

ELECTRONIC SUPPLEMENTARY INFORMATION FOR

Development of novel inorganic electrolyte to engineer rechargeable room temperature sodium metal batteries

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Experimental section

Reagents treatment: Sodium borohydride (98%, Alfa Aesar), sodium tetrafluoroborate (98%, Sigma Aldrich) and sodium iodide (99.6%, Prolabo) were dried under vacuum at 120 °C overnight prior to use. These reagents should be free of iron in order to avoid the reduction of ammonia to NaNH_2 and hydrogen. Metallic sodium (99.8% in kerosene, Sigma Aldrich) was washed with hexane and kept into it. Ammonia (99%, Air liquid) was used as received. The sodium electrode was prepared from Na rods which were rolled flat under hexane in a glove box ($\text{H}_2\text{O} < 0.5\text{ppm}$, $\text{O}_2 < 2\text{ ppm}$). The copper foil was etched using a 1 M HCl solution and then it was washed with distilled water and acetone several times in an ultrasonic bath.

Ammonia-based electrolyte synthesis: The liquid ammoniates were synthesized according to a procedure described by Herlem and co-worker.³⁷ In brief, an excess of ammonia was condensed on the corresponding sodium salt at -50 °C. The resulting solution was colorless. The purification was carried out using solvated electrons: metallic sodium was added into the solution in large excess. Then, the blue color characteristic of the solvated electrons immediately appeared. These electrons reacted with impurities such as H_2O and O_2 . The solution was left to attain room temperature slowly and it was centrifuged. Finally, the electrolyte was stored in a glove box ($\text{H}_2\text{O} < 0.5\text{ ppm}$, $\text{O}_2 < 2\text{ ppm}$). The composition of each electrolyte was determined by weighing. Metallic sodium was stable in the aforementioned electrolytes for weeks.

Physico-chemical characterization of electrolytes: the dynamic viscosity for each ammonia-based electrolyte was determined at 10 °C using an Ostwald viscometer PROTON 3345 (100) by obtaining values relative to those of ultrapure water at the same temperature. The specific conductivity of each ammonia-based electrolyte was determined at several temperatures using a JENWAY 4510 conductivity meter. The density was determined by weighing 10 mL of each electrolyte at 10 °C in a volumetric flask previously standardized with ultrapure water at the same temperature.

Morphological characterization: The morphological characterization of metallic sodium electrodeposited on copper was carried out by means of an optical microscope NIKON (Eclipse E200) with an INFINITY-1 camera for capturing images.

Electrochemical characterization: The electrochemical characterization was performed using both a standard three-electrode electrochemical cell and a two-electrode split cells, both assembled in a N_2 -filled dry glove box ($\text{H}_2\text{O} < 0.5\text{ ppm}$, $\text{O}_2 < 2\text{ ppm}$). For the $\text{NaBH}_4 \cdot 1.5\text{NH}_3$ and $\text{NaBF}_4 \cdot 2.5\text{NH}_3$ electrolytes the cells were kept during measurements in a fridge at 4 °C. In the case of the NaI ammoniate, the experiments were done at room temperature. Sodium, copper and carbon-coated aluminum were used as working electrodes and metallic sodium pieces were employed as reference and counter electrodes. The glass microfiber Whatman 934-AH was used as a separator in

the two-electrode split Cell. Cyclic voltammograms were recorded using an Orignalys potentiostat-galvanostat (OGF-500) and, charge-discharge cycles were recorded using an AUTOLAB potentiostat-galvanostat (PGSTAT-30). The measurements were carried out at scan rates of 20, 10 and 5 $\text{mV}\cdot\text{s}^{-1}$ for cyclic voltammetry and at 10 $\text{mA}\cdot\text{cm}^{-2}$ for the charge-discharge cycling. The working temperature was 25 $^{\circ}\text{C}$ for $\text{NaI}\cdot 3.3\text{NH}_3$ and 4 $^{\circ}\text{C}$ for $\text{NaBH}_4\cdot 1.5\text{NH}_3$ and $\text{NaBF}_4\cdot 2.5\text{NH}_3$. The charge/discharge experiments were performed in a two-electrode split cell after potentiostatic deposition of Na^+/Na at -0.1 V vs Na for 100 seconds. In such way, a thin film of sodium was generated on the copper electrode before proceeding with the charge/ discharge cycles.

