A safe and non-flammable sodium metal battery based on an ionic liquid electrolyte

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Rechargeable sodium metal batteries with high energy density could be important to a wide range of energy applications in modern society. The pursuit of higher energy density should ideally come with high safety, a goal difficult for electrolytes based on organic solvents. Here we report a chloroaluminate ionic liquid electrolyte comprised of aluminium chloride/1-methyl-3-ethylimidazolium chloride/sodium chloride ionic liquid spiked with two important additives, ethylaluminum dichloride and 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide. This leads to the first chloroaluminate based ionic liquid electrolyte for rechargeable sodium metal battery. The obtained batteries reached voltages up to ~ 4 V, high Coulombic efficiency up to 99.9%, and high energy and power density of ~ 420 Wh kg⁻¹ and ~ 1766 W kg⁻¹, respectively. The batteries retained over 90% of the original capacity after 700 cycles, suggesting an effective approach to sodium metal batteries with high energy/high power density, long cycle life and high safety.
High-energy rechargeable battery systems have been actively pursued for a wide range of applications from portable electronics to grid energy storage and electric automotive industry1–6. At higher energies, battery safety becomes increasingly important, evident from high-profile battery fires/explosion accidents in recent years. Rechargeable batteries using flammable organic electrolytes always risk fire/explosion hazards when short circuit or thermal runaway happens, setting a bottleneck in battery design/engineering and requiring innovations of next-generation battery systems with intrinsically higher safety7–9. For organic electrolytes various strategies have been investigated to mitigate the safety concerns, including the use of voltage or temperature-sensitive separators9–11 and overcharge protection additives12. Developing new electrolyte systems that are intrinsically non-flammable has also been actively pursued13–15. In particular, room temperature ionic liquids (ILs) have been widely explored as promising candidates due to their non-flammable nature16–18. Among them, ILs comprised of AlCl3 and 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) are a classical chloroaluminate based electrolyte system with many desired properties including non-flammability, non-volatility, low viscosity, high conductivity, and high thermal stability and chemical inertness17,19. In this electrolyte, AlCl3 complexes with the Cl ion from [EMIm]Cl to produce AlCl4– and EMIm+, and any excess AlCl3 converts a portion of AlCl4– into Al2Cl7–, resulting in the coexistence of AlCl4– and Al2Cl7–:

$$\text{AlCl}_3 + [\text{EMIm}]\text{Cl} \rightarrow \text{AlCl}_4^– + [\text{EMIm}]^+$$ (1)

$$\text{AlCl}_4^– + \text{AlCl}_3 \rightarrow \text{Al}_2\text{Cl}_{7}^–$$ (2)

The AlCl3/[EMIm]Cl-based ILs have been used as electrolytes for rechargeable metal batteries20,21. An example was rechargeable aluminum-graphite battery developed by our group and others with fast and highly reversible AlCl4– intercalation/de-intercalation into graphite positive electrode, and Al2Cl7– plating and stripping on Al negative electrode20. Nevertheless, it is desirable to develop higher voltage and higher energy density battery systems utilizing chloroaluminate IL electrolytes. A promising strategy is replacing Al by more reactive metal negative electrodes with lower standard electrode potentials such as sodium and lithium, which could raise the battery voltage and allow the use of well-established positive electrode materials with higher energy densities. Indeed, researchers have been pursuing this direction since almost 30 years ago. In as early as 1990, Melton et al. reported the first buffered AlCl3/[EMIm]Cl IL system by adding NaCl, eliminating Al2Cl7– and introducing Na ions into the electrolyte22 via

$$\text{Al}_2\text{Cl}_{7}^– + \text{NaCl} \rightarrow 2\text{AlCl}_4^– + \text{Na}^+ + \text{Cl}^–$$ (3)

Thus far, however, reversible and stable deposition and stripping/oxidation of Na metal in buffered AlCl3/[EMIm]Cl ILs towards rechargeable Na batteries have been hindered, with or without the use of a rechargeable electrolyte additives such as HCl23, [EMIm]HCl24,25, triethanolamine hydrochloride26 and thionyl chloride27. These additives can stabilize Na redox to limited degrees, affording Coulombic efficiencies (CEs) of 65–94% for Na plating/stripping23–27. For instance, the CE record of reversible Na redox was 94% achieved with ~ 6 Torr HCl added to NaCl-buffered AlCl3/[EMIm]Cl = 1.7 IL at 6.4 mA cm−2, but it rapidly decayed at a lower current density23. None of the chloroaluminate ILs could afford multicycle Na plating/stripping with sufficiently high CE to pair with sodium positive electrode for Na battery cells17.

