Bismuth Islands for Low-Temperature Sodium-Beta Alumina Batteries

Dana Jin,† Sangjin Choi,† Woosun Jang,‡ Aloysius Soon,‡ Jeongmin Kim,† Hongjia Moon,† Wooyoung Lee,‡ Youinki Lee,† Sori Son,§ Yoon-Cheol Park,§ HeeJung Chang,† Guosheng Li,†∥ Keeyoung Jung,*§ and Wooyoung Shim*†

†Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Korea
‡Department of Materials Engineering and Convergence Technology & RIGET, Gyeongsang National University, Jinju 52828, Korea
§Materials Research Division, Research Institute of Industrial Science & Technology, Pohang 37673, Korea
∥Electrochemical Materials and System Group, Pacific Northwest National Laboratory, Richland, Washington 99352, United States

Supporting Information

ABSTRACT: Wetting of the liquid metal on the solid electrolyte of a liquid metal battery controls the operating temperature and performance of the battery. Liquid sodium electrodes are particularly attractive because of their low cost, natural abundance, and geological distribution. However, they wet poorly on a solid electrolyte near its melting temperature, limiting their widespread suitability for low-temperature batteries to be used for large-scale energy storage systems. Herein, we develop an isolated metal-island strategy that can improve sodium wetting in sodium-beta alumina batteries that allows operation at lower temperatures. Our results suggest that in situ heat treatment of a solid electrolyte followed by bismuth deposition effectively eliminates oxygen and moisture from the surface of the solid electrolyte, preventing the formation of an oxide layer on the liquid sodium, leading to enhanced wetting. We also show that employing isolated bismuth islands significantly improves cell performance, with cells retaining 94% of their charge after the initial cycle, an improvement over cells without bismuth islands. These results suggest that coating isolated metal islands is a promising and straightforward strategy for the development of low-temperature sodium-beta alumina batteries.

KEYWORDS: Sodium-beta alumina battery, low-temperature, liquid metal, wetting, bismuth

INTRODUCTION

The development of liquid metal batteries is rapidly advancing owing to their high specific energy (energy per unit mass) and high energy density (energy per unit volume), with applications in large-scale stationary electricity storage.¹,² In particular, significant efforts have been made in sodium-beta alumina batteries (NBBs) having a liquid Na anode and a β″-Al₂O₃ solid electrolyte (BASE)³−⁵ which have been employed in large-scale renewable energy storage applications. These efforts have highlighted the importance of battery components, but high temperatures are required for electrochemical activity, impeding the realization of low-temperature NBBs that can avoid costly manufacturing and safety issues.⁶,⁷

To realize low-temperature NBBs, β″-Al₂O₃ must have a low resistance and sufficient ionic conductivity (0.2–0.4 S/cm at 300 °C) at low operating temperatures.⁴ These can be attained by thinning β″-Al₂O₃ and producing high-quality β″-Al₂O₃ with fewer bulk impurities such as silicon and calcium that form glassy sodium aluminosilicate phases and intergranular calcium aluminate phases, respectively.⁸−¹⁰ In addition, high ionic conductivity in electrolytes can be achieved by increasing the volume fraction of the β″-phase in two-phase mixtures (β-Al₂O₃/β″-Al₂O₃) via doping with divalent cations such as Mg²⁺, Ni²⁺, Zn²⁺, and Cu²⁺.¹¹,¹² Ionic conductivity is also affected by the microstructure, for example, larger average grains lead to higher conductivity.¹³ Another approach for

Received: August 14, 2018
Accepted: December 24, 2018
Published: December 24, 2018
reducing operating temperatures is to replace $\beta^3\text{Al}_2\text{O}_3$ with other sodium ion conductors such as glass, glass-ceramic electrolytes (e.g., Na$_2$PS$_4$ glass-ceramic electrolyte), and a Na super ionic conductor (NASICON)-type crystal with the general chemical formula of Na$_{1+2y}ZrSiP_{1-y}O_{12}$ ($0 < x < 3$).

Alternatively, improving the wetting behavior of liquid Na on the surface of $\beta^3\text{Al}_2\text{O}_3$ can produce lower operating-temperature NNBs. Typically, the wetting of liquid Na decreases as temperature decreases, meaning that the active area of the wetting interface between liquid Na and $\beta^3\text{Al}_2\text{O}_3$ decreases, degrading battery performance. It is well-known that poor Na wetting is related to the formation of surface oxidation of liquid Na when $\beta^3\text{Al}_2\text{O}_3$ is exposed to moisture-rich conditions (Figure S1), necessitating conditioning cycles to reach full cell capacity. To address this wetting problem, additional metal coatings (e.g., Sn, Bi, and In) or porous nanostructures (e.g., Ni nanowires, Pt mesh, and Pb particles) were applied to the surface of $\beta^3\text{Al}_2\text{O}_3$ to increase the adhesive energy between metal (Na)–metal coating contacts and to prevent moisture from being absorbed onto $\beta^3\text{Al}_2\text{O}_3$. In addition, the application of various Na alloys with Cs, Sn, and Bi, which have a high work of adhesion ($W_{\text{m}}$) with $\beta^3\text{Al}_2\text{O}_3$, has been reported to show improvements in the wetting behavior. Taking advantage of this metal passivation effect, this approach, where metal ions are considered potential impurities, causes a problem with Na ion transport and limits full utilization of the contact area because of the presence of impurity metals on the surface of $\beta^3\text{Al}_2\text{O}_3$. Therefore, metallic elements that can be alloyed with Na in small amounts must be identified such that Na ion transport is unimpeded while effectively protecting the surface of $\beta^3\text{Al}_2\text{O}_3$ and as a result, removing the need for conditioning cycles.