Specific conductivity for each ammonia-based electrolyte at different temperatures

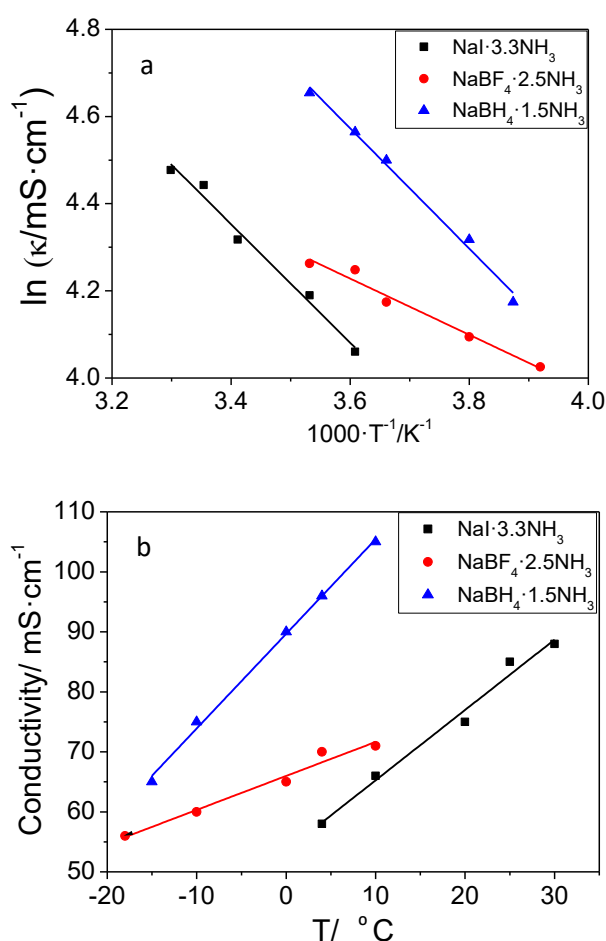


Figure S1. Specific conductivities for each ammonia-based electrolyte at different temperatures: (a) logarithm of the conductivity vs. the inverse of the absolute temperature; (b) specific conductivity in $\text{mS}\cdot\text{cm}^{-1}$ vs. temperature ($^{\circ}\text{C}$).

Specific conductivity/mS·cm ⁻¹	1 M NaClO ₄ / PC	3 M NaFSI /DME
10 °C	4.4	9.6
25 °C	5.5	13.6

Table S1. Specific conductivity of two organic electrolytes commonly used for sodium batteries: 1 M NaClO₄ in propylene carbonate (1 M NaClO₄ / PC) and 3 M sodium bis(fluorosulfonyl)imide (NaFSI) in 1,2-dimethoxyethane (DME) at 10 °C and 25 °C.

Comparative study using two conventional organic electrolyte: 1 M NaClO₄/PC and 3 M NaFSI/DME

