Insertion compounds and composites made by ball milling for advanced sodium-ion batteries

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Sodium-ion batteries have been considered as potential candidates for stationary energy storage because of the low cost and wide availability of Na sources. However, their future commercialization depends critically on control over the solid electrolyte interface formation, as well as the degree of sodiation at the positive electrode. Here we report an easily scalable ball milling approach, which relies on the use of metallic sodium, to prepare a variety of sodium-based alloys, insertion layered oxides and polyanionic compounds having sodium in excess such as the Na4V2(PO4)2F3 phase. The practical benefits of preparing sodium-enriched positive electrodes as reservoirs to compensate for sodium loss during solid electrolyte interphase formation are demonstrated by assembling full C/P2-Na1[Fe0.5Mn0.5]O2 and C/Na3+V2(PO4)2F3 sodium-ion cells that show substantial increases (＞10%) in energy storage density. Our findings may offer electrode design principles for accelerating the development of the sodium-ion technology.

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Considering elemental abundance, the most appealing alternative to Li-based battery technology is undoubtedly sodium. This is reflected in the revival of Na-ion battery (NIB) research, a field in which intense efforts are currently devoted to the search for high-performance electrode materials. Progress in sodium intercalation chemistry is primarily inherited from work on Li-ion materials, with the negative and positive electrodes for sodium systems based on similar structural types \(^1\). For negative electrodes comprising sodium metal, Na\textsubscript{2}Sb is the most attractive\(^2\). Antimony, however, is not the most desirable component considering its scarcity, moderate toxicity and large mass. There is thus great interest in carbon negative electrodes, whose reversible capacity can reach \(300 \text{ mAh g}^{-1}\) after accounting for a \(\sim 25\%\) irreversibility penalty associated with formation of the solid electrolyte interface (SEI) in the first cycle\(^3\). Among the positive electrode candidates, polyatomic compounds such as Na\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}F\textsubscript{3} (NVPF) \((\text{refs} 6,7)\) and Na\textsubscript{2}Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} \((\text{ref.} 8)\), and layered compounds like the O\textsubscript{3}-Na\textsubscript{Ni\textsubscript{0.3}Mn\textsubscript{0.7}O\textsubscript{2} \((\text{ref.} 9)\) and P2-Na\textsubscript{0.67}Fe\textsubscript{0.33}Mn\textsubscript{0.67}O\textsubscript{2} \((\text{ref.} 10)\) phases are presently the most studied. Nevertheless, the performances of NIB prototypes based on the aforementioned materials suffer from the large irreversibility of initial Na-uptake-removal processes at the carbon negative electrode.

The sodium loss in the formation of the SEI is similar to what is observed in the case of Li-ion batteries (LIBs), which has been widely studied. Because the only source of Li in the Li-ion cell is the Li-bearing electrode, compensating for lithium loss in the formation of the SEI at the negative electrode has been of great importance for achieving high energy densities in LIBs, and it is becoming more urgent with the emerging Si anodes, which show larger initial irreversibility than carbon electrodes. Through becoming more urgent with the emerging Si anodes, which show importance for achieving high energy densities in LIBs, and it is becoming more urgent with the emerging Si anodes, which show larger initial irreversibility than carbon electrodes. Through the years various routes have been explored. By adding to the positive electrode either sacrificial lithium species or additional intercalation compounds, the full capacity of a cathode material can be realized with modest weight penalties. For example, Li\textsubscript{1.2}Co\textsubscript{2}O\textsubscript{4} is used as a sacrificial source that decomposes during oxidation to provide extra lithium\(^11\). Alternately, in compounds such as Li\textsubscript{1+x}M\textsubscript{y}Ni\textsubscript{2}O\textsubscript{4}, which contains two redox voltages, the low-voltage \(\sim 3 \text{ V} \) plateau associated with xLi\textsuperscript{+} can be used as a Li reservoir\(^12\). Another approach, mainly applied to Si, is in situ or ex situ pre-lithiation. This can be accomplished either by Li ball milling\(^13\), or by placing Si in contact with Li so that when electrolyte is added formation of the SEI occurs conjoinedly with the uptake of Li by the negative Si electrode (Li\textsubscript{Si}) \((\text{ref.} 14)\).

