemical cells. Based on original research (some data are presented for the first time) and independently published literature, experimental results on silicon, tin, phosphorus, antimony, and lead-containing anodes are critically discussed. The electrochemical properties, charge storage mechanisms, and achievable capacities are considered. The results are compared with the behaviors of the same materials in lithium and sodium cells, and the importance of the volumetric parameters of electrodes is emphasized. Finally, a number of further research directions in these interesting anode materials are suggested. The feature article provides a useful reference for the growing number of researchers and specialists working in the field of emerging metal–ion batteries with non-lithium chemistries.

1. Introduction

Non-aqueous potassium-ion batteries are an exciting new type of “rocking chair” batteries utilizing organic electrolytes and potassium, an abundant chemical element (2.09 wt% in the Earth’s crust), as a shuttle.^[1–3] They are expected to become one of the next generation technologies to replace

state of the art lithium-ion batteries in a range of stationary applications, such as, for example, energy-efficient power grids, localized storage of electricity generated from photovoltaic cells at home and, more generally, storing excess electricity in the downtime periods of energy generation from renewable sources. The future demand for lithium-ion batteries is predicted to increase continuously due to their forecasted widespread use in electric vehicles, portable devices and home battery storage,^[4-6] but there are considerable concerns in the community associated with lithium's rarity (only 0.0017 wt. % in the Earth's crust),^[3] uneven global distribution (predominantly in Chile, Bolivia and China) and the expected increase in the cost of lithium-containing minerals (Li_2CO_3) associated with the increase in demand.^[7,8] These future challenges underpin emerging research interest in alternative, more sustainable and affordable, rechargeable battery technologies. In recent years, sodium-ion batteries have attracted much attention because of the natural abundance of raw materials and the similarity of chemical properties of sodium to those of lithium. Potassium has a similar abundance to sodium in nature and also a number of prospective advantages as a shuttle carrier for "rocking chair"-type rechargeable batteries. These advantages include a higher possible voltage of the potassium-ion batteries (up to 0.2-0.3 V higher than that of sodium-ion batteries),^[1] better conductivity of potassium electrolytes and the possibility to use some key established electrode materials (e.g., graphite)^[9-12] that do not react with sodium ions enough to justify their use in sodium-ion batteries. These attractive characteristics have established potassium-ion batteries as one of the current emerging battery systems of interest for both energy storage and materials science research communities.

In order to justify the feasibility of a new type of high voltage battery systems based on potassium ions, certain initial milestones need to be achieved, including identification of suitable

anode and cathode materials as well as demonstration of initial prototypes of full cell batteries with promising characteristics. These key initial steps have been successfully undertaken over the last two years. Some possible cathode materials have been identified, including Prussian blue (proposed as early as 2004 by Ali Eftekhari),^[13] cyanoperovskite $K_xMnFe(CN)_6$,^[14] $K_{0.3}MnO_2$,^[15] K_xCoO_2 ,^[16] $KVOPO_4$ ^[17] and $K_3V_2(PO_4)_3$.^[18] An important development on the anode side was the realization that graphite can intercalate potassium, just like it can intercalate lithium in lithium-ion battery anodes, to yield stage I intercalation compound KC_8 and theoretical capacity of 278 mAh g^{-1} . Finally, the possibility of obtaining functional full cell potassium-ion batteries has been unambiguously demonstrated by recent studies. In particular, a $K_{0.3}MnO_2$ -hard carbon/carbon black battery and a $K_2C_6O_6$ - $K_4C_6O_6$ cell with organic electrodes have been demonstrated as first working prototypes of potassium-ion batteries.^[15,19] Recently, Komaba et al. have reported a hexacyanoferrate(II)/graphite cell with a high energy density and an operating voltage approaching 4V.^[20] All these exciting developments indicate that rocking-chair potassium-ion batteries are indeed quite promising and will emerge as a viable practical technology over coming years.

Anode materials are the key components of any battery and define, to a large extent, the characteristics and practicality of various battery systems. One of the disadvantages of sodium-ion batteries is that anode materials well-established for lithium-ion batteries such as graphite and silicon, cannot be used in these cells. Indeed, only small amounts of sodium can be intercalated into graphite (the compositions of NaC_{70} ^[21] and NaC_{64} ^[22] have been measured in the intercalation products). Similarly, high capacities of Si in lithium cells (with the theoretical value of 4200 mAh g^{-1})^[23] are not achievable in sodium cells, with no or only limited redox reaction between silicon and sodium.^[24] In practical terms, this means that completely new fabrication and processing methods

need to be established at a large scale in order to manufacture other, alternative anode materials for sodium-ion batteries. In contrast, graphite robustly intercalates potassium and is available as an anode material for potassium-ion batteries.^[9-12] That means that the existing methods for manufacturing battery graphite (for lithium-ion batteries) can be adapted, after certain modification, for the anodes of potassium-ion batteries. Si has not been yet studied as an anode material for potassium-ion batteries. If it could also alloy with potassium (in a similar fashion to how it alloys with lithium), the whole anode chemistry of lithium-ion batteries would be directly transferable to potassium-ion systems, making transition to the implementation of these new batteries easier.

Silicon belongs to a class of the anode materials that are capable of electrochemical alloying with an alkali element (such as lithium or sodium). As a result of such a redox reaction (that can be generalized as $x\text{A} + y\text{M}^+ + y\text{e}^- \leftrightarrow \text{A}_x\text{M}_y$, where A is an alloying element and M is an alkali metal), very high capacities can be achieved. For example, Si, Ge, P, Sn, Sb and Bi are known as lithium-ion battery anode materials with theoretical capacities of 4200, 1600, 2596, 994, 660, 384 mAh g⁻¹, respectively.^[23, 25-27] Similarly, P, Sb and Sn have been established as the anode materials that can electrochemically alloy with sodium (theoretical capacities of 2596, 660, 847 mAh g⁻¹, respectively).^[26, 28-30] The knowledge of how potassium can alloy electrochemically with various elements was, however, quite limited until recently. It has been previously predicted, based on calculations, that Sn and Si are suitable anode materials for potassium-ion batteries and they can alloy with potassium to form KSn and KSi alloys to deliver capacities of 226 and 955 mAh g⁻¹ at average voltage of 0.32 and 0.15 V vs K/K⁺, respectively.^[31] The experimental confirmations were, however, lagging these prior theoretical attempts, and not much information was known about materials that can electrochemically alloy with potassium. This feature article aims to fill this gap and

illustrate the current status of experimental developments of anode materials that can electrochemically alloy with potassium in non-aqueous potassium batteries.

Here, recent progress in the anode materials for potassium-ion batteries that operate via the alloying-dealloying mechanism is presented on the basis of our own experimental results and independent literature data. Silicon, tin, phosphorus and antimony-containing anodes are systematically assessed as possible anode materials, and preliminary understanding of some other chemical systems (e.g., Pb and Sn_3P_4 binary alloy) is presented. The applicability of these alloying materials to the potassium battery anode chemistry is discussed and reaction mechanisms are analyzed. Furthermore, the behavior of these materials in potassium cells is compared with that demonstrated in lithium and sodium cells. We also include a comparative analysis of various alloying systems in terms of their volumetric characteristics in potassium-ion battery electrodes. Finally, the article is concluded by pointing out the existing challenges in this class of anode materials for potassium-ion batteries and suggesting future research directions in this interesting area.

2. Si-based anodes

Silicon is one of the attractive anode materials of interest in lithium-ion batteries, and on-going efforts are currently directed to commercialize it in this application.^[32,33] The attractive properties of silicon in lithium cells include electrochemical activity at low potentials with respect to the lithium metal electrode and its very high theoretical capacity (4200 mAh g^{-1} , through the mechanism of alloying with lithium to yield $\text{Li}_{4.4}\text{Si}$). The synthesis methods for silicon nanoparticles are rather mature, and, furthermore, a number of methods to create composites of Si with carbon have been

established.^[34,35] Moreover, silicon is environmentally friendly and abundant in Earth's crust.^[3] It is naturally of interest to investigate if Si may be an attractive anode material in potassium-ion batteries via a mechanism of alloying with potassium. Previous calculations have suggested that such an alloying mechanism can indeed be possible to yield a theoretical capacity of 955 mAh g⁻¹ (through the formation of a KSi alloy);^[31] however, no experimental studies have been conducted on the behavior of silicon in potassium-ion batteries so far.