We have chosen Bi as metallic coating materials, and several important features critical to the choice of Bi, follow: first, Bi can be alloyed with Na as an oxygen getter, such as a Ti or Al sponge, to reduce the formation of sodium oxide at the interface and therefore improve wetting. The standard Gibbs free energy of formation of Bi$_2$O$_3$ is $-439.0$ kJ/mol at 230 °C (compared to $-350.8$ kJ/mol for Na$_2$O at 230 °C), indicating that Bi$_2$O$_3$ is more likely to be oxidized than Na$_2$O (Table S1), thereby allowing for oxygen getters to prevent formation of sodium oxides on the surface of the liquid Na. Second, the ionic radius of Bi$^{3+}$ is $1.03$ Å, which is similar to that of Na$^+$, 1.02 Å (Table S2), and therefore causes less lattice strain at the $\beta^3\text{Al}_2\text{O}_3$ grain boundary when ion exchange occurs. Previous research has shown that the exchange of Na$^+$ by larger ions such as K$^+$ and Rb$^+$ at $200$ °C causes permanent stress such that the $\beta^3\text{Al}_2\text{O}_3$ fractures. Indeed, when heated to $300$ °C, the $\beta^3\text{Al}_2\text{O}_3$ samples coated with Na–Bi alloys did not fracture (Figure S2), verifying that no strong lattice strain was imposed during any ion exchange. Third, a small amount of Bi is completely miscible when alloying with Na, as shown in its binary phase diagram (inset, Figure S3), which ultimately does not interfere with Na transport. For example, the solubility limit of Bi in Na is $~10^{-3}$ to $10^{-2}$ wt % at temperatures of $<300$ °C (blue dotted line, Figure S3) (log$_{10}$ (at. % Bi) = $7.7169 - 813.16/T + 1.3774 	imes 10^7/T^2$, ($T < 923$ K), which is much lower than that of the alternatives such as Sn, Pb, and Cs.

Additionally, Bi is fully soluble in liquid Na at temperatures $<300$ °C. In this regard, we estimated the upper limit of Bi thin-film thickness for a given volume of liquid Na, where a Na–Bi alloy can form without an excess Bi thin film on the surface of $\beta^3\text{Al}_2\text{O}_3$. The calculated solubility limit of Bi in liquid Na suggests critical thicknesses $l_c$ of ~10, 46, 152, and 505 nm at temperatures of 150, 200, 250, and 300 °C, respectively (Figure S4). In addition, we noted that adding Bi (10$^{-2}$ wt %) to Na did not increase its melting point of 98 °C within detection limits, which would also be beneficial for the potential low-temperature operation of an NBB.

Herein, we describe the improvement of Na wetting behavior on $\beta^3\text{Al}_2\text{O}_3$ that dramatically enhanced battery cell performance. First, we investigated the presence of a kinetically favored Na oxide layer under a moisture-rich environment. It forms quickly but stabilizes thermodynamically, highlighting the necessity of precise control of the water interface on $\beta^3\text{Al}_2\text{O}_3$. Second, we develop a Bi-island approach that (i) is impervious to water yet does not interfere with Na conductivity and (ii) improves the Na ion pathway from an electrolyte to the anode on charging. (iii) As a result, NNBs fabricated using our methods can be operated at much lower temperatures than typical NNBs and without the need for conditioning cycles. Importantly, we found that it was isolated bismuth islands, as opposed to a continuous bismuth film, that significantly improve cell performance, retaining 94% charge after the initial cycle. This methodology represents a major advance toward Na wetting engineering, as it provides a protocol to effectively enhance wettability and ultimately leads to improved battery performance.

### RESULTS AND DISCUSSION

A single Na/NiCl$_2$ cell consists of a liquid Na (anode)/$\beta^3\text{Al}_2\text{O}_3$ (solid electrolyte)/NiCl$_2$ (cathode) added to a liquid secondary electrolyte (NaAlCl$_4$), with a few nanometer-sized Bi metal islands deposited on $\beta^3\text{Al}_2\text{O}_3$. These Bi islands are sandwiched between the anode and electrolyte (Figure 1a). When a Na/NiCl$_2$ cell is typically assembled, a small amount of solid sodium is applied on the surface of $\beta^3\text{Al}_2\text{O}_3$ (anode side), and the anode is almost empty, with a small amount of contact of the sodium with the $\beta^3\text{Al}_2\text{O}_3$. Upon charging the cell during the first cycle, Na ions formed at the cathode diffuse to the anode through $\beta^3\text{Al}_2\text{O}_3$ and then fill the empty anode space by one-electron reduction of the Na$^+$ ion. The higher wettability of liquid Na on the surface of $\beta^3\text{Al}_2\text{O}_3$ induces better charging characteristics, that is, a low overpotential. In this regard, we utilize two Na filling processes during charging (Figure 1b). First, when Na$^+$ ions diffuse on the $\beta^3\text{Al}_2\text{O}_3$ surface, they are reduced to liquid Na by accepting electrons from Bi on the anode side of $\beta^3\text{Al}_2\text{O}_3$ (stage I), and thus, a strong local active area forms at the edge of the Bi for Na reduction. Second, the significant growth of liquid Na in this active area is expected (stage II), given that the diffusivity of the Na$^+$ ion into liquid Na (self-diffusion) is much higher than that into solid Bi (interdiffusion) by a factor of 100–1000 (Figure S5). Given that vacancies should be more abundant in the liquid, the activation energy for vacancy diffusion in liquids (Na$^+$ → liquid Na) is lower than that in solids (Na$^+$ → solid Bi) (Figure 1c). This self-diffusion in liquids leads to a large ratio of entropy to enthalpy and, as a consequence, a lower Gibbs free energy. As a result, further diffusion leads to the conformal filling of the gaps between Bi islands with liquid Na, representing good wetting of liquid Na on the $\beta^3\text{Al}_2\text{O}_3$ surface (stage III).

