Bismuth Vanadate and Molybdate: Stable Alloying Anodes for Sodium-Ion Batteries

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ABSTRACT: Sodium-ion batteries may become an inexpensive alternative to lithium-ion batteries for large-scale stationary storage of energy generated by intermittent renewable sources. The key for the deployment of this technology is the development of suitable anode materials which can rival the graphite anodes used in lithium-ion batteries in terms of energy density, cycle life, rate performance, and safety. Here, we demonstrate that the bismuth metalates, BiVO₄ and Bi₂(MoO₄)₃, as representatives of ternary metalates, can cope with these requirements. High specific capacities (367 mAh/g and 352 mAh/g, respectively), exceptionally high cycling stability for alloying anodes (up to 79% of the first charge capacity is retained over 1000 cycles at ∼1C for Bi₂(MoO₄)₃), better high-rate performance compared to other Bi-based anodes, low environmental load (Bi has low toxicity for a heavy metal), and low manufacturing costs (e.g., BiVO₄ is a commercial yellow pigment) make this novel class of anode materials suitable for large-scale electrical energy storage applications. Operando XANES, ex situ XRD, and DFT analysis suggest that the initial compounds are converted into alloying Bi nanocrystallites confined in a matrix of electrochemically active insertion hosts Na₃+xVO₄ and Na₂+xMoO₄, respectively. The Bi metalate phases are not reformed on charge, and on subsequent cycles the reaction with Bi metal and vanadate/molybdate phases gives rise to the reversible capacity. The nanostructured composite anode thus obtained has excellent high rate performance and retains its capacity over hundreds of cycles.

INTRODUCTION

Rechargeable sodium-ion batteries (SIBs) may become a promising alternative to lithium-ion batteries (LIBs) for large-scale stationary storage of energy generated by intermittent renewable sources. Wide-spread abundancy and low cost of Na makes this technology particularly attractive.¹–³ Similarities in Li and Na chemistries should facilitate a fast and cost-effective scale up of SIB technology.

The analogy to LIB systems is, however, not applicable for graphite, the most commonly used anode in LIBs, due to the inability of graphite to intercalate Na. Hard carbons are the most promising carbonaceous SIB anodes with reversible capacities as high as 300 mAh/g, close to those of graphite in LIBs (372 mAh/g). However, the low operation voltage is problematic with respect to safety concerns and high-rate capability due to risk of Na plating (<0.1 V) during sodiation and removal of Na from enclosed pores in the “house of cards” structure.⁴–⁶ It is therefore fundamental to develop suitable SIB anodes with high specific capacity, excellent cycling stability, safe average operation voltage (>0.2 V), and high-rate utilization.

 Alloying anode materials (group 14 and 15 metals) fulfill most of these requirements (Table S1). The main drawback is that multiple phase transitions and large associated volume changes (>250%) during sodiation and desodiation can cause the cycling stability to deteriorate.⁷,⁸ In some cases smoother...
structural transitions (e.g., with an amorphous intermediate phase) can lead to more stable capacity retention.\textsuperscript{9,10} Even higher capacities can be achieved if the alloying reaction is combined with a conversion-type reaction.\textsuperscript{11,12} Bi\textsubscript{2}O\textsubscript{3} (690 mAh/g) and Bi\textsubscript{2}S\textsubscript{3} (625 mAh/g), for example, exhibit higher capacities compared to Bi metal (385 mAh/g), respectively. These materials can reversibly form Na\textsubscript{2}O and Na\textsubscript{2}S, respectively, in addition to Na\textsubscript{3}Bi during electrochemical cycling. However, conversion often takes place at relatively high voltages (>1 V) which reduces the energy density. Improved cycling stability could in many cases be obtained by crystallite size engineering and careful selection of binder and carbon matrix which play a key role in compensating for the large volume changes and the low electrical conductivity of all or some phases present during electrochemical cycling.\textsuperscript{5}

In continuation of our work on Bi-based alloying and conversion reactions,\textsuperscript{9,15} we attempted a novel type of conversion reaction based on ternary Bi metalates in which the anions consist of electrochemically active transition metals surrounded by four oxygen atoms. A full conversion reaction (formation of Na\textsubscript{2}O) of these compounds would yield high specific capacities. To investigate this novel class of materials and to study their working mechanism, our choice of materials fell on commercially available BiVO\textsubscript{4} and Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}.