In this context, we have attempted to investigate the electrochemistry of a silicon-based anode in potassium-ion electrochemical cells. It is known from the literature that the main challenges for the practical implementation of Si anodes in lithium-ion batteries are a huge volume variation during lithiation and delithiation processes (> 300%) and unstable surface electrolyte interphase (SEI) films; these issues result in pulverization, low cycling efficiency, and permanent capacity loss in electrodes. A common way to overcome these issues is to minimize the size of the silicon particles and control the nature of the electrode-electrolyte interface via preparing an electrode material in the form of Si nanoparticles dispersed in a carbon component.^[36-38] For example, a composite of Si nanoparticles with graphene may be a suitable type of an optimized model system to study the behavior of silicon based electrodes in battery cells.^[39] In order to evaluate Si as a possible candidate for an electrode material for potassium-ion batteries, the need to optimize the structure of the electrodes was taken into account and a sample of a composite of Si particles with graphene (similar to the one used in ref. [39]) with a weight ratio of Si to graphene of 1:1 was purchased from Carbon Allotropes Pty Ltd (Sydney, Australia). Samples of pure Si particles and graphene were also obtained from the same source as additional references.

The Si-graphene model sample was characterized by x-ray diffraction (XRD, Cu K α radiation (1.54 Å)), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA) in flowing air atmosphere. The sample was also evaluated preliminarily in lithium half-cells to ensure that the electrochemical reactivity with Li occurs as expected. The results are shown in **Figure 1**. The XRD pattern of the Si-graphene composite (Figure 1a) matches the standard pattern of silicon (diffraction file JCPDS #00-005-0565). A typical morphology of Si-graphene composite is depicted in Figure 1b. The Si-graphene composite contains micrometer-sized aggregates with visible Si nanoparticles on the surface. The TEM image (Figure 1c) shows Si particles (darker contrast) with sizes from tens of nm to two-three hundred nm and thin sheets of carbon in this material. Approximately 50% weight loss was recorded in a TGA experiment at 500°C (Figure 1d) due to the combustion of graphene. Si nanoparticles are stable against oxidation up to 800 °C due to a protective native oxide layer on their surface. Therefore, we could confirm independently that the mass fraction of Si in the composite was close to 50%. To make sure that our model system is a proper Si-based electrode system for the battery application, we tested the composite in lithium cells first. Lithium metal was used as a reference/counter electrode in a coin cell and 1M LiPF₆ in a mixture of ethylene carbonate (EC), diethylene carbonate (DEC), and dimethyl carbonate (DMC) with a volume ratio of 1:1:1 was used as an electrolyte. Indeed, the sample exhibits a reversible capacity of about 1800 mAh g⁻¹ in the first few cycles (Figure 1e and 1f), in line with our expectations for the behavior of our model material in a lithium cell.

In order to understand the electrochemical performance of silicon in potassium cells, the Si-graphene electrodes were evaluated in two-terminal configuration in coin cells using potassium metal as reference/counter electrodes. The electrolyte was 0.75 KPF₆ in the mixture of ethylene

carbonate (EC) and diethyl carbonate (DEC) in 1:1 volume ratio. The Si and graphene electrodes were tested as well as additional references (**Figure 2**). The electrochemical data for the Si-graphene composite electrodes as well as electrodes containing only Si or graphene are depicted in Figure 2a-2f. All tests were galvanostatic charge-discharge routines carried out under a current load of 50 mA g⁻¹ within potential limits of 2 – 0.01 V vs K/K⁺. As it follows from Figure 2a, the Si-graphene electrode displays reasonably stable capacity above 100 mAh g⁻¹ in the course of fifty cycles (with reversible capacities of 130 and 100 mAh g⁻¹ in the first and last cycles). Note that the specific capacity is based on the total mass of the Si-graphene composite in this measurement. With the exception of the first cycle, the shape of the charge-discharge profiles of the Si-graphene electrode is rather triangular, with rather capacitive response, not typical for the alloying-dealloying process. It indicates that the carbon component may be the main contributor to the apparent capacity, and the contribution of Si is, perhaps, negligible. To verify this, we looked closely at electrochemical performances of individual Si and graphene electrodes. Only tiny capacity can be measured from pure Si electrodes in potassium cells (Figure 2c and 2d), in line with the idea that Si is probably inert towards the alloying process with potassium. The observed minor electrochemical activity is likely to be of a capacitive nature. Indeed, a number of silicon materials with a relatively developed surface area (e.g., arrays of Si nanowires) have been previously considered as supercapacitor electrode materials.^[40] On the other hand, the pure graphene electrode shows elevated reversible capacity at a level of 120-200 mAh g⁻¹ over the first 50 cycles of cycling (Figure 2e and 2f). On the basis of these data, it is reasonable to conclude that the alloying process of Si and potassium does not occur to any significant extent and the charge storage is predominantly due to the contribution of the graphene component.

In order to provide additional evidence, XRD and SEM analyses were performed on the Si-graphene electrodes after cycling. According to the reference source,^[41] Si and potassium may adopt a range of alloys (e.g., KSi, K₁₂Si₁₇, K₇Si₄₆, K₈Si₄₆), and it is reasonable to expect the appearance of at least one of these alloys in the XRD pattern of used electrodes. The XRD patterns of the electrodes after the first charge and discharge in potassium half-cells are shown in Figure 2g and 2h. It can be seen that visible peaks from Si (JCPDS no 00-005-0565) are still present after first discharge and the first charge of the cells, and there is no apparent change in the intensity of those peaks. The rest of the features in the patterns originate from Kapton tape (used for protecting the sample from the exposure to air and moisture; a broad hump at 20-35°), copper substrate and sample holder (minor signals in the range of 40-50°). It is also known that alloying of anode materials with an alkali metal often causes a significant volume change in the electrodes, resulting in the development of cracks and delamination of electrodes. To check the electrodes for this type of developments, post-cycling SEM investigation was carried out on the electrodes after cycling up to 100 cycles at a current rate of 50 mA g⁻¹ (Figure 2h). No major cracks or disruptions is observed in the cycled electrode, indicating that the processes in these electrodes do not cause breakdowns in the mechanical integrity of the electrodes.

To sum up the existing evidence on the behavior of Si-based electrodes in potassium cells, no evidence of alloying of silicon and potassium is visible. In contrary to the behavior expected from earlier calculations,^[31] Si remains inert to any significant electrochemical interaction with potassium in our experiments. Because of the inert nature of silicon in potassium cells, other materials such as tin, phosphorus and antimony need to be evaluated to gain understanding of the feasibility of using

alloying anode materials in potassium-ion batteries. The current results in these alloying systems are reviewed in the following sections.

3. Sn-based anodes

Another known type of anode materials that can alloy electrochemically with alkali metals such as lithium and sodium is based on the incorporation of tin (Sn) as an active component of the electrodes.^[29, 42-45] It has been established previously that Sn possesses high theoretical capacities of 990 mAh g⁻¹ (corresponding to the formation of Li₂₂Sn₅ as the end product of the alloying reaction) in lithium cells and 847 mAh g⁻¹ (to yield Na₁₅Sn₄ product as the end product of alloying) in sodium cells. It is also known that tin experiences significant volume variations during alloying (420% volume change in sodium cells and 260% in lithium cells). For that reason, in order to avoid the mechanical instability of the electrodes, resulting in the fast capacity fading,^[29, 43, 46] a common strategy of incorporation of the tin component in a suitable carbon component is applied.^[47-49] For the assessment of tin-containing electrodes as anodes for potassium-ion batteries, we applied a similar strategy of dispersing tin nanoparticles in a carbon material.