Considering the lower coulombic efficiency of hard carbon in NIBs, that is, \(< 80\%\) \((\text{ref.} 15)\), a strategy to compensate for Na loss to the SEI is sorely needed. It is also equally important to tune the degree of sodiation in cathodes to be used in NIBs, especially in the case of ‘sodium deficient’ P2-type layered oxide electrodes of formula Na\textsubscript{2/3}M\textsubscript{2}O\textsubscript{3} \((M = \text{Mn, Fe, Co...})\)\(^10,16\), which only contain \(\sim 0.67 \text{ Na}^+\) per formula unit. These materials can achieve performances as high as \(200 \text{ mAh g}^{-1}\) but only in half cells against sodium metal which, in excess, enables NaN\textsubscript{2}O\textsubscript{3} compositions to be reached upon cycling. In contrast, the capacity drops by 30% in Na-ion cells because of the lack of a Na reservoir to compensate for the missing 0.33 Na\textsuperscript{+} in the pristine P2 phase. Solving these two issues constitutes the driving force of the present study.

Surprisingly few studies have been conducted before now to address the development of Na reservoir sources and pre-sodiation reagents for NIBs while minimizing energy penalty. Recently, Na\textsubscript{3}N\textsubscript{3} was proposed as a sacrificial Na source, but the generation of N\textsubscript{2} gas during its non-reversible electrochemically driven decomposition upon oxidation is detrimental to the battery. Moreover, the low Na content in Na\textsubscript{3}N\textsubscript{3} \((35\%\) Na by weight) imposes a penalty in energy density\(^17\). Similar to LIBs, Na metal would obviously be the best pre-sodiation reagent for NIBs. However, it is one of the most difficult metals to handle because of its ductility and tendency to stick to metallic surfaces. Following our previous work on preparing Li-alloy through ball milling\(^18\), we report herein the synthesis of Na-based alloys and other insertion compounds via the ball milling of Na-metal with the appropriate chemical elements. We find this approach equally suitable for tuning the amount of Na in insertion electrodes. In particular, we find that Na\textsubscript{5}P-the Na-based compound showing the closest capacity \((804 \text{ mAh g}^{-1})\) to Na metal \((1,165 \text{ mAh g}^{-1})\) and hence offering the minimum weight penalty-can be used as a sacrificial Na source, increasing for instance the reversible capacity of C/P2-Na\textsubscript{2}Na\textsubscript{0.67}[Fe\textsubscript{0.5}Mn\textsubscript{0.5}]O\textsubscript{2} cells by 20%. We begin by describing the ball milling synthesis of Na-alloys, then present the use of the Na-ball milling approach for pre-sodiation of insertion positive electrodes (P2-Na\textsubscript{0.67}[Fe\textsubscript{0.33}Mn\textsubscript{0.67}]O\textsubscript{2}, NVPF), and end with the implementation of both approaches towards the optimization of full Na-ion cells.

**Results**

**Ball milling-driven formation of Na-based alloys.** Na\textsubscript{3}P powders were prepared by adding stoichiometric amounts of Na-lumps and red phosphorous powder into a hardened steel ball milling jar, loaded in an Ar-filled glove box, with a ball/powder weight ratio of 35. Strikingly, room temperature continuous ball milling for 2 h, using a SPEX 8000 milling apparatus, was found to be sufficient to produce well crystalline and single-phase Na\textsubscript{3}P powders as deduced by X-ray diffraction (XRD) \((\text{Fig. 1a,b})\) while shear grinding for 27 h in planetary ball mill was shown to give a mixture of Na\textsubscript{2}P and amorphous phase\(^19\). These powders were mixed with carbon SP \((30\%\) by weight) and further ball milled for 20 min to obtain homogeneous composite electrodes. When cycled versus Na\textsuperscript{+}/Na\textsubscript{0}, these composites showed reversible capacity \((\text{Fig. 1c})\) of \(\sim 600 \text{ mAh g}^{-1}\) based on the weight of Na\textsubscript{3}P.