Following this concept, we coated the $\beta^3\text{Al}_2\text{O}_3$ surface with Bi to isolate the $\beta^3\text{Al}_2\text{O}_3$ surface from moisture (Figure 2a). Briefly, $\beta^3\text{Al}_2\text{O}_3$ was annealed to 450 °C under a vacuum of

DOI: 10.1021/acsami.9b13954

ACS Appl. Mater. Interfaces 2019, 11, 2917–2924
deposited 30 nm thick Bi islands on a rough Na. Then, a Bi thin film was deposited without breaking vacuum such that the $\beta''$-Al$_2$O$_3$ surface was kept clean and dry, reducing the possibility of forming an oxide layer on the liquid Na. Figure 2b shows representative cross-sectional transmission electron microscopy (TEM) images of the $\beta''$-Al$_2$O$_3$ surface in which Bi islands were deposited on the surface. The growth of metal islands on the surface occurred when the cohesive energy (Bi−Bi adatom) exceeded the adhesive energy (Bi/$\beta''$-Al$_2$O$_3$). This occurred when the deposited metal did not fully wet the substrate (contact angle, $\theta > 0$). This growth mode often has been observed in metal-insulator systems. In addition, in the early stage of non-epitaxial Bi deposition, the thin film tends to result in isolated island formation [cross-sectional TEM and in-plane scanning electron microscopy (SEM) images of Bi-coated $\beta''$-Al$_2$O$_3$ (Figures S6 and S7), respectively]. In this manner, we deposited 30 nm thick Bi islands on a rough $\beta''$-Al$_2$O$_3$ surface as in Figure 2b, where the surface was either flat (subpanel row A and B) or had a trench structure (subpanel row C). Note that the conformal coating of Bi islands on the surface of the trench was achieved in this magnetron sputtering deposition. The concept of utilizing Bi for passivation, and in particular forming isolated islands, is distinct from previous studies where it was used for thick layers, but continuous metallic films can enhance Na wettability, as follows.

The contact angles for liquid Na on nonpreheated and preheated $\beta''$-Al$_2$O$_3$ exhibit distinctly different wetting behaviors (Figure S8). For example, in nonpreheated $\beta''$-Al$_2$O$_3$, an oxide layer on the surface of liquid Na was observed (top, Figure 3a), which pinned the drop edges to $\beta''$-Al$_2$O$_3$, thus impeding further wetting as the temperature was increased. On the other hand, no obvious oxide layer formed for the preheated $\beta''$-Al$_2$O$_3$ (bottom, Figure 3a). In addition, we investigated the manner in which decreasing temperatures affect the contact angle of liquid Na. Figure 3b shows that contact angles decreased from 140° to 80° as the temperature increased from 150 to 300 °C for the nonpreheated $\beta''$-Al$_2$O$_3$, but decreased from 120° at 150 °C to 75° at 300 °C for the preheated $\beta''$-Al$_2$O$_3$. Taken together, these data confirm that the surface of $\beta''$-Al$_2$O$_3$ must be clean of moisture and oxygen to prevent oxide formation in the experimental environment, such as in a glovebox, when a sessile drop technique is often used. Because the surface impurities of $\beta''$-Al$_2$O$_3$ cause the contact edges of liquid Na to become pinned by the solid oxide layer, a further reduction in contact angle by completely isolating the surface from moisture- and oxygen-rich environments is advisable and possible.

The wetting properties of liquid Na on Bi-coated $\beta''$-Al$_2$O$_3$ at temperatures of 150, 200, 250, and 300 °C in an Ar atmosphere were studied to validate the effects of Bi coating on Na wetting. Compared to the wetting behaviors of preheated (contact angle of 75° at 300 °C) and nonpreheated $\beta''$-Al$_2$O$_3$ (contact angle of 80° at 300 °C), as shown in Figure 3b, the use of a Na−Bi alloy clearly improves wetting, with a contact angle as low as 60° at 300 °C. These results demonstrate the effectiveness of using a Bi metal coating layer to protect the surface of $\beta''$-Al$_2$O$_3$ from moisture while highlighting the
potential of Na–Bi alloys to enhance wetting. Note that the contact angle at 150 °C was particularly lower than that at 200 °C (Figure 3b), which is because the Bi thin film (15 nm) was beyond \( t_c \) at 150 °C \( (t_c \approx 10 \text{ nm}) \), where excess remained in Bi contacts and Na–Bi alloys (red dotted line, Figure S3). That is, a metal (Na–Bi alloy)/metal (remaining Bi thin film) contact resulted in a low Na contact angle. Above 200 °C where the film thickness was less than \( t_c \), no excess Bi thin film was observed on the surface but instead Bi was completely alloyed with the Na, increasing the contact angle slightly owing to metal (Na–Bi alloy)/ceramic (\( \beta''\text{-Al}_2\text{O}_3 \)) contact, which is in good agreement with the calculated data (blue dotted line, Figure S3).