The detailed preparation procedure can be found elsewhere.^[50] In brief, a Sn-carbon composite with a composition of 70 wt.% Sn and 30 wt.% C was prepared via mechanical ball-milling of tin and graphite powders (**Figure 3**). The Sn-C model sample was characterized by XRD (Cu K α radiation (1.54 Å)) and TEM. The characterization results are shown in Figure 3a-c. The XRD pattern of the Sn-C composite (Figure 3a) matches the standard tetragonal phase of tin (JCPDS # 04-004-7744). An XRD pattern of the original Sn powder is also included for comparison. The graphitic peak

at around 26° is no longer detected in the XRD pattern of the composite due to the loss of well-organized graphitic structure during ball milling. TEM analysis was carried out to get the visual information about the structure of the Sn-C composite. A bright-field TEM image of the sample (Figure 3b) shows the morphology of the composite. An energy filtered image (Figure 3c), composed by overlaying elemental maps of Sn (blue color) and carbon (yellow color), demonstrates the distribution of components of the electrode material. As it follows from the interpretation of the elemental contrast in the image, nanoparticles of Sn are distributed in the carbon component.

To understand the electrochemical performance of Sn-C in potassium cells, the Sn-C electrodes were tested in a two-terminal configuration in coin cells using potassium metal as reference/counter electrodes. The electrolyte was 0.75 KPF₆ in the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) in 1:1 volume ratio. The electrodes assembled using metallic Sn and milled graphite were also tested to evaluate their performance on a standalone basis and estimate possible contribution of the milled carbon component to the measured capacities of the Sn-C composite. Figure 3d shows the cycling performances of Sn-C, pure Sn and milled graphite at a current rate of 25 mA g⁻¹ within a potential window of 2.00-0.01 V vs K/K⁺. The Sn-C composite is capable of delivering a reversible capacity as high as 150-170 mAh g⁻¹ in potassium cells in the first few cycles. However, the capacity decreases afterwards and reaches the value of approximately 110 mAh g⁻¹ after 30 cycles. Similar to the situation in lithium and sodium cells,^[49, 51] the electrode assembled with coarse Sn shows only negligible capacity in a potassium cell as well. It is also important to estimate the contribution of the carbon component in the Sn-C electrode because it is electrochemically active. This can be done by measuring the capacity of the electrode assembled using the sample of milled graphite. From our data, the carbon-only electrode delivered capacity at a

similar level with that of a composite but slightly lower. Figure 3e shows the charge-discharge curves of Sn-C electrodes in selected cycles. An irreversible capacity loss of 148 mAh g^{-1} is recorded initially, which is a common phenomenon in battery electrodes due to a solid electrolyte interphase layer (SEI) formation on the surface of the electrodes at the beginning of cycling.

In order to understand the charge storage mechanism in the Sn component and confirm the presence of a reversible alloying process with potassium, ex-situ XRD analysis of the electrodes extracted from the charged and discharged cells was performed.^[50] The XRD pattern of an electrode discharged to 0.01 V vs K/K⁺ (Figure 3f, lower pattern) demonstrates the formation of tin alloys of a certain kind. Although it was not possible to comprehensively index the pattern, some major peaks coincide with the expected peaks of a K_4Sn_{23} phase (JCPDS no. 04-004-8647) and K_2Sn_5 phase (analogous to a known lithium-tin alloy). It is likely that not the final phase of the alloying process is detected in this experiment but reaction intermediates instead. De-alloying can be confirmed by the analysis of the XRD pattern of the electrode extracted from a cell charged back to 2 V vs K/K⁺ (Figure 3f, upper pattern) as tin diffraction peaks re-appear in the pattern. The experimental evidence suggests that tin is capable of alloying and de-alloying with potassium in a reversible manner.

Follow-up studies on tin electrodes in potassium cells were conducted by Wang et al.^[52] By using a combination of XRD and TEM analyses, these authors were able to pinpoint a possible final phase for the alloying process. The KSn composition is proposed as the final alloy in the electrochemical alloying of tin and potassium.^[52] The process implies a theoretical capacity of 226 mAh g^{-1} , broadly consistent with our measurements (the demonstrating Sn capacity of $150\text{-}190 \text{ mAh g}^{-1}$ after taking the contribution of the carbon component into the account^[50]). A final potassiation phase of KSn has been also suggested by Zhang et al.^[53]

Wang et al.^[52] took characterization of tin electrodes further and conducted in-situ TEM studies of potassiation of tin (**Figure 4**). In such an experiment a transmission electron microscopy – scanning tunneling microscopy (TEM/STM) sample holder is used. This sample holder contains platinum and tungsten rods that can be brought into contact with each other. When a sample of tin nanoparticles is attached to the Pt rod and a piece of potassium metal is affixed to the W rod, a miniaturized battery half-cell is formed when the materials are brought into contact. A thin layer of potassium oxide and hydroxide that forms on potassium metal upon the exposure to air may serve as an electrolyte between the tin and potassium electrodes. The pair of Pt and W rods can be biased to the desired potential, causing tin on one of the electrodes inside the TEM instrument to potassiate and depotassiate. Changes in the working electrode can be monitored in real time. The potassiation of tin is conducted by applying a negative potential of -2V vs potassium metal to the tin electrode (Figure 4a-k). It is implied that the potassiation happens in a two-step mechanism. An initial K-poor phase forms first with a clear phase boundary with tin, and the boundary gradually propagates into the depth of the tin particle (Figure 4b,c). The particle further potassiates without a phase boundary, implying a single phase mechanism in the second step. A KSn phase with a tetragonal structure is detected after potassiation by electron diffraction (Figure 4k). De-potassiation is conducted under beam-blank conditions by applying a positive potential of +1 vs potassium electrode to the working electrode. Formation of nanopores in the particle can be observed, and limited volume shrinkage of tin particles occurs because of the formation of nanopores (Figure 4g-i).

Ramireddy et al.^[54] have recently studied phase changes and stress generation in thin film Sn electrodes. In-situ synchrotron XRD measurements have been conducted during cyclic voltammetry scans. Similarly to the previous study,^[52] a tetragonal KSn phase has been detected upon

potassiation at low potentials in these experiments. The stress measurements during the galvanostatic charge-discharge in the first cycle have demonstrated the development of compressive stress in the beginning of potassiation with the following stress flattening and intermittent release (attributed to plastic deformation and mechanical degradation). The stress reverses towards the tensile direction during the depotassiation stage, and, again, flattening of the stress towards the end of the depotassiation step has been observed. Interestingly, the surface phenomena (formation of the SEI layer) have been observed only during the second potassiation in the potential range of 1.2-1.5 V vs K/K⁺, which is accompanied by some additional compressive stress generation in the electrode. The influence of the potential range on the cyclic stability has been further explored, and it has been demonstrated that restricting the upper potential cut-off to 1.2 V vs K/K⁺ (0.01 – 1.2 V potential range) leads to an improved cyclic stability in thin film Sn electrodes.

A prototype of a full cell battery utilizing a tin anode has been demonstrated by Ji et al.^[55] in the form of the so-called dual-ion battery. While the electrochemical process in the cathode of this cell is related to the intercalation of anions into the graphitic structure, the anode operates via alloying with potassium, and Sn foil is used as an electrode in this work. It has been stated that a potassium-ion-based dual-ion battery using Sn as anode is able to deliver a high reversible capacity of 66 mAh g⁻¹ at a current density 50 mA g⁻¹ over the voltage window of 3.0-5.0 V. The authors of this work have also attempted to investigate the alloying/de-alloying mechanism of Sn in a potassium cell. According to their interpretation, the formation of the K₂Sn alloy composition happens in their tin electrode upon alloying,^[55] different the conclusions of other studies.^[50, 52, 53, 54]

As it follows from the above results, Sn is capable of alloying with potassium, and the final product of alloying (KSn phase, as suggested by the majority of the published studies^[50, 52, 53, 54])

coincides with the phase predicted from calculations.^[31] The findings about the alloying activity of tin with potassium have important implications. Although Si, an established anode candidate for lithium-ion battery anodes, does not react substantially with this element, other materials can alloy with potassium. It is worthwhile to investigate what other systems may be active in electrochemical alloying with potassium and emerge as anode candidates for potassium-ion batteries. In particular, phosphorus (P) and antimony (Sb) are known for their alloying ability with lithium and sodium. The reactivity of these phases with potassium is considered in the next two sections of this article.