To highlight the simplicity of this ball milling synthesis we recall the two approaches previously adopted to prepare Na\textsubscript{3}P powders: (i) electrochemical sodiation of P by making a battery using P and Na metal as working and counter electrode\(^20\), respectively; and (ii) chemical alloying of Na and P, either through a solvothermal reaction at 150°C \((\text{ref.} 21)\), or high temperature annealing \((480^\circ \text{C} \) in evacuated silica ampoules\(^22\). Encouraged by these results, we successfully extended the approach to the synthesis of Na\textsubscript{3}M alloys, where M is selected from the group consisting of Sn, Sb and Pb. For reasons of conciseness, the preparation of single-phase Na\textsubscript{3}Sb powders \((\text{Fig. 1d})\) whose voltage-composition curves fully mirror previous literature data \((\text{Fig. 1e})\)\(^23\) is solely reported herein.

Although speculative, we believe that the key to success for such unexpected reactions depends on the large free energy \((\Delta G)\) of the alloy formation reaction. As depicted in the schematic representations of Fig. 1a, a monolayer of alloy is rapidly created by contact of metal particles with Na lumps, hence separating the Na from the metal container and balls. Ball milling will continuously break the alloy shell to expose fresh surfaces, which rapidly react in a progressive alloying of all the Na, most likely facilitated by local heating. The repeated alloying/fracturing sequences are accompanied by a continuous peeling and breaking of the alloy shell into loose powders.

**Ball milling-driven pre-sodiation of insertion electrodes.** The successful synthesis of Na-based alloys by room temperature Na ball milling encouraged us to exploit the reducing power of both Na and Na\textsubscript{3}P to simulate electrochemical reduction of positive electrode materials so as to increase their sodium content.
We tested this possibility using the P2-type layered oxide phase, Na$_{0.67}$[Fe$_{0.5}$Mn$_{0.5}$]O$_2$, which can be electrochemically reduced at a potential near 1.5 V to form the P'2-Na$_4$[Fe$_{0.5}$Mn$_{0.5}$]O$_2$ phase that delivers a capacity of ~190 mAh g$^{-1}$ (ref. 24). Attempts to synthesize P'2 type Na$_4$[Fe$_{0.5}$Mn$_{0.5}$]O$_2$ through direct solid-state reaction have so far failed, resulting in an O3 type phase with poor capacity$^{10}$. Stoichiometric amounts of Na$_{0.67}$[Fe$_{0.5}$Mn$_{0.5}$]O$_2$ (XRD shown in Fig. 2b) and Na metal were added under argon into a hardened steel ball milling jar using a ball to powder weight ratio of 35. The XRD pattern of the obtained powder (Fig. 2a) is consistent with the reflections reported for the electrochemically produced P'2 phase$^{24}$, which confirms the successful production of fully sodiated P'2-Na$_4$[Fe$_{0.5}$Mn$_{0.5}$]O$_2$ after only 2 h of ball milling. At shorter milling time or when a sub-stoichiometric amount of Na is used, the ball-milled samples are a mixture of the P2 and P'2 phases.

Fig. 2c–e compare the electrochemical behaviour of a Na/P2 cell with that of a Na/P'2 cell with the P2 phase made by ball milling with Na. Note that only 0.45 Na$^{+}$ can be removed from the P2-based cell, as opposed to nearly 0.8 Na$^{+}$ for the P'2 cell, clearly confirming the success of the ball milling-induced sodiation process. Aside from this difference, the cells behave identically in terms of reversible and sustained capacity upon cycling, independently of whether pristine P2 or P'2 obtained by Na ball milling was initially used.

In addition to layered oxides, the polyvalent compound NVPF (Na$_3$V$_2$(PO$_4$)$_2$F$_3$) is also of great interest as a positive electrode in Na-ion cells$^{25,26}$ since it shows high-voltage plateaus near 3.6 and 4.2 V, whose equal amplitudes provide a cumulative capacity of ~110 mAh g$^{-1}$. To generalize our approach, we explored the ball milling-driven reactivity of Na against NVPF.