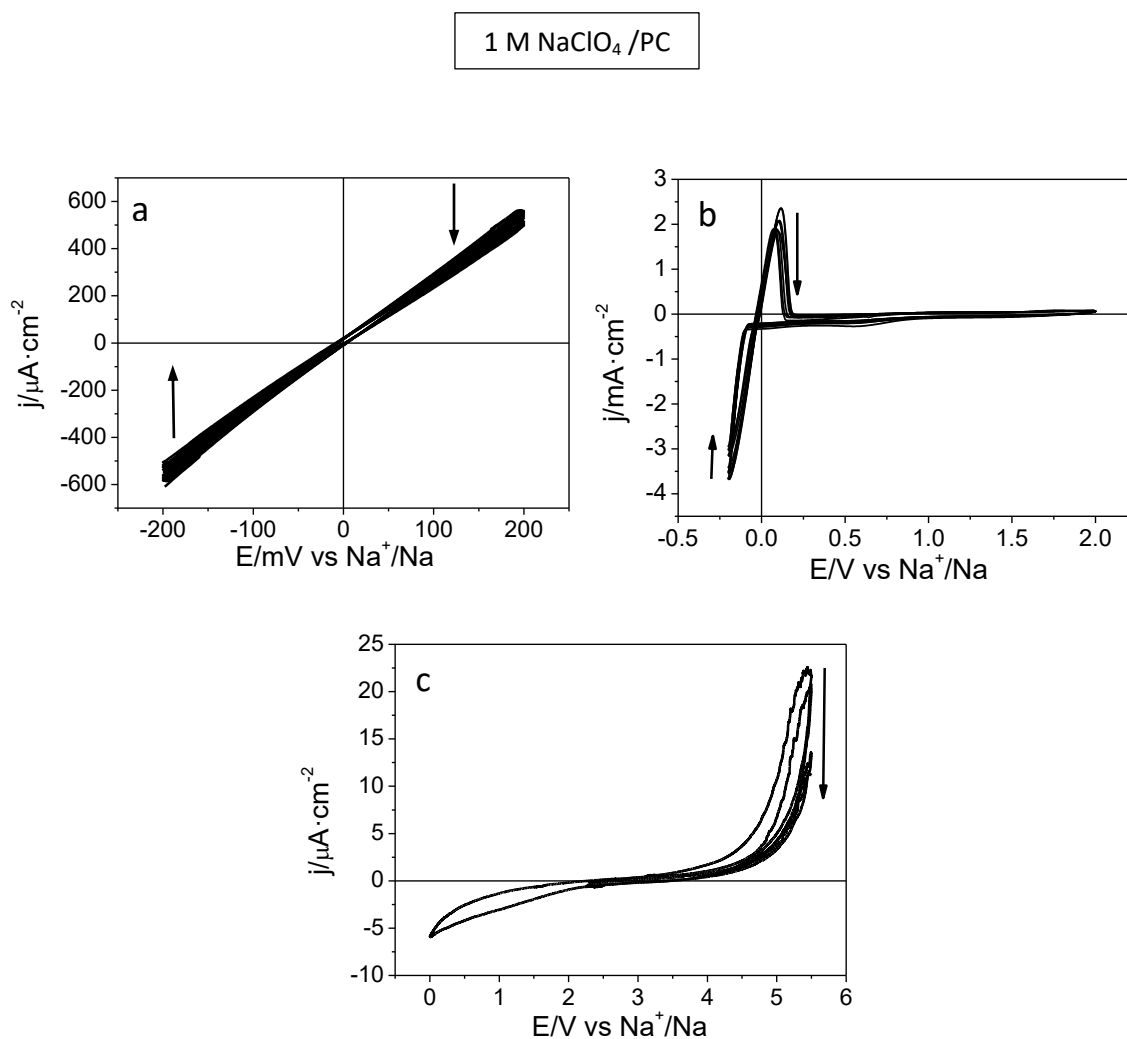


Figure S2. Cyclic voltammograms in 1 M NaClO₄ in propylene carbonate (PC) for (a) sodium deposition on sodium in a three electrode cell at a scan rate of 20 mV·s⁻¹ between ± 0.2 V vs. Na⁺/Na. The Figure shows ten successive voltammograms. (b) Twenty successive voltammograms for sodium deposition on a copper electrode in a three electrode cell at a scan rate of 20 mV·s⁻¹. The potential window goes from -0.2 V to 2 V vs. Na⁺/Na. (c) Voltammograms for determining the working potential window (positive limit) at a scan rate of 5 mV·s⁻¹ using as a substrate Al/C. An oxidation current of the electrolyte could be observed at around 4.5 V vs. Na⁺/Na.