4. P-based anodes

Phosphorus is one of the most interesting materials that can alloy electrochemically with alkali metals. In lithium-ion and sodium-ion batteries this material has a very high theoretical capacity (2596 mAh g⁻¹, based on three-electron electrochemical reactions to form Li₃P or Na₃P alloys.^[56-59] Phosphorus is an element of the fifth group in the Periodic Table and has three main allotropes - white, red and black varieties. Among these three allotropes, white P is chemically unstable and flammable in air at about 50°C, which makes it unsuitable for easy processing and the application in batteries.^[60] In contrast, red and black forms of phosphorus are chemically stable at room temperature. A well-known red phosphorus phase is amorphous in nature and relatively less conductive while the orthorhombic black phosphorus is a thermodynamically more stable allotrope with a higher conductivity, non-flammable and insoluble in most solvents.^[56] Considering the promise of phosphorus-based materials in lithium-ion and sodium-ion batteries (high capacity electrodes containing both red and black phosphorus phases have been reported), it is of a

significant interest to evaluate how phosphorus-containing electrodes can behave as potassium-ion battery anodes.

A phosphorus-based anode has been first reported for the application in potassium-ion batteries by Zhang et al.^[53] A phosphorus – carbon composite (87.5 wt.% P and 12.5 wt.% C) has been produced by mechanical ball milling and tested in a two-terminal coin cell configuration vs potassium metal in 0.8 M KPF₆ in an ethylene carbonate (EC) – diethyl carbonate (DEC) solution (1:1 by volume) as an electrolyte. While a very high potassiation capacity in excess of 2100 mAhg⁻¹ has been recorded in the first cycle, a quick and dramatic capacity decay has been subsequently observed. It has been suggested that a three electron charge storage mechanism to form a K_{3-x}P-type alloy (similar to the reaction mechanisms known in lithium and sodium cells) may be in operation. The authors conclude that an electrode based on a phase of pure phosphorus is not practical due to the observed unstable cyclic behavior, and electrodes containing alloys of phosphorus with other elements (such as Sn₄P₃) should be used instead.

In an independent study, our group has evaluated the electrochemical performance of electrode materials containing black (orthorhombic) phosphorus.^[61] Similarly to the case of a tin-based material described in the previous section, a composite material in the form of nanoparticles of black phosphorus dispersed in a carbon component has been prepared. Black phosphorus powder has been obtained initially by mechanical milling of red phosphorus powder in a planetary ball mill under appropriate milling conditions. Subsequently, two composite materials (with compositions of 50 wt.% P - 50 wt.% C (BP-C 1:1 sample) and 70 wt.% P - 30 wt.% C (BP-C 7:3 sample)) have been prepared by mechanical milling of the mixtures of the black phosphorus powder with graphite, and evaluated in potassium cells. The results of characterization of these samples by XRD (Cu K α

radiation (1.54 Å)) and energy-filtered TEM are shown in **Figure 5**. The XRD pattern of black phosphorus material obtained at the initial stage matches the standard pattern of the orthorhombic phase of black phosphorus (JCPDS #00-009-0020, Figure 5a). The XRD patterns of black phosphorus - carbon composites (BP-C 1:1 and BP-C 7:3) demonstrate that the phase of black phosphorus is retained in the final composite materials. Certain broadening of the diffraction peaks is visible, suggesting a reduction in the size of crystallites. Graphitic XRD peaks are not detected because of the amorphization of the carbon component during milling. The energy-filtered TEM analysis was carried out to visualize the structure of the black phosphorus - carbon composite (BP-C 1:1) and is depicted in Figure 5b,c. An elastic TEM image (Figure 5b) displays the shape and morphology of an area in the sample. The distribution of the elements in the same area is shown in the energy-filtered image (Figure 5c) with elemental contrast (color scheme: red - phosphorus, green - carbon). An excellent degree of mixing between the phosphorus and carbon components is observed. Further mapping of thin areas in the samples by scanning TEM helps to determine that black phosphorus is present in the form of nanoparticles.^[61]

In order to evaluate the electrochemical performance of black phosphorus-carbon composites (BP-C 1:1 and BP-C 7:3), the electrodes have been tested in coin cells using potassium metal as reference/counter electrodes and 0.75 KPF₆ in the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) in 1:1 volume ratio as an electrolyte (**Figure 6**). Figure 6a-c shows the electrochemical performance of black phosphorus-carbon composites (BP-C 1:1 and BP-C 7:3). A reversible capacity of 617 mAh g⁻¹ is measured in the first cycle for the BP-C 7:3 sample (Figure 6a), indicating the maximal level of reversible capacity that can be achieved for the material in a potassium cell. At about 0.6-0.7 V vs K/K⁺, a plateau is recorded in the charge profile, which

indicates a battery-type behavior that may be useful in practical cells. However, a gradual capacity decrease is observed with the increase in the number of cycles. The capacity of the BP-C 1:1 electrode (Figure 6b) is a bit lower (a reversible value of 443 mAh g^{-1} is recorded) and the flat plateau at 0.6-0.7 V is less pronounced; however, a much improved cyclic stability is demonstrated (Figure 6c). It is to note that the content of carbon in the composite electrode plays an important role in the stability of electrodes. A part of this effect is related to the effect of dilution of the phosphorus component by carbon but another contributing factor is a smaller size of black phosphorus particles in the BP-C 1:1 composite.

To elucidate the charge storage mechanism, ex-situ XRD analysis has been conducted on the BP-C 1:1 electrodes extracted from potassium cells after the first discharge and the first charge. It can be seen (Figure 6d) that a group of peaks than can be assigned to a KP phase (JCPDS no. 04-004-2804) appears in the XRD pattern of the electrodes discharged to 0.01V vs K/K⁺. After the dealloying process (the first charge to 2.0V vs K/K⁺), the XRD signature of the electrodes does not contain clearly visible features (Figure 6d), indicating amorphization of the material in the depotassiated state. Based on the detected KP-type alloy phase, a theoretical capacity of 843 mAhg^{-1} has been proposed by us for the phosphorus component.^[61] Considering that capacity of ball milled graphite is about 150 mAhg^{-1} (experimentally evaluated in our previous work),^[50] there is a good match between the expected capacity (on the basis of $\text{P} + \text{K}^+ + \text{e}^- \leftrightarrow \text{PK}$ mechanism in the phosphorus component) and the capacity observed in the experiment. For example, the reversible capacity expected for the BP-C 7:3 electrode is 635 mAh g^{-1} while a similar value of 617 mAh g^{-1} has been indeed measured in an experiment. For the BP-C 1:1 electrode the expected and experimentally measured values are close as well, 496 and 443 mAh g^{-1} , respectively.

The results discussed in this section^[53, 61] indicate that phosphorus is indeed capable of alloying with potassium. Importantly, the measured capacities have the highest values, at this stage, reported for the anodes of potassium-ion batteries. This certainly underpins the importance of developing phosphorus-based electrodes further. An important issue with the lack of clarity at the moment is the reaction mechanism in phosphorus. One electron and three electron redox processes (resulting in theoretical capacities of 843 and in excess of 2100 mAh g⁻¹, respectively) have been proposed by independent studies. Further experiments, e.g. via in-situ methods such as in-situ XRD on operating phosphorus-containing battery cells, are needed to clarify the charge storage mechanism.

5. Sb-based anodes

For quite some time antimony (Sb) has been considered to be a promising alloying anode for high energy density lithium-ion and sodium-ion batteries because of its high theoretical capacity of 660 mAh g⁻¹. This high capacity originates from a redox mechanism that involves the formation of Li₃Sb and Na₃Sb alloys as the end products in lithium and sodium cells, respectively.^[62-64] Similarly to other materials that alloy and dealloy with alkali elements, antimony experiences significant volume variations during functioning in a battery electrode. A number of strategies have been considered to tackle this issue including using intermetallic alloys of antimony with other elements, nanosizing particles, using thin film electrodes and incorporating a suitable amount of nanosized antimony in a carbon component.^[28,62,65,66] The last strategy of dispersing Sb nanoparticles in an appropriate

carbon host has been very successful, and stable cyclic behaviour has been reported for Sb-C composite electrodes in both lithium and sodium half-cells.^[66, 67]

An antimony-carbon anode for potassium-ion batteries has been first reported by McCulloch et al. (**Figure 7**).^[68] A composite sample with a composition of 70 wt.% Sb and 30 wt.% C has been prepared by the mechanical milling of an Sb powder and Super P carbon black in a planetary ball mill. The composite has been initially characterized by XRD (Cu K α radiation), and the XRD pattern of the Sb-C composite is shown in Figure 7a. The pattern matches the expected diffraction peaks of the rhombohedral phase of antimony (JCPDS #01-073-5920). An XRD pattern of pure antimony powder is also included for comparison in Figure 7a. Compared with the XRD peaks of pure unmilled Sb powder, the XRD pattern of the ball milled composite displays diffraction peaks with low intensities and considerable broadening, indicating the reduction in the crystallite sizes of Sb in this sample. The average crystallite size calculated by using Scherrer equation is approximately 15 nm.