In this work we present bismuth vanadate and molybdate as novel and promising anode materials for SIBs. BiVO\textsubscript{4} and Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} show high specific capacities (367 mAh/g and 352 mAh/g, respectively), improved cycling stability vs metallic Bi (up to 79% first charge capacity is retained over 1000 cycles for Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}), excellent high-rate performance, low environmental load (due to the unusually low toxicity of Bi for a heavy metal), and low manufacturing costs (e.g., BiVO\textsubscript{4} is a yellow pigment that is produced by major chemical companies). The formation of an electrochemically active Na\textsubscript{3}VO\textsubscript{4} and Na\textsubscript{2}MoO\textsubscript{4} matrix after the initial, irreversible conversion of BiVO\textsubscript{4} and Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}, respectively, is likely one of the major reasons for the excellent battery performance.

\section*{RESULTS AND DISCUSSION}

\textbf{Ternary Bi Metalate Carbon Composite Anodes.} BiVO\textsubscript{4} and Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} adopt crystal structures in which Bi is surrounded by separated (VO\textsubscript{2})\textsuperscript{3−} and edge sharing (MoO\textsubscript{4})\textsuperscript{2−} tetrahedra, respectively (Figure 1; see Table S2 for crystallographic details). Bi metalate/carbon composites (7:3 by wt) were prepared by ball milling the as-purchased BiVO\textsubscript{4} and Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} and Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} and carbon black for durations of 20 min (Bi\textsubscript{2}O\textsubscript{2}(MoO\textsubscript{4})(C-20min) and Bi\textsubscript{2}(MoO\textsubscript{4})(C-20min) and 24 h (Bi\textsubscript{2}O\textsubscript{2}(MoO\textsubscript{4})(C-24h) and Bi\textsubscript{2}(MoO\textsubscript{4})(C-24h) under Ar. The morphology of the Bi metalate particles and their degree of carbon coating in the as prepared composite samples were investigated using SEM and EDX mapping. Prolonged milling results in smaller Bi metalate particles which are homogeneously dispersed in a carbon matrix for the 24 h samples compared to the larger and only partially carbon coated Bi metalate particles in the 20 min samples (see Supporting Information section on morphology for more details). This is in good agreement with the crystallite sizes determined from the broadening of the Bragg reflections in the diffraction patterns of the as-prepared samples (Figure S7). The Bi metalates were found to be microcrystalline in the 20 min samples and nanocrystalline in the 24 h samples (Table S2). Note that a particle can consist of several crystallites. This is the case in Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}/C-20min where several Bi metalate crystallites seem to be aggregated (Figure S3). In Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}/C-24h agglomerations of 68 ± 16 nm particles are found (Figure S4). The closeness to the crystallite size (58 ± 4 nm) as well as the homogeneous carbon coverage of the Bi metalate in the EDX map (Figure S6) suggest a fine dispersion of the Bi metalate in a carbon matrix, as reported for P/C and Sb/C composites prepared under similar ball milling conditions.\textsuperscript{17,18} HRTEM would be required to confirm these details. Anodes were fabricated by coating conductive carbon black and PAA binder on Al foil. A 1 M solution of NaPF\textsubscript{6} in EC/DEC (1:1 by wt) solution with the addition of 5 wt % FEC was used as electrolyte. The use of FEC as electrolyte additive resulted in better cycling stability (Figure S8). Synthetic and electrochemical testing conditions were fixed to those used in our previous work on Bi anodes for better comparability between the two studies.\textsuperscript{9}