These representative examples of Bi-coated structures highlight how the thicknesses of the Bi coatings are key motifs for wetting experiments (Figure 3c). First, the Bi film thinner than 10 nm does not effectively protect the \( \beta''\text{-Al}_2\text{O}_3 \) surface from moisture such that its contact angle is similar to that of an uncoated \( \beta''\text{-Al}_2\text{O}_3 \) surface. Second, as its thickness increases from 10 to 20 nm, where the Bi islands form on the \( \beta''\text{-Al}_2\text{O}_3 \) surface, the \( \beta''\text{-Al}_2\text{O}_3 \) surface is successfully isolated from moisture, improving the wetting of the Na (darkened band) at 200 °C. Third, a thickness over 20 nm exceeds the solubility limit of Bi for Na in our experiments and a distinct Na/Bi/\( \beta''\text{-Al}_2\text{O}_3 \) interface is maintained. This leads to low contact angles of the Na liquid because of metal–metal contact between the Na liquid and remaining Bi film. However, this is ultimately not desirable for Na ion transport to \( \beta''\text{-Al}_2\text{O}_3 \). In addition, we characterized the Na/Bi/\( \beta''\text{-Al}_2\text{O}_3 \) interface above 200 °C, where the Bi film below the critical thickness (<20 nm) was completely dissolved into the Na liquid. Local elemental mapping of the Na/Bi/\( \beta''\text{-Al}_2\text{O}_3 \) interface by energy dispersive X-ray spectroscopy (EDXS) was performed to probe compositional variations across the interface (Figure 3d). Cross-sectional elemental maps show that the Bi film below 20 nm, within the equilibrium solubility limit of Bi for Na, was completely dissolved into the Na liquid (middle, Figure 3d), while the 100 nm Bi film, which is over the solubility limit, appeared localized in the interface region (right, Figure 3d).

Note that quantitative analysis of Na, Bi, and Al composition variation, however, shows that the interface was not atomically abrupt but rather broadly transitioned over a length scale of a few microns. To provide fundamental insight into the mixing of dissolved Bi in Na, ab initio density functional theory (DFT) calculations were performed, and the thermodynamics of the Na–Bi alloy system were investigated with the aid of the energy convex hull diagram (Figure S9). Under the dilute concentration of Bi in Na, we found that the dissolved Bi atom tends to form the thermodynamically most stable alloy structure, Na3Bi (bottom-left image, Figure 3d), with a negative formation energy of \(-0.40 \text{ eV/atom}\). On the other hand, NaBi was found to be stabilized with a negative formation energy of \(-0.33 \text{ eV/atom}\) as the Bi concentration was increased to reach the 1:1 molar ratio to Na.

Along with its wetting behavior, we also explored the electrical transport of Na ions to investigate its effect on the Bi coating. Two-point probe measurements of the Bi-coated \( \beta''\text{-Al}_2\text{O}_3 \) surface were used to measure conductivity as a function of temperature (Figure S10a). We prepared Bi-coated samples 2.8 cm² in area and 2.03 mm thick (Figure S10b). Electrochemical impedance spectra were measured in the temperature range of 175–300 °C for bare (Figure 4a) and Bi-coated \( \beta''\text{-Al}_2\text{O}_3 \) (Figure 4b). During the first cycle, heating from 175 to 300 °C, Ohmic behavior was dominant in both cases. In our study, the measured total resistance \( (R_{\text{tot}}) \), the sum of Ohmic and polarization resistances, can be analyzed in terms of a change in the contact area and the condition of the interface between the liquid Na and \( \beta''\text{-Al}_2\text{O}_3 \). We focused on the former case because the Ohmic resistance, \( R_{\text{Ohm}} \), varied by contact area. The use of \( R_{\text{Ohm}} \) simplified the identification of the effect of the Bi coating on the wetting behavior as a factor in varying the active area. It is primarily determined by the bulk properties, that is, the ionic conductivity, of \( \beta''\text{-Al}_2\text{O}_3 \) that are relevant to size (area/length), whereas polarization resistance is influenced by parasitic effects that disturb ionic transport at the interface. When the interface is clean (e.g., no parasitic
Therefore, an increase in enhanced, increasing the contact area at the interface. Therefore, decreased such that the wetting of the liquid Na was and 1.0 \( \sigma \). The conductivity of the Bi-coated behavior compared to bare \( \beta''\text{Al}_2\text{O}_3 \) at each temperature during cycle 1. (d) Arrhenius plot (AC) of the Na\(^+\) ion conductivities of bare and Bi-coated \( \beta''\text{Al}_2\text{O}_3 \) at each temperature during the cycle 2. (e) Arrhenius plot (AC) of the Na\(^+\) ion conductivities of Bi-coated \( \beta''\text{Al}_2\text{O}_3 \) at each temperature during 4 cycles.

We characterized the charge/discharge behavior of Na/NiCl\(_2\) cells (Figure S11) to investigate the effect of the Bi coating at 175 °C. Three different surface modifications of the anode sides of \( \beta''\text{Al}_2\text{O}_3 \) were made: bare \( \beta''\text{Al}_2\text{O}_3 \), Bi-coated \( \beta''\text{Al}_2\text{O}_3 \) and scratched Bi-coated \( \beta''\text{Al}_2\text{O}_3 \) (Figure S12). The scratched Bi-coated \( \beta''\text{Al}_2\text{O}_3 \) was prepared by scratching the Bi film with a diamond cutter in a glovebox (H\(_2\)O, O\(_2\) below 1 ppm) to prevent further exposure to ambient moisture. Na/NiCl\(_2\) batteries were assembled in their discharged states. Some liquid Na initially resided in the anode for the electrical contact with \( \beta''\text{Al}_2\text{O}_3 \) and began the charge cycle where Na\(^+\) ions were transported from the cathode to the anode. \(^{34}\) In this sense, the scratched Bi film increased the active area (edge of Bi islands) and the Na\(^+\) ion path across the interface of Bi and \( \beta''\text{Al}_2\text{O}_3 \) (Figure 5a).

Figure 4. (a) Electrochemical impedance spectroscopy (EIS) spectra of bare \( \beta''\text{Al}_2\text{O}_3 \), (b) EIS spectra of Bi-coated \( \beta''\text{Al}_2\text{O}_3 \), (c) Arrhenius plot (AC) of the Na\(^+\) ion conductivities of bare and Bi-coated \( \beta''\text{Al}_2\text{O}_3 \) at each temperature during cycle 1. (d) Arrhenius plot (AC) of the Na\(^+\) ion conductivities of bare and Bi-coated \( \beta''\text{Al}_2\text{O}_3 \) at each temperature during cycle 2. (e) Arrhenius plot (AC) of the Na\(^+\) ion conductivities of Bi-coated \( \beta''\text{Al}_2\text{O}_3 \) at each temperature during 4 cycles.

