



Medium-temperature molten sodium batteries with aqueous bromine and iodine cathodes



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ABSTRACT

Medium-temperature sodium-bromine and sodium-iodine battery systems operating at 3.5 V and 3.0 V, respectively, are presented. The rechargeable molten-sodium systems work at approx. 100 °C and use aqueous bromine/bromide or iodine/iodide solutions as catholyte and sodium-ion conductive NaSICON ($\text{Na}_3\text{Zr}_2\text{Si}_{2.3}\text{P}_{0.7}\text{O}_{11.85}$) as solid electrolyte. The free halogen, which is formed upon charge, is complexed as highly soluble tribromide and triiodide, respectively. These systems can work in both, static and redox-flow setup, respectively, and aim at stationary energy storage applications. The sodium-halogen batteries were shown to run with high coulombic efficiency over several hundred hours. Long-term stability of the NaSICON ceramic material in contact with aqueous electrolytes, however, is still a concern. The sodium-bromine system suffers from a considerable bromine vapour pressure of the tribromide, whereas the sodium-iodine system was shown to operate in a stable manner with a catholyte allowing for a high total iodine concentration (≥ 2.0 M). Catholyte concentrations up to 2.75 M total iodine in redox-flow setup and up to 3.7 M in static setup are possible without iodine precipitation and correspond to specific energies of 198 Wh kg⁻¹ and 228 Wh kg⁻¹, respectively, on total active material level.

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1. Introduction

Molten sodium is the anode of several high-temperature batteries such as sodium/sulfur and sodium/nickel chloride which have been developed in the 1960s and 1970s [1,2]. These batteries use sodium- β'' -alumina as solid electrolyte and are operated at approx. 300 °C as the cathodes used require such temperatures in order to be in the molten state and because the ionic conductivity of the solid electrolyte must be sufficiently high. They show high energy density, combined with reasonable safety and long cycle life. However, at these high temperatures, thermal losses are not negligible and reduce the overall energy efficiency of these systems or limit their use to very large units in the MWh range for stationary applications. Attempts to reduce the operating temperature to reduce thermal losses are accompanied by more difficult wetting of the ceramic material with molten sodium and decreasing sodium-ion conductivity. Coating of the ceramic surface with metals [3,4] or the use of sodium-caesium alloy [5] have been proposed to increase wetting. NaSICON-based materials

are another type of ceramic sodium-ion conductors with high ionic conductivity [6–9]. Battery systems operating at temperatures as low as 100 °C have, to our knowledge, not been presented yet. They could, though, combine the very high specific capacity of sodium metal with high calendar life-time of high-temperature systems like sodium/sulfur and zero self-discharge. Recently, Ingersoll et al. showed a prototype of a sodium-iodine battery based on NaSICON ceramics, and an inorganic NaI/AlCl₃-based catholyte [10]. This battery works at a temperature of 120 °C. Zhu and Kee published theoretical work on an aqueous sodium-iodine system also working at 120 °C (using highly concentrated NaI, which has a boiling point of >120 °C) [11]. NaSICON, contrarily to sodium- β'' -alumina, is reported not to be stable against molten sodium metal at temperatures around 300 °C [12], but even when cycling in Na/Na configuration at 300 °C, several hundred hours of stable cell polarization could be obtained [13]. In the same paper a corrosion rate of <1 μm in 3 years was obtained during immersion in molten sodium at 300 °C. This indicates that the chemical stability vs. liquid sodium at temperatures around 100 °C can be expected to be several years. Aqueous cathodes based on highly soluble redox active species would permit easy preparation, low cost and high energy density. They could, in comparison to existing sodium (or lithium) ion or high temperature sodium systems,

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allow operation in static mode as well as flow-cell mode (redox-flow battery). It would, however, be limited to a relatively narrow operating temperature window between the freezing point of liquid sodium (98 °C) and the boiling point of the aqueous solution, which depends on the concentration of the dissolved species. Bromine and iodine could be suitable cathode materials as they are highly soluble in the reduced state (bromide, iodide) and the oxidized state (as tribromide and triiodide). Several publications are dealing with the question of the stability of NaSICON against aqueous electrolytes and present several materials that show impressive behaviour in alkaline media up to 60–80 °C [10,14] and even >100 °C [15]. This is why we focused on NaSICON as solid electrolyte for these batteries comprising an aqueous catholyte operating at temperatures around 100 °C. We present stability data of NaSICON and sodium- β'' -alumina in Na halogenide solution and Na halogenide solutions containing bromine or iodine at operating temperature which confirm our choice of NaSICON as solid electrolyte. The sodium-halogen batteries can be designed in static and flow-cell setup and permit a high energy density which depends on the concentration of the halogen in the charged catholyte. Such batteries could be used as low-cost alternative for stationary energy storage.