\textbf{Electrochemical Performance.} Prolonged milling leads to improved cycling stability for both materials (Figure 2). Bi\textsubscript{2}O\textsubscript{2}(C-20min) and Bi\textsubscript{2}O\textsubscript{2}(C-24h) have a first charge (desodiation) capacity of 347 mAh/g and 367 mAh/g with 51% and 93% capacity retention over 100 cycles. Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}/C-20min and Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}/C-24h show 333 mAh/g and 352 mAh/g first charge capacity of which 57% and 91% are retained over 100 cycles. Bi\textsubscript{2}O\textsubscript{2}(C-20min) and Bi\textsubscript{2}O\textsubscript{2}(C-24h) exhibit a first cycle Coulombic efficiency of 49% and 56% with a first discharge (sodiation) capacity of 712 mAh/g and 683 mAh/g. Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}/C-20min and Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}/C-24h display 51% and 56% first cycle Coulombic efficiency with 655 mAh/g and 633 mAh/g first discharge capacity. For other Bi-based electrodes the first cycle Coulombic efficiency ranges between 65% and 78%.\textsuperscript{9,13,14,19} In addition to common irreversible processes taking place at the electrode (e.g., SEI formation), the lower first cycle Coulombic efficiency of the Bi metalates is related to the initial irreversible conversion reaction of the Bi metalates, which is discussed below. The Coulombic efficiency lies above 93% and 98% in the 2nd and 100th cycle, respectively, for all samples. The 20 min and 24 h samples furthermore exhibit clearly improved Coulombic efficiency and capacity retention with respect to identically prepared micro- and nanocrystalline Bi anodes (Bi/C-20min and Bi/C-24h, respectively, of our previous study)\textsuperscript{9} as compared in Figure S9. Another advantage of the Bi metalate anodes is that the first discharge capacity is only slightly affected by the increased surface area due to nanosizing compared to, e.g., Bi/C-20min.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{structure.png}
\caption{Crystal structure of (a) BiVO\textsubscript{4} and (b) Bi\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}. Purple, yellow, gray, and red balls represent Bi, V, Mo, and O atoms, respectively. Visualization by VESTA.\textsuperscript{16}}
\end{figure}
and Bi/C-24h with first discharge capacities of 635 mAh/g and 814 mAh/g, respectively. During the first discharge BiVO₄/C-20min exhibits a voltage plateau at 1.15 V, while the other samples show sloped voltage profiles in this voltage range (Figure 2). A possible explanation could be that sodiation of BiVO₄/C-20min proceeds through a two-phase mechanism of well-defined phases similar to Bi₂S₃ while a range of amorphous phases is formed during sodiation of the other samples that does not give rise to pronounced plateau (or dQ/dV peak in Figure S10). After the first discharge a reversible cycling regime is established showing sloped voltage profiles with two discernible plateaus for all samples during charge and discharge.

The voltage drop in the low-voltage plateau (Figure 2, giving rise to the small dQ/dV peaks below 0.3 V, Figure 3 and Figure S10) during the first discharge steps is not produced by a change in potential of the working electrode but by solvent interaction at the Na counter electrode which causes polarization (Figure S11) as initially suggested in ref 22. It disappears with increasing cycle number. Ideally prepared and tested reference cells without addition of FEC to the electrolyte did not show the voltage drop (Figure S12) in the low-voltage plateau during discharge. The voltage polarization is thus attributed to FEC which limits the Na reactivity toward the electrolyte via the growth of a protecting layer and minimizes the capacity degradation of the Na half cells (Figure S8). Similar dQ/dV features are otherwise observed (Figure 3 compared to Figure S13) which indicate that the reaction mechanism is not affected by the use of FEC in the electrolyte.