Here we present an ionic liquid electrolyte based on NaCl-buffered AlCl3/[EMIm]Cl for safe and high energy Na batteries. Two electrolyte additives at the 1 to 4% by mass level i.e., ethylaluminum dichloride (EtAlCl2) and 1-ethyl-3-methylimidazolium bis(fluorosulfonyl) imide ([EMIm]FSI) are key to stabilizing SEI on sodium negative electrode for reversible Na plating/stripping. In a Na/Pt cell containing this IL electrolyte, a CE of ~95% is reached at 0.5 mA cm−2 over ~ 100 reversible Na plating/stripping cycles. With the optimized IL electrolyte, we pair Na negative electrode with sodium vanadium phosphate (NVP) and sodium vanadium phosphate fluoroide (NVPF) based positive electrodes to afford high discharge voltage up to ~4 V, high CE up to 99.9%, and maximal energy and power density of 420 Wh kg−1 and 1766 W kg−1, respectively based on active material mass of positive electrode. In addition, more than 90% of the original capacity is retained after over 700 cycles. Solid-electrolyte interphase (SEI) analysis reveals SEI compositions including NaCl, Al2O3 and NaF derived from the reactions between Na and the anions in the IL electrolyte. The results shed light on future electrolyte and SEI design towards practical sodium metal batteries with high safety and high energy/power densities.

**Results**

**Properties of NaCl-buffered AlCl3/[EMIm]Cl ionic liquid.** Preparation of IL electrolyte (see “Methods” section) started by mixing anhydrous AlCl3 and [EMIm]Cl at a molar ratio of 1:1 to form an acidic room-temperature IL (AlCl3/[EMIm]Cl = 1.5), followed by buffering to neutral with excess NaCl and then adding 1 wt% EtAlCl2 and 4 wt% [EMIm]FSI to afford the final NaCl-buffered chloroaluminate IL electrolyte (referred as ‘buffered Na–Cl–IL electrolyte’) (Fig. 1a). Raman spectroscopy was performed to probe the evolution of AlCl4– and Al2Cl7– species in the IL at different stages (Fig. 1b). Both AlCl4– and Al2Cl7– peaks were observed in the starting acidic IL with AlCl3/[EMIm]Cl = 1.5. After NaCl buffering of the electrolyte to neutral, the Al2Cl7– peaks at 309 and 430 cm−1 disappeared while the AlCl4– peak at 350 cm−1 strengthened, indicating the conversion of Al2Cl7– to AlCl4– by NaCl on the basis of equation (3). Subsequent addition of 1 wt% EtAlCl2 resulted in a noticeable further enhancement of the AlCl4– peak. This was attributed to reactions of EtAlCl2 with trace amounts of protons and undissolved NaCl in the buffered AlCl3/[EMIm]Cl = 1.5 IL with the generation of AlCl4–, C2H6 and Na+ via

$$\text{EtAlCl}_2 + \text{H}^+ + 2\text{NaCl} \rightarrow \text{C}_2\text{H}_6(g) + \text{AlCl}_4^– + 2\text{Na}^+$$ (4)

No obvious change in the Raman spectrum of chloroaluminate species was observed after the addition of 4 wt% [EMIm]FSI (Fig. 1b). The final buffered electrolyte (named buffered Na–Cl–IL hereon) was comprised of Na+, AlCl4–, EMIm+ and FSI– with Na+ and FSI– molar concentration of ~1.76 M and ~0.2 M, respectively.