Figure 1 | Synthesis of Na-based alloys. (a) Schematic diagram showing the ball milling process exemplified for the formation of Na$_3$M alloys (yellow) by reacting Na (blue) with metal M (M = P or Sb) (red). In b c and d e, the Rietveld refined X-ray powder patterns of Na$_3$P and Na$_3$Sb powders are respectively shown together with their corresponding electrochemical voltage-profile in Na-half cells.
Refinement of the synchrotron XRD pattern (Fig. 3c) of the obtained Na$_x$V$_2$(PO$_4$)$_2$F$_3$ was undertaken based on the structural model reported for pristine NVPF by Bianchini et al.\textsuperscript{26} The VO$_6$ octahedra and PO$_4$ tetrahedra arrangement of NVPF is kept, and the best agreement between the observed and calculated patterns was found for the Na positions as listed in Supplementary Tables 1 and 2 and Supplementary Note 1. The Na environments are shown in Fig. 3e. The three distinct Na sites are all seven-fold coordinated with four oxygen and three fluorine atoms, which is analogous to the coordination of NaI in NVF (Fig. 3g). The structural analysis fully confirms the chemical composition (Na$_x$V$_2$(PO$_4$)$_2$F$_3$) and indicates that there is apparently no further space for Na insertion. Lastly, the synchrotron XRD patterns of the sample prepared by ball milling NVPF with Na for 30 min can be perfectly refined with a two phases model: NVPF and Na$_x$V$_2$(PO$_4$)$_2$F$_3$, as shown in Fig. 3b.

The occurrence of Na$_x$V$_2$(PO$_4$)$_2$F$_3$ comes as a total surprise, as no extra capacity has ever been reported for NVPF at low potential. It is however worth noting that the reversible insertion of 1 Na$^+$ at 0.3 V was just recently reported for Na$_3$V$_2$(PO$_4$)$_3$ (ref. 27). Knowing the existence of the two Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and Na$_x$V$_2$(PO$_4$)$_2$F$_3$ end-member phases, we deliberately prepared composites of nominal compositions having different amounts of NVPF and Na$_x$V$_2$(PO$_4$)$_2$F$_3$ that will be denoted hereafter ‘Na$_x$V$_2$(PO$_4$)$_2$F$_3’

In light of our finding on the Na$_x$V$_2$(PO$_4$)$_2$F$_3$ phase, we explored electrochemical intercalation in NVPF down to low voltages. In situ XRD measurements were conducted on a Na/NVPF cell, with XRD patterns collected for every 90 min.

As the cell was being discharged at 0.15 C, we observed the progressive appearance of an additional set of peaks (Fig. 4a,b) corresponding to the Na$_x$V$_2$(PO$_4$)$_2$F$_3$ phase obtained by ball milling. They appear at the expense of the NVPF reflections, which barely change in position but decrease in intensity. By careful refinement of the XRD patterns, we quantified (Fig. 4c) the growing amounts of Na$_x$V$_2$(PO$_4$)$_2$F$_3$, promoted by continuously lowering the reduction voltage; Na$_x$V$_2$(PO$_4$)$_2$F$_3$ constitutes nearly 60% of the composite when the cell potential reaches 0 V. This corresponds to a x value of 0.6 (in ‘Na$_3+x$V$_2$(PO$_4$)$_2$F$_3’

Turning to the charging process, a reverse trend is observed, with the recovery at 3.6 V of an XRD pattern similar to that of the pristine phase indicating the full reversibility of the Na-uptake–removal process (Fig. 4a). However, it is worth noting the drastic difference in the charge and discharge profiles, highlighted in the derivative plot (Supplementary Fig. 4a,b), which is indicative of a different reacting pathway. Moreover, we note the continuous growing of Na$_x$V$_2$(PO$_4$)$_2$F$_3$ when the cell is switched back to stable capacity of $\sim 110$ mAh g$^{-1}$ when cycled between 4.4 and 3 V.