The high-voltage plateaus during charge/discharge are found at about 0.8 V/0.6 V while the low-voltage plateaus occur at about 0.6 V/0.4 V (potential vs Na/Na⁺) for all samples as determined from the differential capacity (dQ/dV) plots shown in Figure S10 and Figure 3. The reaction voltages are in good agreement with the ones determined from the cyclic voltammetry (CV) measurements which were performed at a voltage sweep rate of 0.01 mV/s. The dQ/dV and CV curves are compared in Figure S14. Similar redox voltages were found for nanocrystalline Bi (Bi/C-24h, Figure S15). An analogous alloying mechanism might therefore be expected. Previously we found nanocrystalline Bi (Bi/C-24h) to deviate from the reaction path for microcrystalline Bi (Bi/C-20min) following the equilibrium phase diagram (Bi ↔ NaBi ↔ hexagonal Na₃Bi) and to form cubic Na₃Bi instead. Cubic Na₃Bi provides
a smoother structural transition to NaBi which results in better cycling stability for Bi/C-24h compared to Bi/C-20min (Figure S9). The dQ/dV peaks of the Bi metalate samples, however, appear broadened vs nanocrystalline Bi (Figure S10 and S15). An underlying redox contribution from the metalate anion proceeding through amorphous phases which do not give rise to pronounced dQ/dV peaks might therefore be expected. In subsequent cycles new dQ/dV features, which we believe are associated with the crystallization of sodium metalate phases, become visible as indicated by the black arrows in Figure 3. During the fifth charge/discharge they are found at 0.67 V/0.49 V for BiVO₄ and at lower voltages, 0.59 V/0.25 V, for Bi₂(MoO₄)₃. The average operation voltages were found accordingly at 0.71 and 0.65 V with a voltage hysteresis of 0.26 and 0.28 V for BiVO₄/C-24h and Bi₂(MoO₄)₃/C-24h, respectively. The average operation voltage further largely depends on the group 14 or 15 alloying element in the ternary metalate. In this family of materials it is thus possible to optimize average operation voltage and specific capacity using both the alloying element and the transition metals.

The voltage profiles are only weakly affected by the milling conditions, while prolonged milling drastically improves the long-term cycling stability. BiVO₄/C-24h and Bi₂(MoO₄)₃/C-24h have smaller crystallite sizes, homogeneous carbon coating, and thus improved separation of the Bi metalate particles compared to the 20 min samples (Figure S1 and S2). The sharpening of the dQ/dV peaks associated with the Bi redox reactions with increasing cycle number in the 20 min samples (Figure 3) indicates Bi particle agglomeration (crystallization). This might explain the lower capacity retention compared to the 24 h samples (Figure 2a,b). Similar observations have been reported for Bi₂S₃.15 This point will be addressed by the ex situ XRD analysis which is described below. Note that loss of reversible capacity might also be associated with the electrochemically active metalate phases.

Rate performance and long-term cycling stability were investigated for the 24 h samples (Figure 4). The applied specific current was varied between 150 mA/g [corresponding to a (dis)charge rate (C-rate) of about 0.5C] and 3000 mA/g (∼10C) over 200 cycles. Up to currents of 900 mA/g capacities of more than 300 mAh/g and 250 mAh/g are retained for BiVO₄/C-24h (Figure 4a) and Bi₂(MoO₄)₃/C-24h (Figure 4b), respectively. At the highest applied current (3000 mA/g) both materials still exhibit capacities of about 100 mAh/g. The rate performance of the Bi metalates is summarized in Figure 4c, and better capacity utilization was found compared to other Bi-based materials, MoO₃, and hard carbon.21 The rate performance of an electrode is affected by the amount of carbon, film density, and thickness. Available information from the literature on the different electrodes compared in Figure 4c is therefore presented in Table S3. Despite the stress applied on...
the electrode system by the varying C-rates and application of large specific currents, as much as 91% and 95% of the first charge capacity are retained in the 200th cycle for BiVO₄/C-24h and Bi₂(MoO₄)₃/C-24h, respectively. This further underlines the excellent rate performance and cycling stability for these materials.

The long-term cycling stability of BiVO₄/C-24h and Bi₂(MoO₄)₃/C-24h was further investigated over a total of 1000 cycles (Figure 4d). After the first 100 cycles at a specific current of 150 mA/g (described above) the current was increased to 300 mA/g (∼1C). This C-rate corresponds to the time scales required in large-scale electrical energy storage applications ranging from 15 min to several hours. At 300 mA/g charge capacities of 323 mAh/g and 294 mAh/g in the 101st cycle (first cycle at ∼1C) were found for BiVO₄/C-24h and Bi₂(MoO₄)₃/C-24h, respectively. BiVO₄/C-24h and Bi₂(MoO₄)₃/C-24h retain 68% and 87%, respectively, of the 101st charge capacity in the 1000th cycle. Only 37% and 21%, respectively, of the first charge capacity are lost over a total of 1000 cycles. The less stable capacity retention of BiVO₄/C-24h might be due to instabilities in the cell after the 250th cycle (see spontaneous drop in Coulombic efficiency at this point) and is not necessarily related to the electrode material itself. The first 100 cycles at ∼0.5C lasted for 20 days while the total long-term cycling experiment took 70 days. This indicates that the materials are stable not only with cycle number but also with time. The Coulombic efficiency is improved at higher C-rates (Figure 4a,b,d). It increases from about 98% to above 99% when increasing the current from 150 mA/g to 300 mA/g for both samples (top panel Figure 4d). The reasons for this observation are not understood. A possible explanation is that higher C-rates prevent rate-limited, irreversible side reactions.