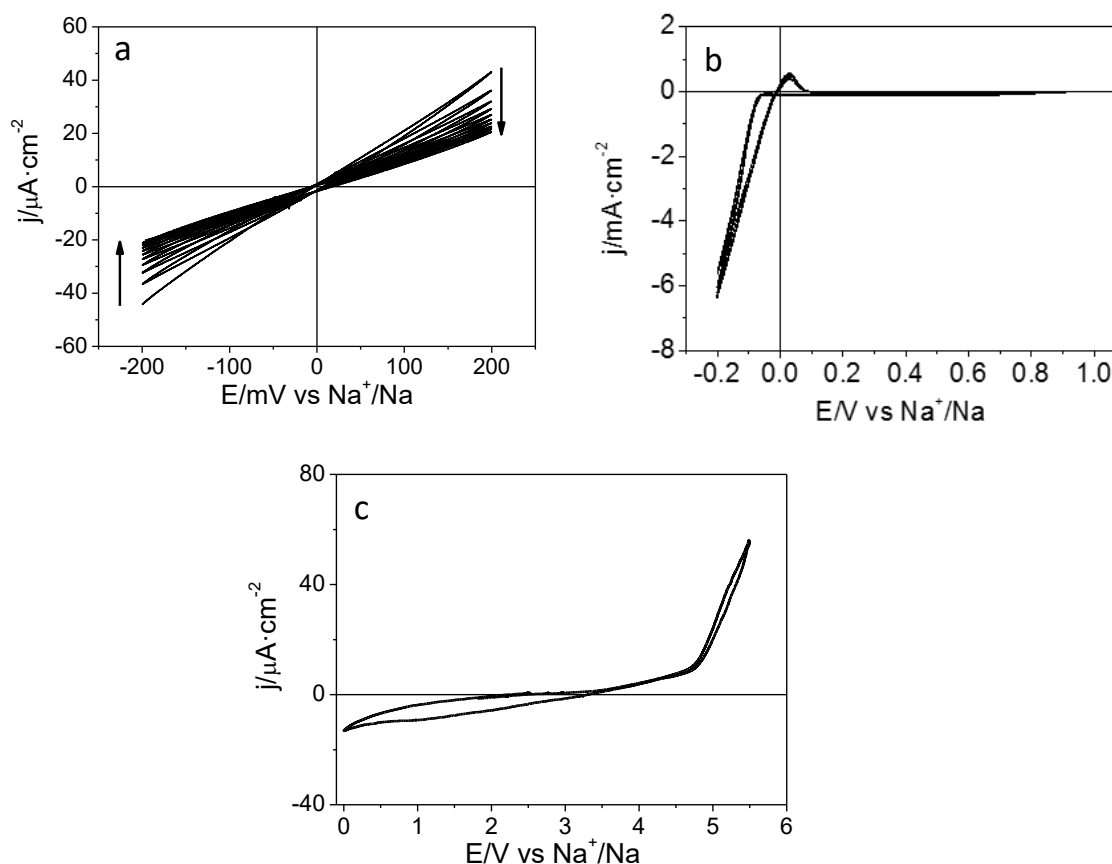


Figure S3. Cyclic voltammogram in the 3 M sodium bis(fluorosulfonyl)imide in 1,2-dimethoxyethane (NaFSI/DME) organic electrolyte for (a) sodium deposition over sodium in a three electrode cell at a scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$ between $\pm 0.2 \text{ V}$ vs. Na^+/Na . (b) Ten successive voltammograms for sodium deposition on a copper electrode in a three electrode cell at a scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$. The working potential window goes from -0.2 V to 1 V vs. Na^+/Na . (c) Voltammogram for determining the working potential window (positive limit) at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ using a substrate Al/C. An oxidation current of the electrolyte could be observed at around 4.75 V vs. Na^+/Na .

