Enabling room temperature sodium metal batteries

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Abstract

Rechargeable batteries based upon sodium (Na^+) cations are at the core of many new battery chemistries beyond Li-ion batteries. Rather than using carbon or alloy-based anodes, the direct utilization of solid sodium metal as an anode would be highly advantageous, but its use has been highly problematic due to its high reactivity. In this work, it is demonstrated that, by tailoring the electrolyte formulation, solid Na metal can be electrochemically plated/stripped at ambient temperature with high efficiency (> 99%) on both copper and inexpensive aluminum current collectors thereby enabling a shift in focus to new battery chemical couples based upon Na metal operating at ambient temperature. These highly concentrated electrolytes have enabled excellent cycling stability of Na metal batteries using Na metal anode and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathode at high rates with very high efficiency.

KEYWORDS: concentrated electrolytes, solid-electrolyte interface, sodium metal batteries.

Introduction

Solid sodium (Na) metal electrodes could enable the production of relatively low cost, high energy batteries with an anode active material derived directly from ubiquitous table salt (NaCl) which is abundant on earth. Commercial, secondary (rechargeable) batteries are presently available which directly employ Na metal as an anode—i.e., Na/NiCl₂ and Na/S, but these batteries need to operate at high temperature (> 250°C) due to the requirement of a solid electrolyte (β "-alumina) to protect the highly reactive Na metal. The high temperature is essential to facilitate Na^+ cation transport within the solid electrolyte and the Na metal (m.p. 98°C) is therefore molten in such batteries. This feature adds considerable complexity and cost to cell manufacturing and operation.

In recent years, a prolific number of research publications have been reported for ambient temperature Na-ion batteries (Fig. 1) in which the Na metal was not used as the anode. Instead, the cells operate in a manner similar to Li-ion batteries, with the cations forming intercalation compounds or alloys with the anode active materials. A large specific capacity penalty is incurred for such anodes, however, due to the need to stabilize the Na^+ cations either with carbon, with alloying metals/phosphorus or within metal oxides/sulfides.¹⁻³ In

addition, the working voltage of such anodes is often well above that of the Na/Na⁺ couple⁴⁻⁹ resulting in a significantly lower battery voltage (than for Li-ion batteries) and thus a much lower specific energy density (the product of the specific capacity and operating voltage) when the anode is paired with a cathode in a battery cell.

The direct use of Na metal as a battery anode would therefore be highly advantageous as it exhibits a much higher specific capacity as compared with carbonaceous materials and other Na intercalation compounds such as Na₄Sn. The direct use of Na metal anode will further accelerate the commercialization of Na based rechargeable batteries¹⁰. A critical challenge to use of Na metal anode, however, is the reactivity of Na metal which is even more problematic than for Li metal. This accounts for the fact that only a handful of publications have been reported for the plating/stripping of Na metal and these have focused primarily on electrolytes based upon molten salt mixtures containing sodium salts and either another inorganic salt or a salt with an organic cation (i.e., an ionic liquid)¹¹⁻²³. The reactivity of these electrolytes with Na metal, however, has limited the plating/stripping Coulombic efficiency (CE) (ratio of charge recovered from stripping and required for plating of the Na metal) to $\leq 95\%$ (typically much lower) which would result in rapid capacity fading for a battery and no extensive cycling data has been reported for a solid Na metal electrode with these electrolytes. Electrolyte formulation optimization has been a difficult challenge for Na-ion batteries²⁴⁻²⁶ and the same holds true for electrolytes for use with Na metal. One notable exception to this is a recent report by She and Cui et al on the use of an electrolyte composed of diglyme and NaPF₆ which demonstrated the ability to reversibly plate/strip Na with very high efficiency.²⁷ However, the full operation of Na metal batteries with Na intercalation compounds has not yet been reported.

We report here the high rate, high efficiency operation of Na metal batteries based on Na/Na₃V₂(PO₄)₃ structure. We demonstrate that solid Na metal can be reversibly plated/stripped on a Cu current collector with an extremely high CE using highly concentrated liquid electrolytes based upon ether solvents (e.g., tetrahydrofuran (THF), 1,2 dimethoxyethane (DME), diglyme, etc.) and the salt sodium bis(fluorosulfonyl)imide (NaN(SO₂F)₂ or NaFSI) demonstrating that solid Na metal battery electrodes may be directly used at ambient temperature.