**Reaction Mechanism Reveals New Route to Stable Alloying Anodes.** The sodiation mechanisms of BiVO₄ and Bi₂(MoO₄)₃ were investigated by operando X-ray absorption near edge spectroscopy (XANES), ex situ X-ray diffraction (XRD), and ab initio calculations.

Figure 5 shows the changes in Bi L₃ edge position for both samples and in Mo K edge position for Bi₂(MoO₄)₃. XANES spectra of Bi and Mo could be acquired quasi-simultaneously on the same cell while the low absorption energy of V did not allow for detection of both Bi and V absorption edges using the same experimental configuration. The absorption energies were calibrated to 13419 eV for the Bi L₃ edge of Bi metal and 20 000 eV for the Mo K edge of Mo metal as described in the Supporting Information section on experimental details. Exemplary operando Bi L₃ and Mo K edge XANES data are shown in Figure S16. The data quality is insufficient for principal component analysis, so only changes in the edge positions were followed during cycling.

In the high-voltage region (>0.7 V) during the first sodiation the Bi L₃ edge shifts irreversibly from 13 424 eV for the Bi(III) metalates to 13 419 eV for metallic Bi, while the Mo K edge spectra remain unchanged. The six Na per Bi₂(MoO₄)₃ that are reduced for both samples after the first irreversible step.

This is in good agreement with the dQ/dV peaks in Figure 3 which are associated with the alloying reaction: Bi ↔ NaBi ↔ NaBi. Note that the slope of the Bi L₃ edge variation is reduced for both samples after the first irreversible reaction. This is not observed for the conversion anode Bi₂S₃/C-20min in ref 15 and can be seen as an indication of reduction of V(V) and Mo(VI), respectively, taking place in parallel with the reversible Bi alloying. Reversible changes in the Mo K edge were indeed observed for Bi₂(MoO₄)₃ (Figure 5b). They are most pronounced below 0.3 V during discharge and below 0.7 V during charge which fits with the assignment of the dQ/dV features in Figure 3. The moderate shift in Mo K edge position as well as the preservation of the pre-edge feature (Figure S16b) which is indicative of the allowed 1s→4d transition in tetrahedral Mo coordination point to an insertion rather than a further conversion mechanism. Due to the analogous behavior of the Bi L₃ edge and the change in Mo oxidation state the V is also expected to be redox active. The reversible alloying in addition to insertion reactions are therefore suggested in equations III and IV in Table 1 for BiVO₄ and Bi₂(MoO₄)₃, respectively.

The suggested reaction mechanisms agree with results obtained from calculating the theoretical reaction energies for the different possible reactions of Na with BiVO₄ and Bi₂(MoO₄)₃ as listed in the Supporting Information section on computational results, and with identifying the most probable reactions by comparing the energy difference. In
The energy difference between products and reactants of the individual steps is considerably smaller compared to the reactants for the reaction to be reversed. For I and II, respectively, and the products are too stable for the metastable cubic Na₃Bi phase which is stabilized during crystallites (formed during the initial conversion step) the first conversion reaction is highly exothermic (−5.478 eV (−529 kJ/mol) and −13.057 eV (−1250 kJ/mol) for I and II, respectively), and the products are too stable compared to the reactants for the reaction to be reversed. For the reversible reactions III and IV several intermediate reaction steps could be identified by the calculations and are indicated in Table 1. The energy difference between products and reactants of the individual steps is considerably smaller compared to the first step (Table 1).