An important property of the buffered Na–Cl–IL was its high ionic conductivity of ~9.2 mS cm−1 at 25 °C, which was 2–20 times higher than those of previously reported IL electrolytes based on bulky cations (e.g., N-butyl-N-methylpyrrolidinium and N-propyl-N-methylpyrrolidinium) for Na batteries29–32 (Fig. 1c). The ionic conductivity was comparable to conventional organic electrolytes, for example, ~6.5 mS cm−1 of 1 M NaClO4 in propylene carbonate (PC), and 6.35 mS cm−1 of 1 M NaClO4 in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 by vol) with 5 wt% FEC additive by thermogravimetric analysis (TGA) (Fig. 1d). The organic electrolyte showed a rapid weight loss above 132 °C, and lost ~85% of the original weight at 230 °C due to decomposition of the carbonate solvents...
in this temperature range. In comparison, the buffered Na–Cl–IL showed a much better thermal stability without severe weight loss until ~400 °C. The non-flammable nature of the buffered Na–Cl–IL electrolyte was confirmed when it was soaked into a porous separator and contacted with flame (Fig. 1e and Supplementary Movie 1) without causing fire. In contrast, the organic carbonate electrolyte easily caught fire and burned immediately (Fig. 1f and Supplementary Movie 2).

**Electrochemistry of Na–Cl–IL electrolyte.** In a Na vs. carbon-fibre-paper cell containing the buffered Na–Cl–IL electrolyte, linear sweep voltammetry scan was performed (Fig. 2a) and revealed a pair of sodium redox peaks on the cathodic side and no obvious electrolyte decomposition was observed until ~4.56 V on the anodic side, indicating high electrochemical stability of the electrolyte for high-voltage sodium battery systems. Sodium reduction/oxidation peaks were clearly observed in cyclic voltammetry (CV) with a Pt working electrode, a Na reference and counter electrode in buffered Na–Cl–IL electrolyte, showing reversible Na plating and stripping on Pt (Fig. 2b). In striking contrast, redox peaks were completely missing in buffered electrolyte without [EMIm]FSI additive, suggesting its critical role of stabilizing Na plating/stripping (Fig. 2c). Galvanostatic charge-discharge test investigated Na plating/stripping on Pt in buffered Na–Cl–IL electrolyte at a plating current density of 0.5 mA cm\(^{-2}\) for 30 min. The CE increased from ~72 to ~91% during the first 5 cycles for SEI formation and then reached ~95%, which is a new record of Na redox for both buffered chloroaluminate ILs and any other ionic liquids based on different cations (including benzyldimethylhexylammonium, butyldimethylpropylammonium, trimethylhexylammonium, dibutylmethylammonium and N-butyl-N-methylpyrrolidinium) and anions (including FSI and TFSI). Reversible Na plating/stripping
cycling was performed for 100 cycles (Fig. 2e), which was the first-time multicycle Na redox was performed in buffered AlCl3/[EMIm]Cl ILs. Without [EMIm]FSI additive in buffered AlCl3/[EMIm]Cl=1.5 electrolyte, plating current was observed but without observable stripping capacity (Supplementary Fig. 1).

The morphology of the plated Na on Cu after five plating/stripping cycles at a current density of 0.5 and 1.5 mA cm$^{-2}$ was investigated by scanning electron microscopy (SEM), showing particle sizes ranging from 5 to 10 μm without obvious dendritic morphology (Supplementary Fig. 2). The inner part of the Na particle was analyzed using focused ion beam (FIB) to expose cross-section of the interior (Supplementary Fig. 3). EDS element mapping of the cross-section revealed the existence of Na as the major element, together with O, Al, F and C, and very little Cl was detected inside the particle, suggesting the distribution of Cl mainly on the surface of Na rather than inside (Supplementary Fig. 4). More detailed analysis of SEI on sodium negative electrodes are shown later in this paper.