The observed currents in Figures S2 and S3 are significantly lower for Na electrodeposition in the organic electrolyte (even when using -200 mV vs Na as the negative limit) than those obtained in the ammoniate-based electrolyte (figure 1 and 2). In addition, the coulombic efficiency obtained from these voltammograms is rather low, in contrast with the close-to-one coulombic efficiency determined in all the ammonia-based electrolytes describe in this paper.

Photographs for Na electrodeposited on Cu

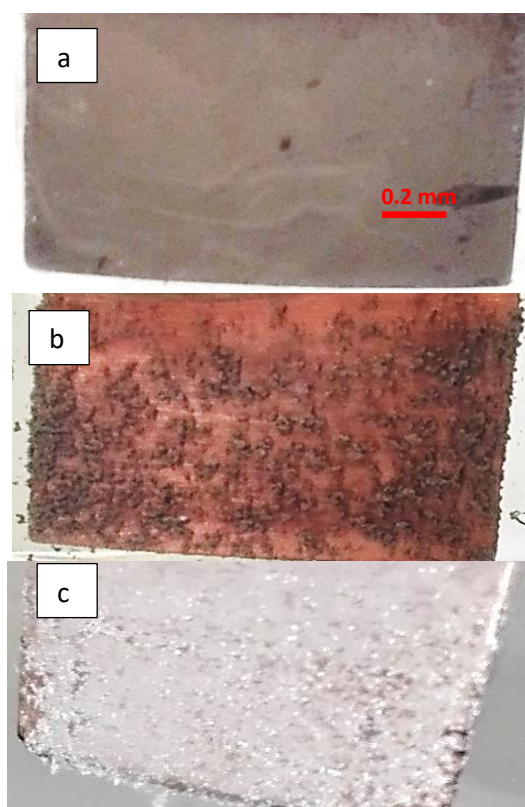


Figure S4. Photographs taken with a digital camera for sodium electrodeposited on copper: (a) 1 M NaClO₄/PC; (b) 3 M NaFSI/DME; (c) NaI·3.3NH₃.

In spite of the fact that the sodium film electrodeposited on Cu from 1 M NaClO₄/PC electrolyte (Figure S4a) seems to be homogeneous and dendrite-free, it is darker which is indicative that Na is reacting with the electrolyte. In Figure S4b shows the morphology of the deposit in the 3 M NaFSI/DME organic electrolyte, it shows aggregates that are not evenly distributed on the Cu surface. In addition, these aggregates are not firmly attached to the substrate. In contrast, for the ammoniate the deposit is homogeneous and it is composed of small submillimetric particles of sodium entirely covering the whole copper surface (Figure S4c). It should be stressed that the ammoniate environment is the only producing a truly metallic-looking Na deposits.