Experimental

Materials. Sodium metal, sodium hexafluorophosphate (NaPF₆), anhydrous tetrahydrofuran (THF), anhydrous 1,4-dioxane and anhydrous 1,3-dioxolane were purchased from Sigma-Aldrich Corporation. Sodium bis(fluorosulfonyl)imide (NaFSI) and sodium bis(trifluoromethanesulfonyl)imide (NaTFSI) were obtained from Solvionic Corporation and dried under high vacuum at 120°C for 24 h before use. The solvents 1,2-dimethoxyethane (DME), diglyme (G2), ethylene carbonate (EC), propylene carbonate (PC) and diethyl carbonate (DEC) (all battery-grade purity) were obtained from BASF Corporation and stored over 4 Å molecular sieves. The electrolytes were prepared by dissolving the desired amount of salt into the solvent (Fig. S1 and S2). Al foil and Cu foil were purchased from MTI Corporation. The materials were stored and handled in an MBraun LABmaster glove box with an Ar atmosphere (< 1 ppm O₂ and < 1 ppm H₂O). Two different notations were used for the electrolyte concentrations: molarity (mol salt L⁻¹ solution) and the solvent-salt

mole ratio to better aid in understanding the relationship between the Na plating/stripping performance and the compositions. For comparison, the 4M NaFSI-DME electrolyte corresponds to a DME-NaFSI 1.6-1 mole ratio.

Electrochemical measurements. The electrochemical performances of the Na plating/stripping processes were studied using CR2032-type coin cells, each of which consisted of a Cu foil (3/4 in diameter) as the working electrode, a Whatman glass fiber separator (3/4 in diameter) and Na metal foil (9/16 in diameter) as the counter electrode. The electrolytes used (100 μ L per cell) include those based upon carbonate or ether solvents and NaPF₆, NaTFSI (i.e., N(SO₂CF₃)₂⁻ anion) or NaFSI (i.e., N(SO₂F)₂⁻ anion). The plating of Na was capacity controlled by setting the deposition time to 1 h for current densities of 0.2, 0.5 and 1.0 mA cm⁻², while the stripping process was voltage controlled by setting the upper cutoff voltage to either 0.5 or 1.0 V vs. Na/Na⁺.

To study the post cycling Na morphologies and to characterize the surface coating compositions after different numbers of cycles, cells were cycled for 1, 5 and 25 cycles at a current density of 0.5 mA cm⁻² for 2 h, while keeping the upper cutoff voltage the same at 1.0 V vs. Na/Na⁺. The Whatman glass fiber separator stuck to the Na metal and also to the deposited coating on the Cu current collector side of the coin cells, so three separators were used instead with a glass fiber separator sandwiched between two Celgard 2400 separators (for the cells which were disassembled for post cycling characterization).

All of the cells were cycled at 25°C in a Lanhe battery testing system. Cells were assembled and disassembled inside an Ar-filled glove box with the H₂O and O₂ concentration < 0.1 ppm. "Plating" and "stripping" refer to the Cu (or Al) working electrode (i.e., "plating" for the Na counter electrode actually corresponds to the stripping of Na metal to plate on the Cu electrode).

A DME-NaFSI (1-1) concentrated electrolyte and Na metal were tested in a full cell with a Na₃V₂(PO₄)₃-carbon composite cathode. The cathode was prepared by mixing 80 wt% Na₃V₂(PO₄)₃-carbon composite (10% carbon in the composite), 10 wt% Super-P, and 10 wt% polyvinylidene difluoride (PVDF) dissolved in *N*-methyl-2-pyrrolidone (NMP) to form a slurry, which was then pasted onto an Al foil current collector. After drying the resulting coating in vacuum at 70°C, the electrodes were punched and tested in coin cells. The electrode loading was 1.5 mg cm⁻². A microporous membrane (Celgard 3501) was used as the separator. Coin cells were assembled in an Ar-filled glove box. The cells were tested using galvanostatic charge-discharge protocols on a BT-2000 Arbin battery testing system at room temperature. The cells were cycled within a voltage range from 2.7 to 3.7 V at different rates (i.e., 10 cycles for each rate of C/10, C/5, C/2, 1C, 2C and 4C, followed by continuous cycling at C/2 (1C = 120 mA g⁻¹)). The specific capacity was calculated based upon the mass of the Na₃V₂(PO₄)₃ active material in the cathode. **Characterization.** Cycled coin cells were disassembled to harvest the Na metal counter electrodes and Cu current collectors for characterization using optical photographs, SEM, powder XRD, XPS and NMR (details provided in the SI). Before analyses, these electrodes were first rinsed with DME solvent three times to remove residual electrolyte and then dried in the vacuum chamber of the MBraun glove box. SEM images of the Na electrodes for both the surfaces and the cross-sections were obtained with an FEI Quanta FESEM at an accelerating voltage of 5 kV. A cross-section of the plated Na was prepared by vertically cutting the Na samples with a razor blade.