The electrodes assembled with the Sb-C composite have been tested in a two-terminal coin cell configuration vs potassium metal using 1.0 M KPF₆ in propylene carbonate (PC) -ethylene carbonate (EC) 1:1 (w/w) as an electrolyte.^[68] Figure 7b shows the galvanostatic discharge-charge profiles of the Sb-C sample in a potassium half-cell at a current rate of 35 mA g⁻¹ within a potential window of 2 – 0.05 V vs K/K⁺. A high capacity including an irreversible component of ~230 mAh g⁻¹ has been recorded in the first discharge of the half-cell, and the capacity of ca. 600 mAh g⁻¹ has been obtained on the charge of the half-cell in the first ten initial cycles. It is important to note that the currents and capacities in the measurements here are calculated per mass of antimony, and the contribution of the carbon component is not evaluated. A final alloy phase of K₃Sb (i.e., a reaction mechanism similar to those known in lithium and sodium cell for antimony) has been proposed on

the basis of the level of capacity obtained. To verify this, the XRD analysis of pristine and fully discharged electrodes has been conducted (Figure 7c). It can be seen that the diffraction peaks of the pristine electrode match those of pure crystalline antimony and the peaks of the fully discharged electrode match the peaks of the cubic K_3Sb phase (JCPDS #00-019-0935). The electrodes with bulk Sb have also been investigated; however, quick capacity fading within just a few cycles have been observed (Figure 7d), which can be attributed to the inability of large Sb particles to tolerate volume expansion during cycling.

In an attempt to improve the cyclic stability of the Sb-C composite electrodes (which otherwise display a stable capacity for only ten cycles), restricted cycling (by limiting the capacity of the Sb-C material to 250 mAh g^{-1}) has been conducted (Figure 7e,f). A stable cyclic performance (a consistent capacity of 250 mAh g^{-1} with the accompanying Coulombic efficiency of 98%) has been observed for 50 cycles, and the drop in capacity has been detected afterwards. McCulloch et al.^[68] have suggested that the drop in capacity is linked to a mechanical phenomenon, i.e. mechanical disintegration and loss of structural integrity in the electrodes. However, it is important to note that the capacity decay may also be associated with the development of polymeric layers on the electrodes that interfere with normal operation of the anode materials. This is known to happen for some of the anode materials in lithium cells, e.g. Si,^[62,69,70] and should be investigated further as a possible failure mechanism in Sb-based electrodes in potassium cells.

Inspired by this work, we have conducted further investigation of the influence of composition and particle size of Sb in Sb-C composites on the electrochemical performance in potassium cells. A previous study has been conducted by Ramireddy et al.^[28] on the influence of these parameters in sodium cells. The original intention in this previous work has been to vary the

carbon content in the Sb-C composites prepared by ball milling but it has been further discovered that a particle size of Sb can be controlled in the composites as well in the range between 50 nm and ~1 nm by varying the Sb:C weight ratio between 9:1 and 1:1. This series of samples represents an excellent model system to study size and composition effects in Sb-C electrodes. Here, we prepared three Sb-C composites with Sb:C weight ratios of 9:1, 7:3 and 1:1 by mechanical milling in the same magneto-ball mill used prior.^[28] The electrodes of different compositions were tested in a two-terminal configuration in coin cells using pieces of potassium metal as reference/counter electrodes. The electrolyte was 0.75 KPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with 1:1 volume ratio. We calculated the currents and capacities per total mass of Sb and carbon in order to account for any capacity from the carbon component. The cyclic stabilities of the three electrodes are shown in **Figure 8**. The Sb-C 9:1 electrode delivers a capacity as high as 550 mAh g⁻¹; however, the capacity becomes unstable and fades rapidly after ten cycles (Figure 8a). Interestingly, a systematic shift in the failure point of the electrodes is noticeable between compositions. The Sb-C 7:3 sample is reasonably stable for the first 20 cycles and fails afterwards (Figure 8b). Finally, the Sb-C 1:1 sample displays the best cyclic stability among the three electrodes and is able to maintain a reversible capacity (achievable on the charge of a half-cell) of 350 mAh g⁻¹ up to 40 cycles. Failure of the Sb-C 1:1 electrode similar to the previous cases occurs afterwards. An interesting aspect of the electrode failure in these instances is a combination of reasonably stable behavior in the initial few cycles with an abrupt decay in capacity after a certain number of cycles that is sensitive to the Sb particle size and the carbon content in the composite. Further studies are needed to pinpoint the origin of such a behavior with the aim of achieving long term cyclic stability in Sb-based electrodes.

It may be concluded that Sb is certainly capable of electrochemical alloying with potassium.

The currently available data point to the presence of a three electron reaction mechanism similar to the mechanisms of antimony alloying in lithium and sodium cells, and the K_3Sb phase appears to be the final product of reaction. Interestingly, Sb-C composite electrodes tend to experience an abrupt drop in capacity after a certain number of cycles, and the onset of such a drop is sensitive to the amount of Sb in the sample and its particle size. Further studies are needed to understand the failure mechanism in the electrodes more and to mitigate the issues with cyclic stability observed in the Sb-C electrodes at this stage.

6. Other alloying anodes

The universe of possible anode materials that alloy with potassium is not limited to tin, phosphorus and antimony. In particular, alloying of lead and Sn_4P_3 has been reported at this stage.^[53,55] Ji et al. have reported that a Pb anode is active in potassium cells.^[55] Further, lead anodes have been trialed in potassium-ion based dual-ion batteries as anodes using expanded graphite as cathodes and 1 M KPF_6 in a mixture of ethylene carbonate, dimethyl carbonate and ethyl methyl carbonate (EC:DMC:EMC, 4:3:2 by volume) as an electrolyte. In general, this publication^[55] has been dedicated predominantly to the prototyping of dual-ion full cell batteries, and electrochemical mechanisms in lead electrodes need to be investigated in the follow-up studies.

In an attempt to improve the stability of phosphorus-based anodes, composites of a Sn_4P_3 phase and C (73.1 wt.% Sn, 14.4 wt.% P and 12.5 wt.% C) have been evaluated by Zhang et al. (**Figure**

9).^[53] The $\text{Sn}_4\text{P}_3\text{-C}$ composite has been produced by mechanical milling of tin, phosphorus and carbon black powders in a planetary ball mill. Sn-C and P-C composite materials have also been prepared for the purpose of comparing with the $\text{Sn}_4\text{P}_3\text{-C}$ material. The XRD patterns of the three materials (collected using $\text{Cu K}\alpha$ radiation) are reproduced in Figure 9a. The XRD pattern of the $\text{Sn}_4\text{P}_3\text{-C}$ material matches a Sn_4P_3 phase (ICSD No.15014). Typical tin diffraction peaks can be observed for the Sn-C sample, while the XRD pattern of the P-C sample appears relatively featureless.

To reveal the electrochemical performance of the $\text{Sn}_4\text{P}_3\text{-C}$ material in potassium cells, the $\text{Sn}_4\text{P}_3\text{-C}$ electrodes have been tested in two terminal coin cells using potassium metal as a reference/counter electrode. 0.8 M KPF_6 in a mixture of ethylene carbonate and diethyl carbonate has been used as an electrolyte. Figure 9b-d shows the obtained data. Cyclic voltammetry curves (Figure 9b) demonstrate a major peak at 0.01 V in the initial cathodic scan, which shifts to 0.1 V vs K/K^+ in the following cycles. Two peaks at 0.8 and 1.15 V vs K/K^+ have been observed in the anodic scans and are associated with the depotassiation process of alloy phases. Figure 9c depicts the discharge-charge profiles of a $\text{Sn}_4\text{P}_3\text{-C}$ electrode for the initial three cycles. A discharge potential plateau at 0.1 - 0.6 V vs K/K^+ is above the plating potential of metal, which might help to limit the possibility of the formation of dendrites during cycling. It has been stated that the $\text{Sn}_4\text{P}_3\text{-C}$ electrode can deliver a reversible capacity of 385 mAh g^{-1} at a current rate of 50 mA g^{-1} . The electrochemical performance (in terms of both capacity and cyclic stability) has been found superior to those of P-C and Sn-C electrodes (Figure 9d). Capacity drop has been observed in the $\text{Sn}_4\text{P}_3\text{-C}$ electrodes after 40 cycles. Investigation of the failure mechanism and developing strategies to limit the eventual drop in capacity will be critical in further work on this material.