Figure 5. (a) Schematic of the Na-filling process of a scratched, Bi-coated \( \beta''\text{Al}_2\text{O}_3 \) cell on charging. (b) Voltage profiles of the initial cycle of bare, Bi-coated, and scratched Bi-coated \( \beta''\text{Al}_2\text{O}_3 \) cells. The Bi-coated sample was charged, with an increasing current of 0.6 mA (for 2 h), 1 mA (for 10 h), 2 mA (for 17 h), 4 mA (for 4 h), and 5 mA (until the cell voltage reached 2.8 V). For the bare and scratched Bi-coated cases, 0.6 mA (for 2 h), 1 mA (for 10 h), and 5 mA (constant) were used. (c) Voltage profiles of Bi-coated (for 7 cycles), scratched Bi-coated (for 21 cycles), and bare \( \beta''\text{Al}_2\text{O}_3 \) cells (for 35 cycles). (d) Cross-sectional schematic, TEM image, and high-resolution EDXS elemental mapping of the scratched Bi-coated \( \beta''\text{Al}_2\text{O}_3 \) surface for Al, Bi, and O, respectively.

Typically, Na/NiCl\(_2\) batteries require conditioning cycles to properly activate them because of the poor initial Na wettability during low-temperature operation below 200 °C. To investigate the initial wetting performance of cells, the voltage profiles of the initial cycle are compared in Figure 5b. In this measurement, a cutoff voltage of 2.8 V (for charging) was selected based on the fact that when the cell was overcharged...
higher than 2.8 V, an undesirable side reaction between Ni and NaAlCl₄ catholyte is known to occur.²² If the cell was overdischarged below a state of charge (SOC) lower than 20% (≈2.4 V), a small amount of Na would remain in the anode chamber, possibly leading to high cell resistance because insufficient Na was available to provide electrical contact between Na and β″-Al₂O₃.²² Note that the presence of a plateau region during the charge/discharge processes indicates the oxidation of Ni to NiCl₂ and reduction of NiCl₂ to Ni.¹⁷,³⁴ respectively, for the initial cycle and as a result of the electrochemical reactions in the Na/NiCl₂ cell. For example, such a plateau was clearly observed for the Bi-coated sample (148 mA h) was higher than that of the bare sample (34 scm). The coatings were deposited from a 2 in. Bi (99.99%) target in an Ar (99.999%) atmosphere. The distance from the substrate to the target was 10 cm. The Bi films were deposited at 10–100 nm at a rate of 0.48 nm/s at room temperature. The discharge power was 10 W. The thickness of the coatings deposited on the β″-Al₂O₃ surface was measured using field-emission scanning electron microscopy (JSM-7001F, and by cross-sectional TEM, JEM-ARM 200F (JEOL, USA)).

**Wetting Test.** The contact angle of liquid Na on the β″-Al₂O₃ surface was measured by a sessile drop technique in an An-protected glovebox. High-purity Na (99.9%) was used and heated to the measurement temperature in an alumina crucible by a hot plate. Drops of Na were transferred to the β″-Al₂O₃ surface using a glass syringe. Bare β″-Al₂O₃ samples were preheated or not preheated to the measurement temperature in a quartz tube chamber which is surrounded by a Kanthal tube furnace (Figure S16). Some β″-Al₂O₃ samples were heated to 450 °C in a high-vacuum (~10⁻⁸ Torr) sputter chamber for 10 h and continuously coated with Bi at room temperature in the same chamber. The temperature range of the wetting test was 150–300 °C and the duration after transference of the Na droplets to the β″-Al₂O₃ surface for wetting angle measurements was 30 min. Angle measurement was performed in a glovebox by a charge-coupled device camera and the SEO surfaceware9 program, which provides an instant contact angle (Figure S17).

**Characterization.** Cross-section analysis of Na on Bi-coated β″-Al₂O₃ was performed using a JIB-4601F focused ion beam (FIB)/field emission-SEM dual-beam system (JEOL, USA). This was done under high vacuum because Na is highly reactive in moisture and air. After preparing the cross section, local elemental mapping of Na/Bi/β″-Al₂O₃ was performed by EDXS. The cross-sectional TEM sample of Bi/β″-Al₂O₃ was also prepared using FIB. To prevent damage from the Ga⁺ ion beam, the Bi/β″-Al₂O₃ substrate was coated with a carbon layer. STEM EDXS elemental mapping was performed using JEM ARM 200F (JEOL, USA).

**Conductivity Measurement.** The electrochemical impedance spectra of the Na/β″-Al₂O₃/Na cell were obtained in the frequency range from 0.1 Hz to 200 kHz at an amplitude of 0.1 V with a potentiostat (HP803, BioLogic, France) as a function of temperature in the range of 150–300 °C. We used bare and one-side Bi-coated β″ Al₂O₃ (Figure S10).