Results and discussion

Fig. 2a reports the CE upon cycling for Cu/Na half cells with a 4M NaFSI-DME electrolyte in which Na metal is plated onto and then stripped from Cu current collectors at three different current densities. The CE of the first few cycles is relatively low for the cells, but this increases upon continued cycling—achieving a value of 99% for the cells cycled at 0.5 and 1.0 mA cm⁻². The lower CE values in the initial cycles (Fig. 2) suggests that—along with the Na metal plating—side reactions are present, but the continuous improvement in the CE over the first few charge/discharge cycles indicates that passivation rapidly occurs.

Cu metal is almost universally used as an anode current collector in Li-ion batteries, despite its high cost and weight, since it is one of the few metals which does not alloy with Li to form intermetallic phases at ambient temperature²⁸. Al is a less expensive, lower weight metal than Cu, making it a much more desirable anode current collector material, but Al does form intermetallic phases with Li leading to the physical transformation of the current collector during cycling²⁹. In contrast, neither Cu nor Al alloys with Na^{30, 31}. When the Cu current collector was replaced with Al, a highly efficient cycling of Na metal with the 4M NaFSI-DME electrolyte was again achieved—comparable to that noted with Cu (Figs. 2b and S12). A high CE was also obtained for the cycling of the Al electrode when a 4M LiFSI-DME electrolyte was used (Fig. 2b), but this was instead due to the highly reversible formation of Al-Li alloys as reflected by the plating/stripping voltage profiles (Fig. S12).

Optical images of the new and cycled electrodes show that a gray (wet status) surface coating builds up on the Cu electrode during the initial cycles (Fig. 3). After continued cycling (10-20 cycles), this becomes a uniform dark gray (wet status) coating which acts as a protective layer shielding the electrolyte from direct contact with the Cu electrode and plated Na metal and thus acts in a similar manner to the solid electrolyte interface (SEI) layer formed on graphite anodes in Li-ion batteries³².

SEM images of the Na metal plated with the 4M NaFSI-DME electrolyte in the 1st cycle (Figs. 4a, b) reveal a flat, interwoven mat of Na metal that closely resembles the morphology of the pristine Na metal of the counter electrode prior to cycling (Fig. S16). Upon continued cycling, the SEM images for both the Cu and Na counter electrodes (Figs. 4c,d, S17) display the surface coating noted in the optical images (which cracks on the Na electrode upon drying). After 50 cycles, coatings formed on the top surface of both Na and Cu electrodes could be obviously seen (Fig. S15). In contrast, SEM images of the Na metal plated with the dilute 1M NaFSI-DME electrolyte in the 1st cycle (Fig. S14) show a rough, non-conformal Na deposit on Cu electrodes. For comparison, the Cu current collector is also carefully characterized (Fig. S13).

In order to further analyze the chemical composition of coating layers, several characterization techniques, including powder XRD, XPS and ²³Na 3Q-MAS NMR, are conducted. XPS results show that the coatings on Cu electrodes cycled in a 4 M NaFSI-DME electrolyte contain a large amount of Na and O elements (Figs. S18, S19), while the coatings formed in a 1 M NaFSI-DME electrolyte contain a lower concentration of O element and a higher concentration of F and S elements (Figs. S20, S21). The EDAX spectra of the surface coating in the 4 M NaFSI-DME electrolyte also reveal the high content of Na and O (Fig. S24). The results of powder XRD and

^{23}Na 3Q-MAS NMR indicate that the high content of Na and O formed in the 4 M NaFSI-DME electrolyte should be attributed to a large fraction of NaOH (Figs. 5a, S26). Noticeably, the ^{23}Na 3Q-MAS NMR also shows the formation of Na_2S in the coating layer (Fig. S25).