7. Reaction mechanisms of alloying materials in potassium cells: comparison with lithium and sodium cells

As stated earlier, an electrochemical alloying reaction of a suitable anode material usually proceeds in a reversible manner according to the following general equation:

where A is an element capable of alloying, M is an alkali element (Li, Na or K), x and y are the stoichiometric coefficients for the chemical formula of the final alloy that forms at a low potential vs the corresponding alkali metal in a half-cell. A number of intermediate alloy compositions are possible between the dealloyed state and the final alloy composition at the lowest potential. The presence of particular reaction intermediates (when the reaction follows a specific path) affects the shape of the charge-discharge profile of a given material, which is usually a combination of several plateaus and sloping regions. The nature and composition of the final alloy phase A_xM_y in the alloying process are very important as these parameters define the theoretical capacity of the material and the magnitude of the volume change that the material experiences in the course of the reversible alloying reaction. Interestingly, the mechanisms of alloying of the same materials with different alkali elements (lithium, sodium and potassium) are not necessarily the same, and considerable differences are observed in some cases. In this section we discuss the known reaction mechanisms and accompanying theoretical capacities of tin, phosphorus and antimony (as representative examples) in lithium, sodium and potassium cells. The corresponding properties of these anode materials in various cells are summarized in **Table 1**.

Among the materials under our consideration, tin is probably the most extensively studied anode material in lithium cells because it is not only a common metal well known in various applications but also a material with a high gravimetric capacity. The $\text{Li}_{22}\text{Sn}_5$ phase has been identified as the final alloy phase in the reaction process.^[42, 71-74] The formation of this final phase implies a theoretical capacity of 990 mAh g^{-1} that can be established by calculating the number of electrons required to complete the transformation in the alloying process for a gram of tin. During delithiation, the formation of LiSn has been detected at 0.78 V vs Li/Li^+ and Sn has been found to form at about 1 V vs Li/Li^+ .^[75,76] The reaction mechanism of tin in sodium cells has been found to be somewhat different.^[29,44] The final fully sodiated product is $\text{Na}_{15}\text{Sn}_4$, and the alloying process delivers a theoretical capacity of 847 mAh g^{-1} . As it is commonly the case with many materials that can be used in both lithium and sodium cells, the redox potentials for the formation of Na-Sn alloys with respect to Na/Na^+ are a few hundred mV lower than those for the formation of Li-Sn alloys with respect to Li/Li^+ . During desodiation, the $\text{Na}_{15}\text{Sn}_4$ phase transforms back to Sn through the formation of Na_9Sn_4 , NaSn , and NaSn_5 intermediate phases at 0.2 , 0.3 , 0.56 and 0.7 V vs Na/Na^+ , respectively.^[46] Interestingly, totally different values of capacity have been measured for tin-containing electrodes in potassium cells. For example, we have previously estimated that the capacity of the tin component of a Sn-C electrode is only between 150 and 190 mAh g^{-1} .^[50] This has been further confirmed by Wang et al.^[52] and evidence has been demonstrated that the KSn alloy is the final product in the potassiation reaction, resulting in a theoretical capacity of 226 mAh g^{-1} . Volume changes of up to 197% have been estimated for Sn in the course of alloying with potassium by *in-situ* TEM observations. The data available for tin vividly illustrate the possibility of considerably

different reaction mechanisms for the same alloying materials in lithium, sodium and potassium cells.

Unlike tin, phosphorus is believed to have a similar reaction mechanism (to form either Li_3P or Na_3P alloy in a three-electron redox process) in both lithium and sodium cells.^[57, 59, 77] Such a process results in a high theoretical capacity of 2596 mAh g^{-1} in both cases. The data in the potassium cells are not entirely conclusive at this stage. Zhang et al.^[53] have suggested the presence of a similar three-electron mechanism. However, some of the main diffraction peaks of the K_3P phase have not been located in the XRD pattern of an electrode after its full discharge in a half-cell. Instead, a possibly partially amorphous K_{3-x}P phase has been proposed as the final alloy to explain the experimental results. We have evaluated the behavior of electrode materials containing black (orthorhombic) phase of phosphorus.^[61] A different, lower level of capacity has been measured experimentally. Based on the value of the measured capacity and diffraction peaks of the KP alloy visible in the XRD patterns of an electrode after alloying, we have proposed a theoretical capacity of 843 mAh g^{-1} . Due to a conflicting nature of current results, we do expect further studies from other groups to verify the storage mechanism in phosphorus electrodes and investigate if different processes may occur in different phosphorus phases present in electrodes. A possible switch from a three-electron process (to form Li_3P or Na_3P alloys) to a one electron process (to form the KP alloy) may influence not only the capacity of phosphorus in various cells but also the shapes of charge-discharge profiles, which are of an utmost importance for creating full cell devices based on these electrodes. A clear advantage of the phosphorus-containing electrodes in lithium and sodium cells has been the presence of a pronounced plateau in their voltage profile, which a classical battery-type behavior of an electrode. A plateau is still located in a charge-discharge profile of electrodes

based on black phosphorus in potassium cells at about 0.6-0.7 V vs K/K⁺; however, the plateau coexists with sloping sections in the voltage profiles, which will have implications for the characteristics of full cell devices assembled with phosphorus-containing electrodes.

Antimony represents a contrasting case with tin and phosphorus. While different mechanisms have been either directly observed or at least suspected in the latter materials, the alloying mechanisms of Sb are quite consistent between various types of cells. The alloying reaction of antimony with lithium, sodium or potassium produces similar phases of Li₃Sb, Na₃Sb and K₃Sb, respectively, as the final products of the electrochemical reactions.^[63, 66, 68] This corresponds to a consistent theoretical capacity of 660 mAh g⁻¹ in all three types of cells. During the discharge in lithium half-cells, Sb electrochemically reduces and produces a crystalline Li₂Sb phase initially.^[63] The final phase of Li₃Sb forms upon further lithiation. In contrary, Li₃Sb transforms into Sb in one step upon delithiation, indicating different electrochemical reaction paths for the two parts of the reversible reaction.^[63,78] In the case of antimony electrodes with coarse particles in sodium cells, the presence of only amorphous intermediates has been observed between the initial phase and the highly crystalline hexagonal Na₃Sb final structure. During desodiation an unknown amorphous intermediate phases a-Na_{3-x}Sb and a-Na_{1.7}Sb has been observed.^[79] Interestingly, there are indications that the reaction mechanism in electrodes with nanocrystalline antimony (5-15 nm particles) is different, and crystalline reaction intermediates have been observed by Ramireddy et al.^[28] The reaction mechanism of Sb in potassium cells has been probed by McCulloch et al.^[68] A final cubic K₃Sb phase has been directly observed in the XRD patterns of potassiated electrodes. Based on the shapes of CV curves and charge-discharge profiles, existence of a KSb intermediate of some kind has been also proposed.

As it follows from our discussion, the alloying mechanisms can be quite different in different types of cells. Antimony is the most consistent out of the three considered materials, with similar final compositions of alloys in the form of Li_3Sb , Na_3Sb and K_3Sb in each instance. However, the exact structural characteristics of each phase are different. For example, hexagonal phase of Na_3Sb is the final product in the sodium cells^[79] but a cubic phase of K_3Sb tends to form in potassium cells.^[68] While there is no complete clarity on the exact reaction mechanism for phosphorus in potassium cells (and the reaction mechanism may appear different between the amorphous and crystalline forms of phosphorus), it is quite obvious that the alloying of tin in potassium cells proceeds differently and terminates at a KSn stoichiometry, a tin-rich alloy with respect to the final phases in lithium and sodium cells. These results underpin the importance of careful studies of the reaction mechanism of these and other materials in the new potassium cells, as the reaction mechanisms will directly define the capacity, volume change and the voltage charge-discharge profiles of the electrodes.