The trends in our calculated voltages for the various steps (Table 1) correspond well to the experimental observations. The closeness in voltages for Bi and V as well as Mo redox reactions fits with our previous assumption that they may take place in parallel. It should be noted that if Na₃MoO₄ crystallizes in the Pnma structure our calculated voltage for reaction IVc becomes 0.79 V which is too high compared with the experimental results. When we used the energy of the metastable phase (i.e., the P213 structure, Table S4) we got 0.46 V which fits better with the experimental observations. This finding clearly indicates that in the Na₃MoO₄ nanocrystallites (formed during the initial conversion step) the metastable phase is stabilized. A similar situation was identified for the metastable cubic Na₃Bi phase which is stabilized during electrochemical sodiation of nanocrystalline Bi.

The electrochemical activity of Na₃VO₄ and Na₃MoO₄ was tested without Bi. Na₃VO₄ and Na₃MoO₄ carbon composites exhibit negligible reversible capacities (Figure S17). Also the cycling stability of Bi/C composites is worse than that of the Bi metalate samples (Figure S9). The intimate mixing of the Bi and metalate phases at the nanoscale appears to give rise to the improved electrochemical performance.

The ex situ XRD profiles of Bi₃(MoO₄)₃ collected after the first sodiation and desodiation (Figure S18) confirm the nanocrystalline nature of the electrode material after the irreversible conversion of Bi₃(MoO₄)₃ (equation 1). The positions of the broad diffraction features indicate mainly cubic Na₃Bi and Bi phases for the sodiated and desodiated samples, respectively. The signal is dominated by the Na–Bi phases, and it was impossible to identify any Mo containing phases using XRD. Total scattering analysis could reveal more quantitative information on the local order of involved phases, their particle/cluster sizes, and weight fractions.

The low first cycle Coulombic efficiency of the Bi metalate electrodes (49% to 56%) is partly due to the irreversible conversion reactions (equations I and II, with single headed arrows, in Table 1) which take place during the first sodiation. These give rise to a loss of 248 mAh/g and 179 mAh/g of reversible capacity for BiVO₄ and Bi₂(MoO₄)₃, respectively.

Note that the first cycle Coulombic efficiency is also caused by other irreversible processes which is reflected in the only slightly higher values (65% and 75%) for other Bi-based electrodes.

For subsequent cycles a reversible regime based on equations III and IV is established. Calculations suggest alloying of Bi in two steps (Bi ↔ NaBi ↔ Na₂Bi) which is in good agreement with the Bi L3 edge shifts, the dQ/dV peaks (Figure 3), and ex situ XRD (Figure S18). The calculations further indicate insertion of Na into Na₃MoO₄ and Na₂MoO₄ with x ≤ 1 (equations IIIc and IVb, respectively). Note that although the Mo XANES and the dQ/dV/ features (Figure 3) support an insertion reaction the amount of Na inserted (x) could not be quantified. The theoretical capacities of reactions III and IV with x = 1 are 331 mAh/g and 269 mAh/g, respectively. The measured specific capacities are larger than the theoretical ones which confirms that one Na can be inserted into Na₃MoO₄ and Na₂MoO₄ (x = 1). The extra observed capacity could be due to the added carbon contributing to the reversible capacity.

Ex situ XRD profiles collected after 100 discharge/charge cycles confirm particle agglomeration with cycle number for both Bi₃(MoO₄)₃/C-20min (Figure S18) and Bi₃(MoO₄)₃/C-24h (Figure S19) as indicated by the sharpening of the Bi dQ/dV features. The crystallization is much more pronounced for the 20 min sample which in addition forms NaBi and Na₂Bi residual phases. The capacity degradation due to Na–Bi particle agglomeration seems to be favored by the larger and/or only partially carbon coated Bi metalate particles in the 20 min vs 24 h samples (Figures S1 and S2).