Na metal cells based on Na–Cl–IL electrolyte. Next, we made a Na metal battery by pairing a Na negative electrode with a positive electrode formed by coating Na$_3$V$_2$(PO$_4$)$_3$@reduced graphene oxide (NVP@rGO) particles on a carbon-fibre-paper.
substrate (see Method). NVP was a widely explored positive electrode material for rapid and reversible Na ion insertion/deinsertion in its lattice, and the interconnected conducting network formed by rGO sheets further enhanced the charge transfer process\textsuperscript{37,38}. Powder X-ray diffraction (XRD) measurements showed a NASICON-type framework with R3c space group with high crystallinity of the synthesized NVP@rGO particles (Supplementary Fig. 5). SEM and transmission electron microscopy (TEM) showed NVP particles several hundred micrometers in size blended with rGO sheets (Supplementary Figs. 6 and 7). The lattice fringes with d-spacings of 0.44 and 0.34 nm were assigned to the (104) planes of rhombohedral NVP and (002) planes of multi-layered rGO respectively\textsuperscript{37}. The rGO content of the NVP@rGO hybrid was around 1.1 wt% determined by thermogravimetric analysis (TGA, Supplementary Fig. 8).

Cyclic voltammetry of a Na/NVP@rGO cell with the optimized buffered Na–Cl–IL electrolyte (see supplementary Fig. 9 for electrolyte optimization) showed a pair of oxidation and reduction peaks corresponding to the redox reactions of V\textsuperscript{3+}/V\textsuperscript{4+} couples, and the CE increased to ~99.9 % within four cycles and then stabilized (Fig. 3a). A mass loading of NVP@rGO ~3.0 mg cm\textsuperscript{-2} was used unless specified otherwise. A charge-discharge plateau at ~3.4 V was seen with a specific discharge capacity of 93.3 mA g\textsuperscript{-1} based on the mass of NVP@rGO at a rate of 25 mA g\textsuperscript{-1} (Fig. 3b). In striking contrast, the buffered Na–Cl–IL electrolyte without [EMIm]FSI additive showed a negligible discharge capacity (0.03 mAh g\textsuperscript{-1}) (Fig. 3b). The Na/NVP@rGO cell in buffered Na–Cl–IL electrolyte showed good rate capabilities at higher rates (Fig. 3c), with a specific capacity of ~70 mAh g\textsuperscript{-1} at 500 mA g\textsuperscript{-1} (~4.3 C), which was ~71% of the specific capacity at 25 mA g\textsuperscript{-1} (Fig. 3d). The Na/NVP@rGO cell could retain ~96 % of the initial capacity for over 460 cycles at 150 mA g\textsuperscript{-1} (~0.4 mA cm\textsuperscript{-2}) with a high average CE of 99.9 % (Fig. 3e). This was the first time >99 % CE was achieved for Na metal battery in buffered chloroaluminate IL electrolytes. In comparison, a Na/NVP@rGO cell based on a conventional organic carbonate electrolyte, 1 M NaClO\textsubscript{4} in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 by vol) with 5 wt% fluoroethylene carbonate (FEC) only retained 79 % of the initial capacity after 450 cycles at 150 mA g\textsuperscript{-1} (Supplementary Fig. 9).

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**Fig. 3** Na/NVP@rGO cell performances in buffered Na–Cl–IL electrolyte. a CV curves of a Na/NVP@rGO cell using buffered Na–Cl–IL electrolyte at a scan rate of 2 mV s\textsuperscript{-1}. b Initial galvanostatic charge-discharge curves of a Na/NVP@rGO cell using buffered Na–Cl–IL electrolytes with and without [EMIm]FSI additive at 25 mA g\textsuperscript{-1}. c Galvanostatic charge-discharge curves of a Na/NVP@rGO cell using buffered Na–Cl–IL electrolyte at varied current densities from 25 to 400 mA g\textsuperscript{-1}. d, e Rate and cyclic stability of a Na/NVP@rGO cell using buffered Na–Cl–IL electrolyte. The boxed region of (e) corresponds to the rate performance of (d) at varied current densities from 20 to 500 mA g\textsuperscript{-1}. After that, a current density of 150 mA g\textsuperscript{-1} was used for cycling.
1, 2 and 3 represent three different IL electrolytes based on 1 M NaBF4, NaClO4 and NaPF6 salts, respectively. Using buffered NaCl electrolyte, the NVP@rGO cell based on buffered NaCl electrolyte was stably cycled, but CE fluctuation was significantly lower than ~96% based on the same NaCl electrolyte (Supplementary Fig. 11). A cyclic stability of a Na/NVPF@rGO cell using buffered Na–Cl–IL electrolyte at 300 mA g⁻¹ method, which was the first time NVPF@rGO hybrid was prepared via a one-step and low-temperature (120 °C) method without any freeze drying or annealing treatments (see Method). XRD patterns (Supplementary Fig. 12) indicated the prepared NVPF and NVPF@rGO mainly comprised of tetragonal Na₃V₂(PO₄)₂F₃ (ICDD PDF No. 01-089-8485) with an average size of ~100 nm. The NVPF particles were uniformly hybridized with rGO sheets, affording an interconnected conducting network with rGO sheets, affording an interconnected conducting network.