8. Gravimetric and volumetric parameters of alloying electrode materials in potassium cells

Most of the previous discussion in this feature article is focused on gravimetric capacities that can be obtained in various electrodes. In fact, this is not the only important metric to pay attention to. Not only the weight but also the size and footprint of a battery are often important for many practical applications. In order to control the size and footprint of the resulting battery, the efforts are focused on minimizing the sizes and thicknesses of various cell components, i.e. making various parts more compact. In this context the most important thing for battery electrodes is to contain as much

capacity within a limited volume as possible, and a concept of volumetric capacities, expressed in the units of mAh cm^{-3} , is used. Obviously, a high gravimetric capacity does not always translate into a high volumetric capacity for a given electrode material because of the influence of the material's density. While addressing various materials that can alloy with potassium electrochemically, it is important to discuss their volumetric characteristics.

In order to provide meaningful input parameters for discussion, we use the data we obtained for Sn-C, P-C and Sb-C composite electrode materials (with the same weight ratio of components of 70 and 30 %) in potassium and sodium cells. For the phosphorus-containing electrode, the data obtained with black (orthorhombic) phase are used. Tapped density D (g cm^{-3}) was determined for each electrode material. In order to measure tapped density, 2g of each material were loaded in a measuring cylinder and shaken to allow the material to settle. As our electrodes are hand-made, we cannot guarantee the entirely uniform thickness of the coating and determining the volume of electrodes by a direct measurement may be not accurate. To bypass this experimental complication, a volumetric parameter $D \times C_K$ (also expressed in mAh cm^{-3}) was calculated instead (C_K is an experimentally measured gravimetric capacity for a material). While not representing true volumetric capacity, the $D \times C_K$ parameter allows us to compare volumetric characteristics of the electrodes between each other and see if any difference with the use of the same materials in other types of cells, e.g. sodium cells (we have also calculated $D \times C_{Na}$ parameters for sodium cells), exists. The results of the measurements and calculations are shown in **Table 2**. The tapped densities for the Sn-C, P-C and Sb-C electrodes are 1.43, 0.91 and 1.82 mAh cm^{-3} , respectively. As it follows from the calculation of the $D \times C_K$ parameters (229, 561 and 882, respectively), Sb-C electrodes are expected to have the highest volumetric capacities, followed P-C

and Sn-C electrodes. The values for the P-C and Sn-C electrodes are lower in the potassium cells as the expected end phases of alloying are KP and KSn stoichiometries resulting from one electron reaction mechanisms. It is perhaps worth noting that the idea of precisely determined volumetric capacities is quite relative for the alloying electrode materials, due to the significant volume changes they may experience during potassiation and depotassiation. However, discussing this point further is beyond the scope of this article.

To highlight the differences between different battery chemistries, it is useful to compare the results with those obtained for the same materials in sodium cells. The experimentally measured capacities for Sn-C, black P-C and Sb-C electrodes as well as the corresponding $D \times C_{Na}$ parameters are given in the last two columns of Table 2. The key difference originates from different alloying mechanisms of tin and black phosphorus in sodium cells. As a result, the Sn-C and black P-C electrodes are capable of demonstrating higher experimentally measured gravimetric capacities of approximately 350 and 1300 mAh g⁻¹. When the $D \times C_{Na}$ parameter is calculated, black P-C composite emerges as a material with the highest possible volumetric capacity out of the three, followed by Sb-C and Sn-C electrodes that have noticeably smaller values of $D \times C_{Na}$. The difference between Sb-C and Sn-C electrodes is also not that significant anymore, with values of $D \times C_{Na}$ of 756 and 501, respectively. As it follows from this exercise, the nature of the material that exhibits the highest capacity per volume is dependent on the chemistry of cell and differs between potassium and sodium cells. The Sb-C composite material is the most attractive from this perspective in potassium cells, while black P-C composite material is a leader in sodium cells. It is important to keep these differences in mind while selecting appropriate anode materials for full cell batteries with various chemistries.

It is worthwhile to note the approximate nature of the above consideration, as this is done with the purpose to highlight differences in volumetric characteristics between various cell chemistries. Ideally, it would have been advantageous to use the exact measured volumes of electrodes and the actual volumetric capacities to discuss the differences. This was however not possible to do directly in this case due to experimental limitations. Nevertheless, we feel that discussing volumetric parameters defined via the tapped density of materials is appropriate (although less accurate) in order to highlight the differences between gravimetric and volumetric values of electrodes in various cells.

9. Summary and outlook

Anode materials that are able to alloy with the corresponding alkali metals have been known for a while in lithium-ion and sodium-ion batteries. Impressively, one of these materials, silicon, is in the phase of active commercialization at the moment in various countries. The most striking advantage of the materials that can alloy electrochemically with alkali elements is their enviable gravimetric and, in many cases, volumetric capacities; this has been fully recognized by the battery community. Until recently, however, little knowledge was available on materials that can alloy electrochemically with potassium. The initial results on the key candidate phases (e.g., Sn, P, Sb)^[50,53,55,61,68] as well as some original data from our group have been summarized in this feature article. It is appropriate now to state with confidence that a number of materials are indeed capable of alloying with potassium and display a promising level of capacities in excess of that of graphite. Disappointingly, silicon has demonstrated no apparent electrochemical reactivity with potassium in our experiments;

however, other phases including Sn, amorphous and black phosphorus, Sb, Pb and certain intermetallic phases (with the first example of Sn_4P_3) are all exciting candidates to be explored further. It will be of a great academic interest and practical importance to study these materials and their appropriately engineered composites for the application in potassium-ion batteries.

An obvious future avenue to pursue is the expansion of the range of the candidate phases. While we have a circle of the initial candidate phases now, not all possible alloying materials have been covered. For example, Ge and Bi are known to be alloying successfully with the alkali elements in lithium and sodium cells^[80-85] and it is definitely worthwhile to assess them in potassium cells as well. Another almost untouched area is the universe of intermetallic phases, in which various elements (that are known or suspected to be able to alloy with potassium) are combined with each other or an inert (not capable of alloying) element within the same material. A Sn_4P_3 phase has been a very interesting initial phase to get evaluated in this space.^[53] Theoretical calculations should be a useful guide in the search of suitable materials. The results of prior calculations of Si and Sn have been indeed very useful in early work, although the experimental results have mainly confirmed the theoretical predictions for one of these materials while no alloying activity have been found in silicon in preliminary experiments.

Studies of the reaction mechanisms will be paramount in the future work. It has been already established that the reaction mechanisms of electrochemical alloying in potassium cells may be quite different from those in previously assessed lithium and sodium cells. That will have implications for the capacity levels of these materials, both in the gravimetric and volumetric senses, and for the shapes of charge-discharge profiles in potassium cells. Failure mechanisms of electrodes, e.g. through their mechanical breakdown or SEI phenomena, need to be understood, and the

acquired knowledge should form a basis for the optimization of the cyclic behavior. A related problem that needs to be looked at is a relatively poor Coulombic efficiency often observed in the alloying electrodes of potassium cells. The Coulombic efficiency may be up to a few percentage points lower than that of state of the art electrodes of lithium-ion batteries. Experiments in this area should include optimization of electrolyte formulations, trialing electrolyte additives (the known ones may not be so effective; e.g. fluoroethylene carbonate (FEC) does not improve the behavior of anodes in potassium cells)^[20,86] and experimenting with binders.

Binders can be indeed the key to the performance optimization of the anode materials that alloy with potassium. At present, the data on the influence of the choice of a binder on the performance of these materials are largely absent in literature. Furthermore, it is probably safe to state that only one systematic study of the influence of binders on potassium-ion battery anode performance has been published at this stage. Komaba et al.^[9] have evaluated the influence of binders on the performance of graphitic anodes and concluded that the initial Coulombic efficiency and cyclic stability may vary depending on the binder chosen for the electrode assembly. For example, the highest Coulombic efficiency (89 %) has been achieved with sodium carboxymethylcellulose as a binder, while the optimal cyclic stability has been noted with sodium polyacrylate as a binder (negligible performance degradation over 50 cycles). We would like to encourage the battery community to conduct similar studies on the anode materials that alloy with potassium. The binders may have a strong influence on the performance characteristics of these materials in electrodes.