Morphological characterization of metallic sodium electrodeposited on copper

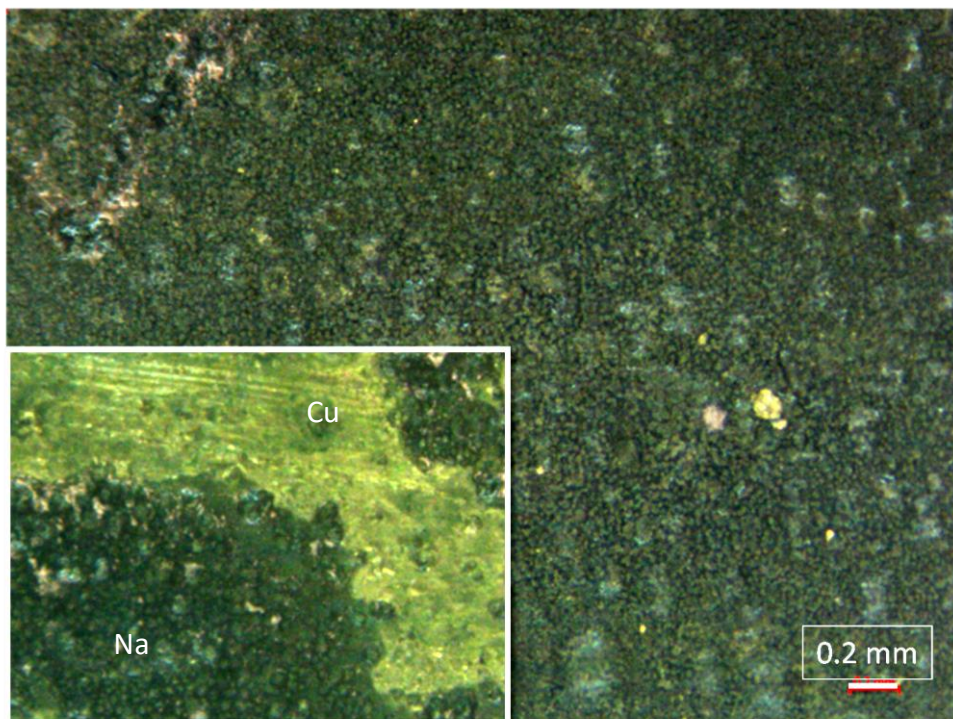


Figure S5. Morphological characterization by optical microscopy of metallic sodium electrodeposited on copper from the NaI ammoniate. The Na electrodeposit was obtained by applying a potential of -0.1 V on a copper electrode for 400 s. The inset shows the sample after mechanical manipulation leading to the detachment of part of the Na deposit and thus exposing the Cu substrate.

Sodium deposition on Al/C at $20 \text{ mV}\cdot\text{s}^{-1}$ in $\text{NaI}\cdot 3.3\text{NH}_3$

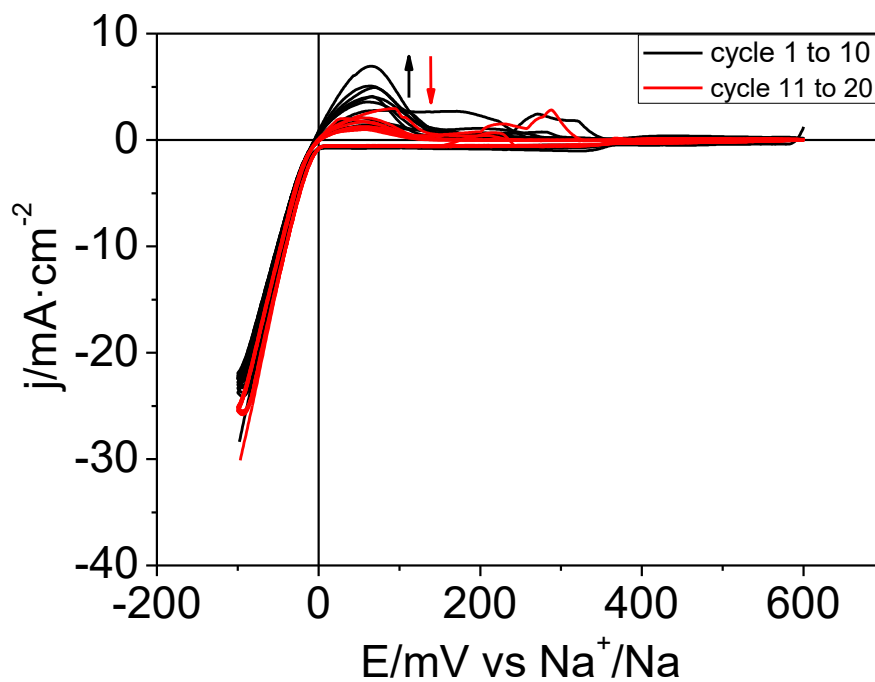


Figure S6. Twenty successive cyclic voltammograms for Na deposition/stripping on Al/C at a scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$ in a three-electrode cell containing $\text{NaI}\cdot 3.3\text{NH}_3$. The working potential window goes from -0.1 V to 0.6 V vs Na^+/Na .

As observed in Figure S6, the anodic current is increasing progressively until reaching cycle 10 (black lines). Then, it decreases due to the mechanical instability of the deposit of sodium on Al/C (cycle 11 to 20, red lines).