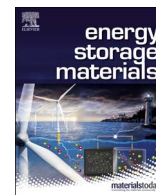




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# Large-scale stationary energy storage: Seawater batteries with high rate and reversible performance



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## ABSTRACT

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  $\text{Na}^+$  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  $\text{Na}^+$  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 ( $\text{M} = \text{Li}, \text{Na}$ , etc.) batteries in that it can receive unlimited  $\text{Na}^+$  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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