With a stable voltage window up to ~4.6 V (Fig. 2a), the buffered Na–Cl–IL electrolyte was compatible with higher voltage positive electrodes such as Na₃V₂(PO₄)₂F₃@rGO to afford Na metal battery cells with higher discharge voltage and energy density. We synthesized NVPF@rGO by a facile hydrothermal method, which was the first time NVPF@rGO hybrid was prepared via a one-step and low-temperature (120 °C) method without any freeze drying or annealing treatments (see Method). XRD patterns (Supplementary Fig. 12) indicated the prepared NVPF and NVPF@rGO mainly comprised of tetragonal Na₃V₂(PO₄)₂F₃ (ICDD PDF No. 01-089-8485) with an average size of ~100 nm. The NVPF particles were uniformly hybridized with rGO sheets, affording an interconnected conducting network with rGO sheets, affording an interconnected conducting network. XRD patterns (Supplementary Fig. 12) indicated the prepared NVPF and NVPF@rGO mainly comprised of tetragonal Na₃V₂(PO₄)₂F₃ (ICDD PDF No. 01-089-8485) with an average size of ~100 nm. The NVPF particles were uniformly hybridized with rGO sheets, affording an interconnected conducting network with rGO sheets, affording an interconnected conducting network.

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(0.16 to 1.6 mA cm\(^{-2}\)) current densities and CEs from 95 % to ~99 % (Fig. 4a, b). The maximal energy density was ~420 Wh kg\(^{-1}\) based on the mass of NVPF@rGO. With an increase of NVPF mass loading from 3.0 to 8.0 mg cm\(^{-2}\), both the specific capacity and energy density were well retained, with an energy density of ~394 Wh kg\(^{-1}\) at a mass loading of NVPF@rGO ~8.0 mg cm\(^{-2}\) operated under a 50 mA g\(^{-1}\) (~0.4 mA cm\(^{-2}\)) for 20 cycles and stopped at fully charged state prior to characterization.

The Na/NVPF@rGO cell with a NVPF@rGO mass loading of 3.0 mg cm\(^{-2}\) showed excellent cycling stability in our IL electrolyte, retaining more than 90% of the initial specific capacity after 710 cycles at a current density of 200 mA g\(^{-1}\) (~0.81 mA cm\(^{-2}\)) with an average CE of 98.5% (Fig. 4e). At a higher NVPF@rGO mass loading of 5.3 mg cm\(^{-2}\), a Na/NVPF@rGO cell could retain 91% of the initial specific capacity after 360 galvanostatic charge-discharge cycles at 150 mA g\(^{-1}\) (~0.7 mA cm\(^{-2}\)) with an average CE of 98.2% (Supplementary