Finally, creating full cell prototypes of potassium-ion batteries with anode materials incorporating alloying components is the next important task. Although a successful attempt to use

alloying anodes (Sn and Pb) in a dual-ion potassium battery (that is, the battery that utilizes potassium ions for the electrochemical reaction in the anode and anions for the reaction in the cathode)^[87,88] has been reported,^[55] the demonstrated prototype is not a potassium-ion battery (with a classical “rocking chair” mechanism) strictly speaking but rather a battery utilizing different ions in the anode and cathode reactions. The same comment applies to another hybrid potassium-ion/oxygen cell reported by McCulloch et al.,^[68] who used Sb-based anodes and an electrocatalytic cathode in their prototype. While these early battery prototypes are without any doubt innovative and interesting, it may also be of interest to trial more conventional full cells involving intercalation cathode hosts for potassium such as hexacyanoferrates, layered oxides or polyanionic compounds. As cathode chemistry for potassium-ion batteries develops, we should look forward to many exciting reports in this area.

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Figure 1. A Si-graphene composite sample used for the electrochemical evaluation: a) an XRD pattern; b,c) SEM and TEM images; d) thermogravimetric curve (in the atmosphere of flowing air); e,f) capacity levels and charge–discharge profiles in a lithium half-cell.

Figure 2. Evaluation of Si-graphene, Si, and graphene electrodes in the potassium cells: a,b) capacity vs cycle number and charge–discharge profiles for a Si-graphene electrode; c,d) capacity vs cycle number and charge–discharge profiles for a pure Si electrode; e,f) capacity vs cycle number and charge–discharge profiles for a graphene electrode; g) the XRD patterns of the Si-graphene electrode after the first discharge and charge of the cell; h) an SEM image of the electrode after 50 cycles.

Figure 3. Evaluation of Sn-C composite electrode in potassium cells: a) XRD patterns of Sn-C materials and a metallic Sn powder; b,c) a bright-field TEM image and an energy-filtered image with an elemental contrast (color scheme: C-yellow; Sn-blue) of the Sn-C composite; d) cycling performances of Sn-C composite material, milled graphite, and pure Sn at a current rate of 25 mA g⁻¹ within a potential window of 2.00–0.01 V vs K/K⁺; e) galvanostatic discharge-charge profiles of the Sn-C electrode in the selected cycles; f) XRD patterns of Sn-C electrodes after the first discharge and the first charge in potassium half-cells. Adapted with permission.^[50] Copyright 2016, The Royal Society of Chemistry.

Figure 4. Reaction process of Sn nanoparticles during the first potassiation–depotassiation cycle. a) Morphology of pristine Sn nanoparticles. b–c) First-step potassiation of Sn nanoparticles. The yellow arrows indicate the propagation direction of the phase boundary. d–f) Second-step potassiation of Sn nanoparticles, without a phase boundary. g–i) Depotassiation-induced nanopores in the nanoparticles. j) A thick layer of KOH (≈ 10 nm) is observed on the surface of potassiated nanoparticles. k) Electron diffraction pattern of the fully-potassiated nanoparticles, which can be indexed as KSn and KOH phases. l) Electron diffraction pattern of the fully-depotassiated nanoparticles, which can be indexed as the β -Sn phase. Reproduced with permission.^[52] Copyright 2017, American Chemical Society.

Figure 5. X-ray and TEM analysis of composites of black phosphorus with carbon: a) XRD patterns of amorphous red phosphorus, black phosphorus, and two nanocomposite anode materials with phosphorus/carbon weight ratios of 7:3 and 1:1 (BP-C 7:3 and BP-C 1:1); b) an elastic TEM image of a black phosphorus-carbon nanocomposite (BP-C 1:1); c) an overlay of energy-filtered three-window maps (color scheme: phosphorus (red), carbon (green)). Adapted with permission.^[61]

Figure 6. The electrochemical performances of the phosphorus-carbon electrodes: a) charge-discharge profiles of the BP-C 7:3 sample at a current rate of 50 mA g⁻¹; b) charge-discharge profiles of the BP-C 1:1 sample at the same current rate; c) cyclic stabilities of the two samples; d) XRD patterns of the BP-C 1:1 electrodes after discharge and charge in potassium half-cells. Adapted from [61].

Figure 7. Electrochemical performance of Sb-C composite electrodes in potassium cells: a) XRD patterns of the Sb-C composite and pure antimony powder; b) galvanostatic discharge-charge profiles of the Sb-C electrode in the selected cycles; c) XRD pattern of a pristine Sb-C electrode and a fully discharged electrode; d) galvanostatic discharge-charge profiles of bulk Sb in the first few cycles; e, f) discharge-charge curves in the first few cycles as well as Coulombic efficiency and capacity for the first 55 cycles under cycling conditions restricting capacity of the Sb-C electrode to 250 mAh g⁻¹. Note that the currents and capacities here are calculated per mass of antimony.

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Figure 8. Cyclic stabilities for Sb–C composites with various weight ratios of Sb to C in potassium half-cells: a) Sb–C 9:1; b) Sb–C 7:3; and c) Sb–C 1:1. The potential window for the test is 2–0.01 V vs K/K⁺ and the current rate is 50 mA g^{−1}.

Figure 9. Electrochemical properties of Sn₄P₃–C composite electrodes in potassium cells: a) XRD patterns of Sn₄P₃–C, Sn–C and P–C materials; b) cyclic voltammograms of a Sn₄P₃–C electrode for the first five cycles; c) galvanostatic discharge–charge profile of a Sn₄P₃–C electrode in the first three cycles; d) cycling behaviours of the Sn₄P₃–C, Sn–C and P–C electrodes in potassium half-cell at the current density of 50 mA g^{−1}. Adapted with permission.^[53] Copyright 2017, American Chemical Society.

Table 1. Mechanisms of alloying of selected materials (Sn, P, and Sb) in various types of alkali cells.

Material	Type of cell	Stoichiometry of the final product of alloying	Theoretical capacity (mAh g ⁻¹)	Volume change, %	References
Sn	Li	Li ₂₂ Sn ₅	990	676	[74]
	Na	Na ₁₅ Sn ₄	847	420	[29]
	K	KSn [*]	226	≈180	[52]
P	Li	Li ₃ P	2596	200	[77]
	Na	Na ₃ P	2596	390	[77]
	K	K _{3-x} P [*]	≤2596	Not known	[53]
		KP [*]	843	190 ^{**}	[61]
Sb	Li	Li ₃ Sb	660	147	[74]
	Na	Na ₃ Sb	660	390	[66]
	K	K ₃ Sb	660	407	[68]

^{*}Inconsistent results have been obtained in independent studies

^{**}Volume change is calculated by the authors of this feature article for the phase of black P

Table 2. Gravimetric and volumetric parameters of composite electrode materials containing 70 wt% of alloying materials and 30 wt% of carbon components (data from our experiments)

Material	Tapped density D, g cm ⁻³	Gravimetric capacity in potassium cells C _K , mAh g ⁻¹	Volumetric parameter D×C _K , mAh cm ⁻³	Gravimetric capacity in sodium cells C _{Na} , mAh g ⁻¹	Volumetric parameter D×C _{Na} , mAh cm ⁻³
70 wt.%Sn – 30 wt.% C	1.43	160	229	350	501
70 wt.%P – 30 wt.% C	0.91	617	561	1300	1183
70 wt.%Sb – 30 wt.%C	1.82	490	882	415	756

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Anode materials are the key components of a new type of rechargeable metal-ion batteries based on potassium. A class of high capacity anode materials that operate through the mechanism of electrochemical alloying with potassium is discussed. Electrode systems incorporating Sn, P and Sb are given particular attention, and the current state of the field as well as future research directions are considered.

Keyword: Alloying, potassiation, potassium-ion batteries, anode materials

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Potassium-ion battery anode materials operating through the alloying-dealloying reaction mechanism

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