In contrast with the use of the highly concentrated ether electrolytes with NaFSI, when Cu electrodes were instead cycled with comparable concentrated electrolytes with either NaPF_6 or NaTFSI (e.g., bis(trifluoromethanesulfonyl)imide or TFSI⁻), only limited Na metal plating occurred suggesting that side reactions consumed most of the applied current for the plating process (Fig. S3-S6 and S8). Poor cycling performance was also found for dilute DME-NaFSI electrolytes (Figs. S3, S5 and S6), while excellent cycling performance was noted for highly concentrated NaFSI electrolytes with other ethers such as diglyme and THF (Fig. S11). In addition, NaFSI-PC electrolytes also show very poor cycling performance (Fig. S7), indicating the solvents play a very important role for the coating layer formation. Furthermore, the addition of mixture salts like NaTFSI and NaPF_6 is detrimental to the cycling performance (Figure S9, S10). The XPS measurements reveal that the SEI coating formed in a 1 M NaPF_6 -EC/DEC electrolyte contains higher concentration of C element, especially in the top SEI layer (Figs. S21, S22). In contrast, the SEI coatings formed in NaTFSI-DME electrolytes contain higher concentration of F element in comparison with that from NaFSI-DME electrolytes based on XPS results (Figs. S23, S24). This is consistent with the results obtained by the powder XRD that NaTFSI tend to generate a large amount of NaF in the SEI layer (Fig. 5b).

The limited oxidative stability of ether solvents with cathodes has always been one of the limitations to their use as electrolyte components for Li-ion batteries. It has been reported, however, that the oxidative stability is greatly improved when all of the ether solvent is coordinated to Li^+ cations^{33,34}. The same is expected for Na^+ cations. Therefore, to demonstrate that the concentrated DME-NaFSI electrolytes are compatible with battery cathodes, full cells were prepared with Na metal as the anode and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ used as the cathode active material^{35,36}. Excellent cycling performance was achieved in terms of both rate performance and the near 100% Coulombic efficiency of the cathode (Fig. 6) confirming that the concentrated DME-NaFSI electrolytes is a very promising electrolyte that enables the use of Na metal anode for room-temperature Na metal-based batteries.

Conclusion

In this work, we have demonstrated that solid Na metal can be reversibly plated/stripped at ambient temperature with an extremely high Coulombic efficiency. The electrolytes that enable this behavior are highly concentrated ether-NaFSI mixtures that largely passivate the Na metal surface, thus minimizing side degradation reactions during cycling. The Na metal is plated as a flat, interwoven mat that is non-dendritic in morphology. These highly concentrated electrolytes permit the Na metal anode to be coupled with a cathode tailored for Na-ion batteries to create full batteries capable of being discharged at high rates with high efficiency.

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Author contributions

J.-G.Z. and W.A.H. conceived and designed the experiments. R. C. and K. M. performed electrochemical measurement with the help from X.L.L and J.Q. M.H.E., M.E. B, performed the SEM and XPS measurement, respectively. K.S.H. and K.T.M. performed NMR measurements. W.A.H., R. C. and J.-G.Z. prepared the manuscript with input from the other authors.

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Figure 1 | Number of publications by year (SciFinder) relevant to Na-ion batteries.

Figure 2 | Alkali metal plating/stripping. **a**, Coulombic efficiency of Cu/Na cells with 4M NaFSI-DME electrolyte cycled at different current densities. **b**, Coulombic efficiency of Al/Na and Al/Li cells with 4M NaFSI-DME or 4M LiFSI-DME electrolytes, respectively, cycled at a rate of 0.5 mA cm⁻². **c**, Voltage profiles for cycling of Cu/Na cell with a 4M NaFSI-DME electrolyte and 1.0 mA cm⁻² current density. The cycle numbers are indicated in the figure.

Figure 3 | Photographs of the Cu (working) and Na (counter) electrodes for a cell cycled with 4M NaFSI-DME. a, New. b, 1st cycle plating. c, 1st cycle stripping. d, 5th cycle plating. e, 5th cycle stripping. f, 25th cycle plating. g, 25th cycle stripping.

Figure 4 | SEM images of electrodes after cycling in the 4M NaFSI-DME electrolyte. a, Na metal on Cu after 1st cycle plating. **b,** Magnified image shown in **a**. **c,** Na metal on Cu working electrode after 5th cycle plating. **d,** Na metal counter electrode after 5th cycle plating (on Cu working electrode).

Figure 5 | Powder XRD patterns of surface coating layer harvested from coin cells with different electrolytes after the 25th stripping cycle. a, 4M NaFSI-DME. **b,** 3M NaTFSI-DME (indexing: blue-NaOH, gold-Cu, red-NaF). The broad peak centered near 30° is due to the glass capillary tube.

Figure 6 | Cycling characteristics of a $\text{Na}/\text{Na}_3\text{V}_2(\text{PO}_4)_3$ full cell. Rate performance and cathode CE for a cell cycled with a 2.5M NaFSI-DME electrolyte.