

Large-scale stationary energy storage: Seawater batteries with high rate and reversible performance



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A B S T R A C T

A new electrolyte (anolyte) for the negative electrode of seawater batteries, based on the combination of two ionic liquids (ILs), a sodium salt, and a SEI-forming additive, is herein reported. The quaternary anolyte is composed of N-methyl-N-propylpyrrolidinium bis(fluorosulfonyl)imide (0.6 mol fraction), N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl) imide (0.3 mol fraction), and sodium bis(fluorosulfonyl)imide (0.1 mol fraction). Ethylene carbonate (5 wt% with respect to the ILs and salt mixture) is added to promote SEI formation. The thermal, physicochemical, and electrochemical characterization of the quaternary electrolyte indicate its suitability as an anolyte, as well as the formation of a highly stable interface with the negative (hard carbon) electrode. Lab-scale seawater full cells employing a hard carbon anode and the ionic liquid-based quaternary anolyte show remarkable results in terms of capacity, cyclability, and rate capability at room temperature. Additionally, these cells showed better energy efficiency (voltage efficiency) and cyclability than those based on a conventional organic carbonate-based anolyte.

1. Introduction

Energy storage systems (ESSs) are becoming increasingly important to the utilization of renewable energy sources such as solar, wind, and tidal energies. Li-ion battery (LIB)-based rechargeable systems have been used in small and medium-scale ESSs because of their high feasibilities, long cycle life, and high energy densities and efficiencies [1–3]. However, instability and shortages in the supplies of lithium and, especially, cobalt resources, which are key factors in determining the price of LIBs, complicates the use of LIBs in large-scale ESS applications [4,5]. Na-ion batteries (SIBs), which working on the same principle as LIBs, have been considered as an alternative solution due to the abundance of sodium and their other raw materials [6–10]. However, despite having the advantage of a production process similar to that of LIBs, the large-scale production of SIBs has been hindered by their lower gravimetric and volumetric energy densities.

Our group has proposed the development of an electrochemical storage device using seawater at the cathode side as an innovative and large-scale ESS solution [11–14]. This battery chemistry, called Na-seawater batteries (see Fig. 1a) make use of multiple electrolytes, i.e.,

seawater as the catholyte (as well as the cathode material), a solid electrolyte physically separating the two electrode compartments, and a non-aqueous anolyte. Typically, the Na-ion conducting ceramic $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NASICON) is used as the solid electrolyte [15]. The anode compartment, in which Na^+ cations are stored at a low potential upon charging, is sealed, while the cathode compartment is open to the environment, i.e., seawater is flowed into it. Because natural seawater is also the active material in the open-structured cathode, the Na-seawater battery can be supplied infinitely with Na^+ cations, which are transferred to the anode side during charging. The process can be reversed during discharge, delivering electricity on demand. This battery chemistry differs from that of typical metal-ion ($M = \text{Li}, \text{Na}, \text{etc.}$) batteries in that it can receive unlimited Na^+ cations via the open cathode. Thus, unlike LIBs and SIBs, Na-seawater batteries are not limited by the need to store metal ions in the cathode material initially, which allows the use of anode materials affected by coulombic efficiency ($Q_{\text{discharge}} < Q_{\text{charge}}$) in the first cycle. Even during further cycling, small coulombic efficiencies only result in slightly lower energy efficiency, rather than inhibiting the operation of the cell, as in sealed batteries (LIB, SIB, and also Ni-MH). This characteristic enables

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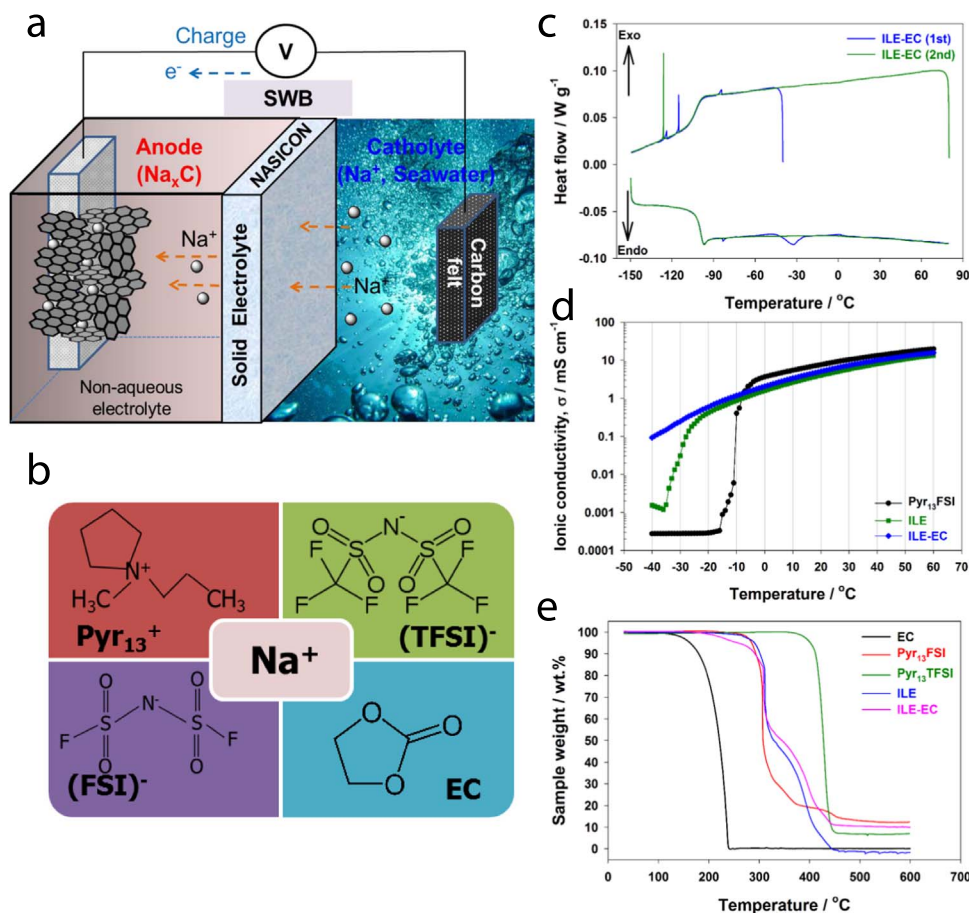