Figure 2 | Synthesis of the P 2 phase by Na ball milling. XRD powder pattern profile matching and schematic representation of the structure of (a) P2-Na$_x$(Fe$_{0.5}$Mn$_{0.5}$)O$_2$ obtained using ball milling with Na and (b) pristine P2-Na$_{0.67}$(Fe$_{0.5}$Mn$_{0.5}$)O$_2$. The refined cell parameters are in agreement with reported ones for both P2 and P 2 phases. The change of symmetry from P2 to P2 accounts for the distortion of the MnO$_6$ octahedral due to the Jahn-Teller effect of reduced Mn$^{3+}$; voltage profiles of (c) P2-Na$_x$(Fe$_{0.5}$Mn$_{0.5}$)O$_2$, (e) P2-Na$_{0.67}$(Fe$_{0.5}$Mn$_{0.5}$)O$_2$ and their corresponding cycling performances in Na-half cells (d). The peak marked with an asterisk (*) in a is attributed to Be window used to measure such a moisture sensitive sample.
oxidation, further implying a complex Na-uptake–removal process. We believe this partial reduction to be nested in kinetics blockages that are most likely due to the growth of a thick insulating SEI layer due to copious electrolyte decomposition and/or the formation of peculiar self-limiting core/C0-shell-like ‘Na3V2(PO4)2F3’ particles upon reduction. Besides, attempts to modify the SEI with the use of fluoroethylene carbonate (FEC) did not result in subsequent changes in increasing the amount of the Na4V2(PO4)2F3 phase (Supplementary Note 2). In comparison, there are two specific aspects that facilitate the production of pure Na4V2(PO4)2F3 in the case of ball milling synthesis. They enlist the absence of SEI formation because of the lack of electrolyte, and the continuous formation of highly reacting fresh surfaces due to repeated fracturing.

These examples highlight the benefits of ball milling-driven Na-reduction reactions, which are free of the complexities associated with handling reactive solutions or using mild temperature processing to prepare fully reduced materials. The synthesized P2-Na0.67[Fe0.5Mn0.5]O2 and ‘Na3.5V2(PO4)2F3’ show similar cyclic and rate performance (Supplementary Fig. 6) as the pristine P2-Na0.67[Fe0.5Mn0.5]O2 and NVPF, respectively, demonstrating that the short ball milling time does not bring any detrimental effect to its electrochemical performance. Such reactions, leading to the transformation of P2 to P02, or NVPF to Na4V2(PO4)2F3, are topotatic since the host structural frameworks are unaltered, and can simply be viewed as insertion reactions. Thus, the reactivity is simply dictated by the redox potential associated with the insertion of Na in various compounds. As shown in the electrochemical energy scale schematic representation in Fig. 5b, although Na3P is a milder reducing reagent than Na (0.5 V versus Na+/Na0), it is also expected to reduce P2 and NVPF. To test this point, as we have done for Na, a survey of various ball milling times together with various amounts of Na3P were conducted and the obtained composites were periodically checked for phase purity. We find the possibility to successfully prepare the Na4V2(PO4)2F3 phase (Fig. 5a) as well as the P02 phase (Fig. 5c) by ball milling powdered mixtures of NVPF and P2 with 1 and 0.2 molar amounts of Na3P, respectively. The reaction between Na3P and NVPF could be classified as chemical sodiation. The successful sodiation of NVPF by Na3P suggests that the reduction potential of NVPF should be higher than the potential for Na3P oxidation, that is, ~0.5 V. The advantage of Na3P as compared with Na metal is the fact it is a powder, although there is a compromise for...
this convenience with the requirements of excess amounts of Na₃P and longer ball milling time.