**Cell Assembly.** Detailed methods for cathode material preparation and the planar cell assembly procedure have been reported previously.¹⁵ The planar cell consisted of battery cases for the cathode and anode, an α-Al₂O₃ fixture, a β″-Al₂O₃ disc (INOTEC, 3 cm² active area), and current collectors (Mo foil for the cathode and stainless steel shim for the anode) between the electrode end-cap and the base. A schematic of the planar cell used in this work is shown in Figure S11. The β″-Al₂O₃ discs were glass-sealed in an α-Al₂O₃ fixture to separate cathode and anode chambers. The β″-Al₂O₃ discs were used in bare and surface-treated states on the anode side of β″-Al₂O₃.
performed with the projector-augmented wave method as implemented in the Vienna Ab initio Simulation Package (VASP).\textsuperscript{36–38} Self-consistent, van der Waals-corrected, semilocal-type exchange–correlation functions (optB86b-vdW) were used,\textsuperscript{39} with a plane-wave kinetic energy cutoff of 300 eV. The reciprocal space integration was performed under the Γ-centered k-point grid with 0.2 Å between each reciprocal point. For the geometrical relaxation of the structures, atomic positions were relaxed until the forces acting on the atoms were <0.02 eV/Å. The convex hull of each Bi–Na configuration was obtained from the Open Quantum Materials Database.\textsuperscript{41} Formation energy ($E_{\text{form}}$) is defined as $E_{\text{form}} = E_{\text{tot}} + N_{\text{Na}} \times E_{\text{Na}} + N_{\text{Bi}} \times E_{\text{Bi}} - N_{\text{Bi}} \times N_{\text{Na}} \times E_{\text{Na-Bi}}$, where $E_{\text{tot}}$, $E_{\text{Na}}$, $E_{\text{Bi}}$, $E_{\text{Na-Bi}}$, $N_{\text{Na}}$, and $N_{\text{Bi}}$ denote the total energy of the system, bulk Na, bulk Bi, number of Na atoms, and number of Bi atoms, respectively.

**Computational Methodology.** All DFT calculations were performed with the projector-augmented wave method as implemented in the Vienna Ab initio Simulation Package (VASP).\textsuperscript{36–38} Self-consistent, van der Waals-corrected, semilocal-type exchange–correlation functions (optB86b-vdW) were used,\textsuperscript{39} with a plane-wave kinetic energy cutoff of 300 eV. The reciprocal space integration was performed under the Γ-centered k-point grid with 0.2 Å between each reciprocal point. For the geometrical relaxation of the structures, atomic positions were relaxed until the forces acting on the atoms were <0.02 eV/Å. The convex hull of each Bi–Na configuration was obtained from the Open Quantum Materials Database.\textsuperscript{41} Formation energy ($E_{\text{form}}$) is defined as $E_{\text{form}} = E_{\text{tot}} + N_{\text{Na}} \times E_{\text{Na}} + N_{\text{Bi}} \times E_{\text{Bi}} - N_{\text{Bi}} \times N_{\text{Na}} \times E_{\text{Na-Bi}}$, where $E_{\text{tot}}$, $E_{\text{Na}}$, $E_{\text{Bi}}$, $E_{\text{Na-Bi}}$, $N_{\text{Na}}$, and $N_{\text{Bi}}$ denote the total energy of the system, bulk Na, bulk Bi, number of Na atoms, and number of Bi atoms, respectively.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b13954.

Detailed process of the Bi coating; solubility of Bi in liquid Na; wetting test; DFT-calculated energy convex hull of a Na–Bi system; two-point probe measurements; structure of the planar cell; SEM images and schematics of the samples; additional charge/discharge experimental results; Ca contents in β″-Al2O3; Gibbs free energies of formation of metal oxides; and ionic radii of metal ions (PDF)

Liquid Na wetting test on bare β″-Al2O3 (AVI)

Liquid Na wetting test on Bi-coated β″-Al2O3 (AVI)

**REFERENCES**

1. Kim, H.; Boysen, D. A.; Newhouse, J. M.; Spatocco, B. L.; Chung; B.; Burke; P. J.; Bradwell; D. J.; Jiang; K.; Tomaszowska; A. A.; Wang; K.; Wei; W.; Ortiz; L. A.; Barriga; S. A.; Poizeau; S. M.; Sadoway; D. R. Liquid Metal Batteries: Past, Present, and Future. Chem. Rev. 2013, 113, 2075–2099.


Supporting Information

Bismuth Islands for Low-temperature Sodium-beta Alumina Batteries

Dana Jin¹, Sangjin Choi¹, Woosun Jang¹, Aloysius Soon¹, Jeongmin Kim¹, Hongjae Moon¹, Wooyoung Lee¹, Younki Lee ², Sori Son³, Yoon-Cheol Park³, HeeJung Chang⁴, Guosheng Li⁴, Keeyoung Jung³* & Wooyoung Shim¹*

¹Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Korea, ²Department of Materials Engineering and Convergence Technology & RIGET, Gyeongsang National University, Jinju 52828, Korea ³Materials Research Division, Research Institute of Industrial Science & Technology, Pohang 37673, Korea ⁴Electrochemical Materials and System Group, Pacific Northwest National Laboratory, Richland, WA 99352, USA

* e-mail: keeyoung.jung@rist.re.kr, wshim@yonsei.ac.kr

This PDF file includes:

Supplementary Figures 1 to 17

Supplementary Table 1 to 3

Brief description of Supplementary Movies 1-2
Figure S1. Schematic of the water interface of the $\beta''$-Al$_2$O$_3$. Moisture absorbed in the $\beta''$-Al$_2$O$_3$ causes oxidation of liquid sodium, causing a thick layer of sodium oxide which is related to the poor Na wetting on $\beta''$-Al$_2$O$_3$. 
Figure S2. Photograph of used Na- β"-Al₂O₃ sample after measuring the contact angle. Deformation or fracture of β"-Al₂O₃ caused by ionic exchange was not observed in Bi coated β"-Al₂O₃. The ionic radius of Bi³⁺ is 1.03 Å, which is similar to that of Na⁺ (1.02 Å) and causes less strain at the β"-Al₂O₃ grain boundaries when ion exchange occurs.
Figure S3. The upper limit of solubility of Bi in liquid Na at measured temperatures (blue dotted line) and Bi content in the Na droplet of the wetting experiment sample (red dotted line). Inset: Phase diagram of Bi-Na system. The solubility limit was calculated based on the Na-Bi phase diagram by \( \log_{10} (\text{at.\%Bi}) = 7.7169 - \frac{8131.6}{T} + 1.3774 \times 10^6/T^2 \), \( T < 923 \text{ K} \). Dotted lines are a guide to the eye.
Figure S4. The upper limit of solubility of Bi in liquid Na according to Na-Bi phase diagram (black) and the calculated critical thickness of the Bi film (red) at each temperature (right axis). Critical thickness (red dotted line) indicates the maximum Bi thickness according to the solubility limit when considering Na droplet volume. Gray dot indicates the solubility and critical thickness of Bi at 175 °C. To determine the proper Bi thickness, the Bi solubility equation was used and it was found that ~ 30 nm of Bi is in the solubility range at 175 °C. Dotted lines are a guide to the eye.
Figure S5. Initial part of voltage profiles of the first charging of the scratched Bi-coated $\beta''$-Al$_2$O$_3$ cell. Plateaus at red dotted lines indicate electrochemical reactions of additives, and the plateau of the gray line indicates the oxidation of Ni. There is no discernable plateau showing the intercalation of Na ions into Bi (0.63 and 0.42 V). Bi does not appear to participate in the electrochemical reactions.
Figure S6. Cross-sectional TEM image and high resolution EDS elemental mapping of the β″-Al$_2$O$_3$ deposited by (a) 20 nm, (b) 30 nm, (c) 50 nm, and (d) 100 nm of Bi. When the thickness was less than 50 nm, Bi formed islands. The Bi formed a continuous coating on the 50 and 100-nm thick Bi films on the β″-Al$_2$O$_3$. Columns represent: The TEM image, the composite chemical map, Al, Bi, and O, respectively.
Figure S7. SEM top-view image and high-resolution EDS elemental mapping of the $\beta''$-Al$_2$O$_3$ deposited by (a) 20 nm, (b) 30 nm, (c) 50 nm, and (d) 100 nm of Bi. The Bi coating is formed uniformly even though there are some pores in the surface of the $\beta''$-Al$_2$O$_3$. Columns represent: The SEM image, and the chemical maps of Al, Bi, and O, respectively.
Figure S8. a) Experimental procedure of non-preheating and continuous process using one sample for the entire series of contact angle measurements (Exposure time: about 180 min). As the liquid Na was continuously exposed to the moisture, the formation of the oxide film became severe, as shown in photographs even in the Ar atmosphere of glove box. b) Experimental procedure of non-preheating (black dotted line) and preheating (red line) process using one liquid Na sample for each temperature to reduce the exposure time. In these experiments, liquid Na in the alumina crucible was prepared on the hotplate heated to 150 °C and then transferred onto the $\beta''$-$\text{Al}_2\text{O}_3$ using the sessile drop technique. The $\beta''$-$\text{Al}_2\text{O}_3$ was then transferred to the quartz tube that was heated to temperatures of 150, 200, 250, and 300 °C under Ar atmosphere. The time interval between the $\beta''$-$\text{Al}_2\text{O}_3$ load inside the quartz tube and contact angle measurements was 30 min to stabilize the contact line of liquid Na on the $\beta''$-$\text{Al}_2\text{O}_3$. 

S-9
**Figure S9.** DFT-calculated energy convex hull of Na-Bi system as a function of Na concentration. The atomic structure of Bi-Na alloy used in calculating the formation energy was obtained from the Open Quantum Materials Database (OQMD). Formation energy ($E_{\text{form}}$) per atom, which is labeled as a heat of formation ($\Delta H$) on the graph, is defined as

$$E_{\text{form}} = \frac{E_{\text{tot}} - N_{\text{Na}} E_{\text{Na}} - N_{\text{Bi}} E_{\text{Bi}}}{N_{\text{Na}} + N_{\text{Bi}}}$$

where $E_{\text{tot}}$, $E_{\text{Na}}$, $E_{\text{Bi}}$, $N_{\text{Na}}$ and $N_{\text{Bi}}$ denotes total energy of the system, bulk Na, bulk Bi, number of Na atoms, and number of Bi atoms, respectively. Dashed line is a guide to the eye.
**Figure S10.** a) Schematic of a two-point probe measurement of the symmetric Na/$\beta''$-Al$_2$O$_3$/Na cell which is coated on one side with 15 nm of Bi on the $\beta''$-Al$_2$O$_3$ surface, for measuring the conductivity as a function of temperature. b) Photograph of the Bi-coated $\beta''$-Al$_2$O$_3$ (2.8 cm$^2$) disc which is glass-sealed in an $\alpha$-Al$_2$O$_3$ fixture for experiments.
Figure S11. Digital photo and schematic of the planar Na-NiCl₂ cell. The Na-NiCl₂ cell (charged state) consists of the anode (liquid Na), cathode (cathode granules comprising NaCl, Ni, NiCl₂ and additives with liquid secondary electrolyte, NaAlCl₄), current collectors and solid electrolyte, β"-Al₂O₃ discs which was glass-sealed in an α-Al₂O₃ fixture to separate cathode and anode chambers.
Figure S12. SEM images of the bare, Bi-coated, and scratched Bi-coated $\beta''$-Al$_2$O$_3$. 
Figure S13. Voltage profiles of the Bare $\beta''$-Al$_2$O$_3$ cell during 26 cycles.
Figure S14. Schematics of the interface of the Na/β″-Al₂O₃, Na/Bi-coated β″-Al₂O₃ and Na/scratched Bi-coated β″-Al₂O₃. The scratched Bi coating may have an increased surface area (active area) supporting Na transport across the interface of the Bi and β″-Al₂O₃.
Figure S15. a) SEM image and EDS spectra of $\beta''$-Al$_2$O$_3$. b) XRD patterns of $\beta''$-Al$_2$O$_3$. About 1.6 at.% of Ca impurity was detected in the surface of $\beta''$-Al$_2$O$_3$. 
Figure S16. a) Experimental setup for contact angle measurement. The quartz furnace is in an Ar-protected glove box. b) The quartz furnace comprises a Kantal furnace, a thermos couple to monitor the temperature of the chamber and a sample tray. c) CCD camera for the angle measurement. The quartz furnace is sealed with a transparent quartz window so that the image of the Na drop can be captured with CCD Camera.
Figure S17. a) Angle measurement by the sessile drop method using a contact angle analyzer (Phoenix HT500). b) Digital SLR camera image. An instant contact angle measurement (a) was provided by SEO surfaceware9 program (Phoenix HT500). Free software provided in the website (https://shaeod.tistory.com) was also used for angle measurement by an image taken with a Digital SLR camera (b).
<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (K) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298</td>
</tr>
<tr>
<td>K₂O</td>
<td>-322.1</td>
</tr>
<tr>
<td>Rb₂O</td>
<td>-294.3</td>
</tr>
<tr>
<td>Cs₂O</td>
<td>-327.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>-379.1</td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>-493.5</td>
</tr>
<tr>
<td>Sn₂O</td>
<td>-519.8</td>
</tr>
<tr>
<td>CaO</td>
<td>-603.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>-741.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>-889.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-1532.0</td>
</tr>
</tbody>
</table>