Fig. 1. (a) Schematic illustration of the Na-seawater battery (SWB). (b) Chemical structure of the ions in the selected ILs and Na-salt, and ethylene carbonate (EC). (c–e) Characterization of the ionic liquid electrolytes (ILE and ILE-EC) and their components: (c) DSC curves of ILE-EC; (d) ionic conductivity (heating scan after an annealing step) of the ILEs and the component Pyr₁₃FSI, which exhibited the lowest melting point; and (e) TGA curves of the ILEs and their components.

the use of low-cost, sustainable hard carbon materials for Na-ion storage in the anode. However, in the anodic compartment, a problem still exists related to the anolyte, i.e., the liquid electrolyte in direct contact with the anode material. Specifically, the use of conventional, non-aqueous electrolytes as anolytes introduces safety and long-term stability issues. With respect to safety, these electrolytes are composed of mixtures of highly volatile (and flammable) organic carbonates as solvents, which may leach out of the sealed anode compartment. Additionally, the best performing conductive salt identified thus far, sodium hexafluorophosphate (NaPF₆), is highly hygroscopic and prone to release HF upon hydrolysis. Regarding the long-term stability issues, a key requirement for the electrolyte is a wide electrochemical stability window (ESW), especially in the low voltage region, to prevent gas evolution and anolyte drying during cell operation. This issue has not yet been resolved. Non-aqueous, organic carbonate-based electrolytes generally have a limited ESW at low voltages (i.e., near the Na/Na⁺ potential). When these electrolytes are used as anolytes in a sealed compartment, reductive side reactions at the anode/anolyte interface consume the electrolyte and generate gases, causing battery swelling. This unwanted behavior may result in stability problems and shorten the battery cycle life. Additionally, the overpressure generated in the sealed anode compartment may crack the NASICON layer that separates the anolyte from the catholyte, resulting in the direct reaction of water with the sodiated anode.

To address the issues associated with the use of conventional, non-aqueous liquid anolytes, we have developed and tested a sustainable ionic liquid (IL)-based electrolyte. ILs are highly suitable for battery applications. Their negligible vapor pressure (practically, they can be considered non-volatile) and high thermal stability, and the resulting

low flammability and potential contamination, make them particularly safe and sustainable for use in batteries [16–18]. Additionally, IL-based electrolytes can provide the required ionic conductivities (even at low temperatures) and wide ESWs [19].

In this work, an IL-based electrolyte composed of sodium bis-(fluorosulfonyl)imide (NaFSI, 0.1 mol fraction), N-methyl-N-propylpyrrolidinium bis-(fluorosulfonyl)imide (Pyr₁₃FSI, 0.6 mol fraction), and N-methyl-N-propylpyrrolidinium bis-(trifluoro-methanesulfonyl)imide (Pyr₁₃TFSI, 0.3 mol fraction) is reported. This electrolyte was designed to provide room temperature ionic conductivity comparable to that of conventional, non-aqueous liquid electrolytes. Among the ILs, Pyr₁₃FSI is known to have a relatively low melting point and viscosity, while Pyr₁₃TFSI has a wide ESW and high thermal stability [20]. Finally, based on a recent report, the use of EC (5 wt% with respect to the total weight of the IL and Na-salt) as an additive in ionic liquid electrolyte enables the formation of a stable and protective layer (namely, the solid electrolyte interphase (SEI) [21,22]) on reactive anode surfaces when used in combination with the FSI anion [23,24].

An initial investigation into the suitability of the designed quaternary electrolyte as an anolyte in Na-seawater batteries has been carried out via ESW determination, electrochemical impedance spectroscopy (EIS), and X-ray photoelectron spectroscopy (XPS). Further tests performed using hard carbon/Na cells showed that the IL-based anolyte successfully forms a SEI layer, which provides greater stability than a conventional, organic carbonate-based electrolyte. In fact, these cells showed excellent electrochemical performance, exhibiting high reversible capacity with stable cyclability and good rate capability. To the best of our knowledge, such high reversibility and durability at room temperature have never been reported for an IL-based electrolyte.

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