**Na-enriched phases for highly efficient Na-ion batteries.** The successful preparation of Na-rich Na₄V₂(PO₄)₂F₃ or composites with known amounts of NVPF and Na₄V₂(PO₄)₂F₃ enables control over the extra Na content by playing with ball milling times, and is of great importance for enhancing the performances of C/NVPF Na-ion cells. This situation closely mirrors the use of Li₁₋ₓMn₂O₄ as a Li source in C/LiMn₂O₄ Li-ion cells⁶, since the extra Na⁺ ions present in NVPF can be removed at low potential without an added weight penalty with exception to the weight of the x added Na. As a proof of concept, we assembled various electrochemical cells having carbon as the negative electrode and either the pristine NVPF phase or the 'Na₃₋ₓV₂(PO₄)₂F₃' composites as the positive electrode. For conciseness, we focus on Na₄V₂(PO₄)₂F₃ and P'2-Na₁[Fe₀.₅Mn₀.₅]O₂ phase by Na₃P ball milling. The XRD Rietveld refinement of (a) Na₄V₂(PO₄)₂F₃ and the profile matching of (c) P'2-Na₁[Fe₀.₅Mn₀.₅]O₂ phase obtained by ball milling using Na₃P as a reducing reagent are shown together with in the middle an electrochemical scale ranking the various used compounds in terms of redox potentials (b). In a,c the orange open circles, black continuous line and bottom grey line represent the observed, calculated, and difference patterns, respectively. Vertical blue tick bars mark the Bragg reflections.
respectively. The cells were cycled at a 0.2C rate (C rate being defined as the weight ratio of cathode to anode is 2.7 and 1.9 for C1 and C2 cell, respectively. The cells were cycled at a 0.2C rate (C rate being defined as the extraction of 2 Na from NVPF). For both cells a 1M NaClO4 in EC/DMC (50/50 by volume) electrolyte was used. The capacity is calculated based on the weight of positive materials. Inset in (b) shows the capacity retention in the first 20 cycles.

Figure 6 | Performances of C/Na3.5V2(PO4)2F3 Na-ion cells. The voltage-composition profiles are reported for two first cycles for cell C1 using Na3.5V2(PO4)2F3 (b) and cell C2 using Na3.5V2(PO4)2F3 (a). The weight ratio of cathode to anode is 2.7 and 1.9 for C1 and C2 cell, respectively. The cells were cycled at a 0.2C rate (C rate being defined as the extraction of 2 Na from NVPF). For both cells a 1M NaClO4 in EC/DMC (50/50 by volume) electrolyte was used. The capacity is calculated based on the weight of positive materials. Inset in (b) shows the capacity retention in the first 20 cycles.

Here only on the performance for the optimum x value. This value was estimated to be equal to 0.5 for compensating the ~25% irreversible capacity related to the SEI. Details about the balancing of cathode and anode are described in Supplementary Fig. 7 and Supplementary Note 3. Figure 6 shows the electrochemical performances of cells C1 and C2, having pristine NVPF and composite Na3.5V2(PO4)2F3 as positive electrodes, respectively. The cells were tested electrochemically between 1.5 and 4.3 V. The voltage trace for C1 mirrors reports in the literature for similar cells with a charging capacity of 129 mAh g−1 and a discharge capacity of 89 mAh g−1, which remains stable upon cycling. Providing sacrificial Na in the form of Na-rich NVPF (C2) strongly modifies the voltage profile: an initial capacity near 0.5 V corresponds to the removal of Na from Na3.5V2(PO4)2F3 to compensate for the SEI formation at the negative electrode; afterwards the potential rises, associated with removal of Na from NVPF. The C2 cell exhibits an overall charging capacity of 167 mAh g−1 and a discharge capacity of 110 mAh g−1, which is a 24% enhancement compared with cell C1. This corresponds to an overall 10% increase in energy density as described in Supplementary Note 4. Lastly, there is no evidence to suggest that use of the Na-rich phase jeopardizes the cycle life, with the capacity remaining nearly constant over 20 cycles (the maximum we have tried). Needless to say that further optimization of cell balancing via the use of three electrodes is being pursued to fine tune the proper value of x for achieving optimum performance.