**Table S1.** Gibbs free energies of the formation metal oxides at three temperatures.
<table>
<thead>
<tr>
<th>Material</th>
<th>Ionic radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$^+$</td>
<td>1.67</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>1.52</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.38</td>
</tr>
<tr>
<td>Bi$^{3+}$</td>
<td>1.03</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.02</td>
</tr>
</tbody>
</table>

**Table S2.** Ionic radius of metal ions.
<table>
<thead>
<tr>
<th>Ni / NaCl molar ratio</th>
<th>NaCl (g)</th>
<th>Ni (g)</th>
<th>Additive (g)</th>
<th>Cathode weight (g)</th>
<th>Theoretical Capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>0.342</td>
<td>0.622</td>
<td>0.036</td>
<td>1</td>
<td>157</td>
</tr>
</tbody>
</table>

**Table S3.** Cathode material and theoretical capacity

The Na-NiCl$_2$ cell is assembled as the discharged state; therefore, we just applied a very small amount of Na (< 5 mg) on the surface of $\beta''$-Al$_2$O$_3$ (anode side) for an initial electrical contact. The amount of Na (x) loaded in the anode (fully charged state) can be calculated by the weight of NaCl (0.342 g) loaded in the cathode. The theoretical specific capacity ($Q_{\text{theoretical}}$) of Na-NiCl$_2$ cell (Ni / NaCl ratio = 1.8) are 157 mAh/g which is obtained from following reaction:

$$2\text{Na} + \text{NiCl}_2 \leftrightarrow 2\text{NaCl} + \text{Ni}$$

The theoretical capacity of a cell can be calculated by Faraday’s law:

$$Q_{\text{theoretical}} = \frac{n\cdot F}{3600\cdot M_w} \cdot \frac{\text{Activated Ni weight}}{\text{Cathode weight}}$$

where n, F and $M_w$ denote the number of charge carrier, Faraday constant and molecular weight of active material (Ni), respectively. The calculated maximum weight of activated Ni is 0.172 g when the whole amount of NaCl (0.342 g) participates in the electrochemical reaction with the stoichiometric ratio between Ni and NaCl, 1:2.

The amount of Na (x) loaded in the anode of the Na-NiCl$_2$ can be calculated by the weight of NaCl (0.342 g) loaded in the cathode:
Molar mass (g/mol) ratio between Na and Cl, Na : Cl = 22.990 : 35.453 = 1 : 1.542

The amount of NaCl that participates in the electrochemical reaction = 0.342 g

If the mass of Na which moved from cathode to anode after charging is \( x \),
\[ x + 1.542 \times x = 0.342 \text{ (g)} \]
\[ \therefore x = 0.135 \text{ g} \]

Therefore, the amount of Na loaded in the anode (fully charged state) was calculated as 0.135 g and we applied a very small amount of Na (< 5 mg) on the surface of \( \beta''\text{-Al}_2\text{O}_3 \) (anode side) for an initial electrical contact.
**Movie S1.** Liquid Na-wetting test on bare $\beta''$-$\text{Al}_2\text{O}_3$. Liquid Na drop were transferred to the surface of bare $\beta''$-$\text{Al}_2\text{O}_3$ by a sessile drop technique and the wetting test (at 175 °C) was conducted for 1 hour. After 1 hour, liquid Na was removed from surface of $\beta''$-$\text{Al}_2\text{O}_3$ very clearly by rolling off from the surface of bare $\beta''$-$\text{Al}_2\text{O}_3$ owing to the poor wetting of liquid Na on bare $\beta''$-$\text{Al}_2\text{O}_3$.

**Movie S2.** Liquid Na-wetting test on Bi coated $\beta''$-$\text{Al}_2\text{O}_3$. Liquid Na drop were transferred to the surface of Bi coated $\beta''$-$\text{Al}_2\text{O}_3$ by a sessile drop technique and the wetting test (at 175 °C) was conducted for 1 hour. After 1 hour, it is difficult to cleanly remove the liquid Na drop from the contact area of liquid Na/ Bi coated $\beta''$-$\text{Al}_2\text{O}_3$, and the small amount of liquid Na remained owing to Na-Bi alloying that result in high adhesive force between Na and Bi.
Reference