### Table 1. Possible Reaction Steps with Calculated Reaction Energies, Voltages, and Theoretical Capacities

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>Energy (kJ/mol)</th>
<th>Voltage (V)</th>
<th>Capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>3Na + BiVO₄ → Bi + Na₂VO₄</td>
<td>1250 kJ/mol</td>
<td>0.62</td>
<td>248</td>
</tr>
<tr>
<td>II</td>
<td>6Na + Bi₂(MoO₄)₃ → Bi + 3Na₂MoO₄</td>
<td>119 kJ/mol</td>
<td>0.62</td>
<td>179</td>
</tr>
<tr>
<td>IIIa</td>
<td>Na + Bi + Na₂VO₄ → NaBi + Na₂VO₄</td>
<td>−0.62</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>IIIb</td>
<td>Na + NaBi + Na₂VO₄ → NaBi + Na₂VO₄</td>
<td>−0.55</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>IIIc</td>
<td>2Na + NaBi + Na₂VO₄ → NaBi + Na₂VO₄</td>
<td>−0.91</td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>IVa</td>
<td>(6 + 3x)Na + 2Bi + 3Na₂MoO₄ → 2NaBi + 3Na₂₋ₓMoO₄</td>
<td>−1.23</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>IVb</td>
<td>4Na + 2NaBi + 3Na₂MoO₄ → 2NaBi + 3Na₂MoO₄</td>
<td>−1.82</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td>IVc</td>
<td>3Na + 2NaBi + 3Na₂MoO₄ → 2NaBi + 3Na₂MoO₄</td>
<td>−1.39</td>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>

*) Components whose oxidation states change are marked in bold and x ≤ 1. Single and double headed arrows indicate irreversible and reversible reactions, respectively.

**CONCLUSION**

Both Bi metalates, BiVO₄ and Bi₂(MoO₄)₃, exhibit better high-rate capacity utilization than other Bi-based anodes and excellent cycling stability, which were demonstrated over 200 and 1000 cycles, respectively. Bi₂(MoO₄)₃, for example, retains 79% of its first charge capacity at −1C over 1000 cycles which is very unusual for alloying anodes. The Bi metalates operate in the optimal voltage range for SIBs with respect to safety and energy density. They have low environmental load with respect to the low toxicity of Bi compared to other heavy metals and low manufacturing costs. For these reasons the Bi metalates are suitable candidates for anode materials in large-scale electrical energy storage applications.

Operando XANES, ex situ XRD, and DFT analysis suggested that during the conversion of BiVO₄ and Bi₂(MoO₄)₃ nanocrystalline Bi (which allows for smoother alloying/dealloying reactions with Na⁺) and the electrochemically active Na₃₋ₓMoO₄ and Na₂₋ₓMoO₄, respectively, are formed. The Bi
metalate phases are not reformed on charge, and on subsequent cycles the reaction with Bi metal and vanadate/molybdate phases gives rise to the reversible capacity (Table 1). Na$_3$V$_2$O$_7$ and Na$_3$Mo$_2$O$_7$ are believed to provide a suitable matrix for the Bi nanocrystallites, giving high rate performance and stable capacity retention over hundreds of cycles.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b04699.

Overview of Na alloying anode materials; experimental details; SEM images and EDX maps of Bi metalate carbon composites; crystallographic information, XRD profiles, and Rietveld refinements; electrochemical, cycling performance, dQ/dV, and CV plots with and without addition of FEC to the electrolyte and compared to Bi; information on the electrodes for which the rate performance is compared in Figure 4c; Li L$_3$ and Mo K edge XANES spectra; electrochemical performance of Na$_3$V$_2$O$_7$ and Na$_3$Mo$_2$O$_7$; ex situ XRD profiles of Bi$_2$(MoO$_4$)$_3$ electrodes at different stages of cycling; and DFT work showing reaction path associated reaction energies and theoretical structures for Na$_3$Mo$_2$O$_7$ (PDF).

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

C-rate, (dis)charge rate; CV, cyclic voltammetry; DEC, diethyl carbonate; dQ/dV, differential capacity; EC, ethylene carbonate; EDX, energy dispersive X-ray spectroscopy; FEC, fluoroethylene carbonate; HRTEM, high resolution tunneling electron microscope; LIB, lithium ion battery; PAA, poly(acrylic acid); SEM, scanning electron microscope; SIB, sodium ion battery; XANES, X-ray absorption spectroscopy; XRD, X-ray diffraction

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