We next implemented a similar approach in the optimization of C/P2-type Na0.67[Fe0.5Mn0.5]O2 Na-ion systems. In contrast to NVPF, the positive P2-Na0.67[Fe0.5Mn0.5]O2 phase cannot act as an extra source of Na since Na-rich Na0.67[Fe0.5Mn0.5]O2 does not exist. This is easily overcome by first preparing the P2-Na2[Fe0.5Mn0.5]O2 phase by Na-ball milling and then homogeneously mixing the P2 phase with the proper amount of Na-P to compensate for the carbon irreversible capacity. We here use extra Na3P, rather than Na metal, as it is easily added as powders to positive electrode materials to make homogeneous composite electrodes. Upon charging the cell, the added Na3P will oxidize to compensate for the Na consumed in SEI formation during the first cycle. This leaves behind elemental phosphorous, which remains as an electrochemical spectator within the cell upon subsequent cycles (Supplementary Fig. 8), but which also has the capability to act as a safety buffer by reinserting Na at a constant voltage in case of cell over-discharge.

A series of full Na-ion cells were assembled using carbon negative electrodes and composite positive electrodes made of P2-Na0.67[Fe0.5Mn0.5]O2 (cell D1), P2-Na1[Fe0.5Mn0.5]O2 (cell D2) and P2-Na1[Fe0.5Mn0.5]O2 + 10 wt.% Na3P (cell D3). The corresponding voltage profiles for the cells, collected upon cycling between 0 and 4.3 V at a current rate of 0.1C, are shown in Fig. 7a–c. The D1 cell shows a charge capacity of 112 mAh g−1 and a discharge capacity of only 71 mAh g−1 that is maintained upon subsequent cycling. These capacities are considerably lower than those obtained for Na/Na0.67[Fe0.5Mn0.5]O2 half cells (168 mAh g−1), due to the replacement of the Na anode by carbon, and hence the absence of a Na source to enable formation of the P2 phase and to compensate for losses to the SEI at the carbon electrode. In contrast, the D2 and D3 cells show charge capacities of 185 and 247 mAh g−1, respectively, with corresponding discharge capacities of 128 and 155 mAh g−1 that stabilized to 110 and 131 mAh g−1 after 20 cycles (Fig. 7d), the maximum we have tried so far. Note that cell D3, as opposed to cell D2, presents an extra voltage feature below 1 V in the first charge. The feature mirrors the voltage charge profile of a NaP/C cell (Fig. 7e), which nicely demonstrates the way Na3P works as a sacrificial Na source in a full Na-ion cell. Owing to its 0.5 V redox potential versus Na+/Na0, Na3P initially clamps the positive electrode voltage at a lower potential than that of the negative electrode-carbon starts to uptake Na+ at solely 1.5 V versus Na+/Na0, thus resulting in a negative output voltage of the cell to start with. Once the cell is charged, Na+ ions are released from Na3P to compensate for the irreversible SEI formation on carbon with the cell voltage climbing to 1 V; afterwards Na+ is released from the P2 part of the positive electrode so that the voltage profiles of both cells become nearly identical. Application wise the observed increase in reversible capacities from 71 to 128 and 155 mAh g−1 for the D1, D2, and D3 cells, respectively, which occurs without any sacrifice to the capacity retention behaviour upon cycling (Fig. 7d), clearly demonstrates the benefits of pre-producing the P2 phase and incorporating Na3P as a Na reservoir. Such capacity improvements increase the energy density by 30% between C/P2- Na0.67[Fe0.5Mn0.5]O2 and C/P2-Na1[Fe0.5Mn0.5]O2 Na-ion cells, and by an additional of 7% using P2-Na1[Fe0.5Mn0.5]O2/Na3P composites rather than solely P2-Na1[Fe0.5Mn0.5]O2 powders as positive electrodes (Supplementary Note 4).