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**Fig. 5** Morphology and solid-electrolyte interphase (SEI) probing of the plated Na in buffered Na–Cl–IL electrolyte. **a–d** High-resolution XPS spectra for Na Auger and O1s (a), F 1s (b), Al 2p (c) and Cl 2p (d) of the Na negative electrode from a Na/NVP@rGO cell with NVP@rGO mass loading of 5.0 mg cm\(^{-2}\) at different depths, respectively. The cell was cycled at 100 mA g\(^{-1}\) (~0.5 mA cm\(^{-2}\)) for 20 cycles and stopped at fully charged state prior to characterization. **e** Cryo-TEM image of Na-plated Cu grid at a current density of 0.1 mA cm\(^{-2}\). Scale bar, 500 nm. **f, g** High-resolution Cryo-TEM images and diffraction patterns (inset) of SEI concerning Al\(_2\)O\(_3\) and NaCl. Scale bars in (f, g), 5 nm. **h** High-angle annular dark-field (HAADF) and the corresponding element mapping images for SEI composition probing using STEM. Scale bar, 100 nm

Performance over previous NVPF-based positive electrodes in IL electrolytes\(^{29-32,41}\) was attributed to the 2- to 20-fold higher ionic conductivity of the Na–Cl–IL electrolyte, and the novel NVPF@rGO hybrid that facilitated charge transfer\(^{42,43}\).
Solid-electrolyte interphase chemistry of Na–Cl–IL electrolyte.

It is well known that SEI plays a critical role in stabilizing the interface between alkali metal negative electrodes and electrolytes. Due to the unusual composition of our IL electrolyte, the SEI chemistry could be different from that in conventional organic electrolytes. To this end, we first analyzed the elemental composition and depth profile by X-ray photoelectron spectroscopy (XPS) of a Na negative electrode from a Na/NVP@rGO cell with the mass loading of NVP@rGO 5.0 mg cm$^{-2}$. The cell was cycled for 20 cycles at 100 mA g$^{-1}$ (~0.5 mA cm$^{-2}$) and stopped at a fully charged state (Na plated on negative electrode). Surface XPS profile identified the presence of Na, O, C, Cl, F, Al and N (Supplementary Fig. 19). XPS profiling by Ar sputtering showed pronounced Na Auger peak at 535.7 eV at all sample depths (Fig. 5a). The O 1s peaks at 531.2, 529.4, 532.2 and 533.6 eV indicated the presence of Na$_2$CO$_3$, Na$_2$O, Na$_2$SO$_4$ and NaOH, respectively (Fig. 5a). The presence of NaOH was only at the surface, as it was generated from the contamination by water when the sample was briefly exposed to air during transfer to XPS. Part of the Na$_2$CO$_3$ could also be from reaction with water and carbon dioxide in air and decreased in intensity after sputtering. In contrast, the intensity of Na$_2$O and Na$_2$SO$_4$, formed by FSI anion and sodium metal showed no obvious decrease during sputtering, indicating their existence in SEI. As expected, the F 1s peak at ~685.5 eV confirmed the presence of NaF as the major F-based SEI (Fig. 5b). The FSI anions in [EMIm]FSI were responsible for F-based SEI via reactions with the highly reactive Na metal, consistent with previous literature. The Al 2p peaks at 74.5 eV indicated the presence of Al$_2$O$_3$ as a major Al-based SEI component with a small portion of metallic Al observed (Fig. 5c). The two pronounced peaks at ~198.4 and 199.8 eV corresponded to Cl 2p$_{1/2}$ and Cl 2p$_{3/2}$ peaks, suggesting NaCl as another major SEI component (Fig. 5d). The weak Na 1s peak at ~400 eV indicated the presence of Na-based species generated from the decomposition of FSI anion (Supplementary Fig. 20), consistent with previous literature based on LiFSI-based organic electrolytes. Overall, a hybrid SEI formed on sodium metal comprised of NaF, Na$_2$O, Na$_2$SO$_4$, Al$_2$O$_3$, Al and NaCl contributed to the reversible plating/stripping process of Na in buffered Na–Cl–IL electrolyte.

To gain a deeper insight into the Na plating process in buffered Na–Cl–IL electrolyte, cryogenic transmission electron microscope (Cryo-TEM) was used to probe the morphology and elemental composition of plated Na on Cu grids without exposing the sample to air (see "Methods" section). Cryo-TEM was demonstrated recently as a powerful tool in probing the morphological and component information of beam-sensitive battery materials such as Li metal, but not yet used for investigating SEI on sodium thus far. We first investigated the initial Na plating on a Cu grid, which involved Na growth and SEI formation at the initial stage. The plated Na (without exposing to air) demonstrated a spherical morphology (Fig. 5e).