Discussion

We have reported the preparation of Na-based alloys (NaSb, Na3P and so on) via an approach that relies on the ball milling of Na metal and have demonstrated that such an approach, using either Na or Na3P as reducing agents, can equally be used to easily prepare P2-Na1[Fe0.5Mn0.5]O2 layered oxide insertion compound, and to produce Na3.5V2(PO4)2F3 composites with the x = 1 composition being a single phase never reported so far. Such findings provide new insights for combating the irreversible capacity of NIBs, thereby significantly enhancing their
performances. We demonstrate the feasibility of assembling full Na-ion cells showing marked enhancements in energy storage density (10–30%) by using Na3P for electrode materials, including Na3P for D3 cell. The negative electrode is C. The weight ratio of positive to negative electrode is 2.6, 1.6 and 1.4 for D1, D2 and D3 cell, respectively. The cells were cycled at 0.1 C rate. The capacity is based on the weight of positive materials, including Na3P for D3 cell. The capacity retention of D1, D2 and D3 cell is given (Supplementary Fig. 3).

Figure 7 | Performances of C/P2-Na0.67[Fe0.5Mn0.5]O2 Na-ion cells. The voltage-composition profiles are reported for the two first cycles for cells using (a) as-made P2-Na0.67[Fe0.5Mn0.5]O2 (cell D1), (b) P2-Na0.67[Fe0.5Mn0.5]O2 made by Na ball milling (cell D2) and (c) for a P2-Na1[Fe0.5Mn0.5]O2/Na3P composite (cell D3) as positive electrode. The negative electrode is C. The weight ratio of positive to negative electrode is 2.6, 1.6 and 1.4 for D1, D2 and D3 cell, respectively. The cells were cycled at 0.1 C rate. The capacity is based on the weight of positive materials, including Na3P for D3 cell. The capacity retention of D1, D2 and D3 cell is given (d), and (e) shows the first charge profile of a C/Na3P cell. For all cells a 1 M NaClO4 in EC/DMC (50/50 by volume) electrolyte was used.

Methods

Synthesis of Na3P. Stoichiometric amounts of metallic sodium as bulk (Sigma) and red phosphorus (Alfa, 325 mesh) were filled into a hard steel ball-milled jar (30 cm3) of a Spex 8000M ball-miller in an Ar-filled glove box and equipped with seven hard steel balls each having a weight of 7 g and a diameter of 12 mm. These solid materials were ball-milled for 2 h to obtain Na3P particles. The mass ratio of balls to Na3P was maintained at 35. A similar protocol was used to prepare the reported Na3Sb powders.
Electrochemical tests. Coin cells were used to study the electrochemical performances. 1 M Na2CO3 solution in a mixture of EC/DMC in 1:1 ratio was used as electrolyte for the full cells with C as negative electrode. 5% FEC was systematically added in half cells when Na metal was used as counter electrode. The only exception regards the cells made of NVPF as positive electrode that were initially discharged because of experimented interferences between the decomposition potential of FEC and the insertion reduction potential of Na into NVPF (Supplementary Figs 4 and 5). Two pieces of Whatman glass fibres soaked with the electrolyte were used as separator between the positive and negative electrode. The powders of active materials were mixed with 20% carbon SP using Spez 8000M mixer mill. A typical weight of 3 mg of active electrode material was used per cell whatever Swagelok’s or coin cells. The cells were galvanostatic charged/discharged with a VMP automatic cycling/data recording system (Biologic Co., Clai, France) using various ranges of scanning potential and C rates with 1 C corresponding to the uptake or removal of 1 Na+ and 2 Na+ per formula unit in 1 h for P2- Na0.66Fe0.33Mn0.33O2 and NVPF, respectively. Note: While the present manuscript was under review, the NaV1/3PO4F2 phase was predicted, but not synthesized, ‘through computational calculation by Ceder’s group’.

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Author contributions

B.Z. carried out the synthesis; B.Z., R.D. and J.-M.T. conducted the electrochemical work and designed the research approach; and P.R. performed P2 phase. G.R. analysed the crystal structure and diffraction patterns; A.M.A. carried out the transmission electron microscopy test; and B.Z., G.R. and J.-M.T. wrote the manuscript. All authors discussed the experiments and final manuscript.

Additional information

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