Discussion

Compared with previous IL electrolytes for Na cells, the Na–Cl–IL electrolyte system is interesting in several ways. First, the high ionic conductivity (~9.2 mS cm$^{-1}$ at 25 °C) outperforms previously reported IL electrolytes based on bulky cations (e.g., benzylidene-methylammonium and N-butyl-N-methylpyrrolidinium) and anions (e.g., FSI$^-$ and TFSI$^-$), allowing for both high-energy density and rate capability/power density of the Na metal cells (Supplementary table 1). Secondly, the EMIm cation is unique among other cations since it provides delocalized positive charge around the imidazolium ring, effectively increasing the cation-anion distance and affording lower viscosities than ILs with other cations, owing to reduced Coulomb (electrostatic) interactions between ion pairs. Second, the SEI components are unique with the inclusion of AlO$_x$ and NaCl due to Na reaction/passivation by chloroaluminate species, which facilitates the stabilization of Na plating/stripping cycling. This led to a cycle life of over 700 cycles, the longest among all the reported IL-based Na cells.

We found that although FSI anions was indispensable for a stable SEI in our system, FSI alone was not sufficient for long cycle life of Na negative electrode. This was based on inferior cycling stability of Na/NVP@rGO cell in a non-chloroaluminate based electrolyte 1 M NaFSI in [EMIm]FSI IL electrolyte, displaying low and fluctuating CE of only ~90%, despite the fact that it had a much higher FSI anion concentration of ~6 M compared with only ~0.2 M in the buffered Na–Cl–IL electrolyte (Supplementary Fig. 21). Similarly, the Na/NVP@rGO cell using NaFSI in N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide IL electrolyte (molar ratio of 2:8) showed fluctuating CE after ~50 cycles when cycling at 150 mA g$^{-1}$ (Supplementary Fig. 22). In addition, an inferior rate performance was demonstrated using NaFSI/N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide IL electrolyte compared with that based on buffered Na–Cl–IL electrolyte (Supplementary Fig. 23).

Another important aspect was that previous IL electrolytes with highly concentrated F-based species (e.g., over 5 M of FSI anion concentration in NaFSI–N-propyl-N-methylpyrrolidinium) FSI electrolyte with a molar ratio of 2:8) were much higher in cost than conventional organic electrolytes due to expensive FSI species. A...
much lower FSI concentration of only ~0.2 M was needed for the buffered Na–Cl–IL electrolyte, and at the same time reaching better cell performances (power density, CE, cycle life and discharge voltage etc.) than previous room temperature IL electrolytes (Supplementary Table 1). The buffered Na–Cl–IL electrolyte could be a promising candidate for affordable, high safety and high performance sodium batteries with high safety and high performance, and can be potentially extended to a broad range of rechargeable battery systems such as Li and K batteries.

Methods

Preparation of IL electrolytes. IL electrolytes were prepared in an Ar-filled glove box with water and oxygen content below 2 ppm. [EMIM][AlCl4], IL was first made by mixing 1-ethyl-3-methylimidazolium chloride ([EMIM][Cl]) and anhydrous AlCl3 (≥99.0%, Fluka). [EMIM][Cl] was dried at 80 °C under vacuum for 24 h to remove residual water. For a certain molar ratio, e.g., 1.5 of AlCl3/[EMIM][Cl], 1.78 g of [EMIM][Cl] and 2.4 g of AlCl3 were weighed into two glass vials respectively. A small portion of AlCl3 was then slowly added into [EMIM][Cl] to avoid decomposition by heat generation during the mixing. This process was repeated until all the AlCl3 were introduced, and the mixture was stirred until all the solid was dissolved, followed by adding around 0.3 g of aluminum foil for purification. 1.8 g of the obtained light-yellow, clear liquid was kept at 70 °C for 1 h under vacuum for removal of water, followed by adding 0.172 g NaCl (99.99 %, Sigma-Aldrich) and allowed to stir for 24 h. The supernatant was collected, and stirred with 1 wt% NaCl and [EMIm]Cl and allows reversible Na plating/stripping upon addition of two additives, i.e., ethylaluminum dichloride (≥99.2 %, Sigma-Aldrich) in anhydrous dimethyl carbonate (≥99.0 %, Sigma-Aldrich) for removal of the metal ion on surface, cutting off the surface oxidation with blades, and pressing a fresh piece into a thin foil. Two nickel tabs (EQ-PLIB-NTA3, MTI) and one piece of glass fiber filter paper (GE/A, Whatman) were served as the current collector and separator, respectively. The obtained pouch was heated in an 80 °C vacuum oven for 8 h, and then transferred into an argon-filled glove box with water and oxygen content below 2 ppm to fill in the electrolyte (200 μL for each cell). The pouch was heat-sealed in the glove box before transferring out for further electrochemical measurement. Cyclometric velocity was performed on a CH760E electrochemical work station. The charge-discharge performances of the cells were measured with a Neware battery testing system (CT-4008-5V50mA-164-U). All the cells were allowed to age for 6 h before charge-discharge measurement. The specific capacity, energy and power density were calculated based on the total mass of NVP@rGO and NaPF6@rGO.

Characterization. For Raman spectra, IL electrolytes were injected and sealed into transparent plastic pouches in an Ar-filled glove box. The spectra were acquired (250–500 cm−1) using an Ar laser (532 nm) with 0.8 cm−1 resolution. The conductivity measurement was performed on a conductivity meter (FiveEasy Plus, Mettler Toledo). Prior to characterization, the electrodes were rinsed with anhydrous dimethyl carbonate for 6 times, and dried under vacuum at room temperature. They were further sealed in Ar-filled pouches and quickly transferred into the vacuum chamber to avoid too much exposure to air. The Na ion concentration of the buffered Na–Cl–IL electrolyte was measured using a Thermo Scientific ICAP 6300 Duo View Spectrometer. SEM images were acquired from a Hitachi S-4800 scanning electron microscope (SEM) operated at 15 kV, and EDS analysis was performed on a Horiba/Ex-450 EDS spectroscope. FIB-SEM was performed on a dual-beam field-emitting focused ion beam microscope (VERSA 3D DualBeam) with an accelerating voltage of 20 kV. TEM image of NVP@rGO was obtained with a JEOL JEM-2100F operated at 200 kV. XRD pattern was measured with a Bruker D8 Advance powder X-ray diffractometer with Cu Ka radiation. TGA measurement was performed on a PerkinElmer/Diamond TG/DTA thermal analyser at a heating rate of 5 °C min−1 in air for NVP@rGO and NaPF6@rGO, and in nitrogen for IL and organic electrolyte. TEM image of NaF@Al2O3 precipitate was taken at 180–460 °C, and the weight loss below 180 °C was due to water removal that is used to determine the water content of products synthesized in aqueous solution. XPS spectra were collected on a PHI 5000 VersaProbe XPS Microprobe. All the binding energy values were calibrated with C1s peak (284.6 eV). Depth profile was conducted using Ar ion sputtering at 1 kV and 0.5 μA over a 2 × 2 mm2 area, corresponding to a S2p sputter rate of 2 nm min−1. Glass fibre separators soaked with electrolyte were used to test the flammability of the electrolyte. Cryo-TEM was performed on an FEI Titan Krios cryogenic transmission electron microscope operated at 300 kV. Na was plated on a Cu TEM grid in a 2023 type transmission electron microscope at a current density of 1 mA cm−2 using 150 μl NaCl–water and one glass fibre as electrolyte and separator, respectively. The coin cell was disassembled in an Ar-filled glove box, followed by removing the residual electrolyte on Na-plated Cu TEM grid using anhydrous DMC and drying it under vacuum. The TEM grid was then carefully mounted onto a TEM cryo-holder and transferred into the chamber of Cryo-TEM without exposing to air. Other processes were performed for element mapping using a FEI Titan Themis 60-300 transmission electron microscope equipped with a cooling sample holder.

Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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Additional information

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