2. Experimental Procedure

2.1. NaSICON preparation

NaSICON solid electrolyte disks were prepared according to the route published by Shimizu et al. [16], except that no excess of sodium was used. First, stoichiometric amounts of 0.3 M solution of Na_2SiO_3 ($\geq 98\%$, Sigma-Aldrich, Germany) and 0.3 M solution of $\text{NH}_4\text{H}_2\text{PO}_4$ ($\geq 98\%$, Alfa-Aesar, Germany) were mixed, then a stoichiometric amount of 0.3 M solution of $\text{ZrO}(\text{NO}_3)_2$ (99%, Sigma-Aldrich) was added over 30 min under vigorous stirring to form a viscous sol. The remaining amount of silicon was added as $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) ($\geq 99\%$, Sigma-Aldrich) under stirring and the solution was further stirred for 60 min, until all the TEOS has reacted. Then the sol was heated to 60 °C and stirred at that temperature for approx. 5 h until half of the volume evaporated. The resulting gel was heated to dryness at 110 °C. The white product was ground in a mortar and further ball-milled for 2 h to form a white powder. This powder was calcined at 750 °C for 1 h, followed by further ball-milling. Then, disks of 20 mm and 40 mm diameter were prepared by pressing uni-axially at 80 and 200 kN, respectively, for 10 min. The obtained green bodies were sintered at 1050 °C for 6 h to form disks of 17 mm and 33 mm diameter, respectively. These disks were sandpapered and polished to form regular disks with a thickness of 600–1000 μm .

2.2. Cell assembly

Molten sodium does not react with polyolefine, therefore polymethylpentene (PMP) was chosen for the anode cell body as it has a high melting point of approx. 240 °C which guarantees sufficient mechanical stability at 100 °C. The cell body was machined from a block obtained from Goodfellow (UK). The cathode cell body must resist elementary bromine which limits the choice of materials very much. Only highly fluorinated polymers as polytetrafluoroethylene (PTFE), ethylene tetrafluoroethylene (ETFE), polyvinylidenedifluoride (PVdF) and polychloro trifluoroethylene (PCTFE), etc. can be assumed to resist the aggressive medium on long term. Out of these PCTFE was chosen, due to its hardness up to high temperatures and the very low diffusion of bromine in the material which limits bromine losses upon operation of the cell. The PCTFE for the cathode cell body was purchased from Schmidt + Bartl (Germany). O-rings were cut out of

1/20" perfluoroelastomer mat (FFKM, Kalrez 6375, CKD Dichtungstechnik, Germany) and 1/20" ethylene propylene diene monomer rubber mat (EPDM, Reiff, Germany) for the cathode and anode part, respectively. As current collector at the anode 1.0 mm aluminium wire ($\geq 99\%$, Alfa-Aesar, Germany) was chosen and for the cathode an Ir-plated 300 μm thick tantalum sheet ($\geq 99.9\%$, Sigma-Aldrich) welded on 1 mm diameter Ta-wire ($\geq 99.9\%$, Sigma-Aldrich) was used. Ir-plating was made from a home-made plating solution containing 10 g L^{-1} Ir as H_3IrBr_6 , 1.8 g L^{-1} oxalic acid ($\geq 99\%$, Sigma-Aldrich) and 40 g L^{-1} boric acid ($\geq 99\%$, Fluka, Germany) at 80 °C and pH 5. The H_3IrBr_6 solution was obtained by reacting iridium black (99.8%, Alfa-Aesar) with Na_2O_2 (95%, Riedel-de-Haën, Germany) at 500 °C for 2 h, dissolving in 10% HBr (made from 47% HBr, for analysis, Merck, Germany), precipitating iridium hydroxide with NaOH solution ($\geq 99\%$, Roth, Germany), washing and dissolving with 47% HBr. Ethylene tetrafluoroethylene (ETFE) tubes were used for the flow cell (diameter 1/16"), together with ETFE ferrules and PEEK nuts (all from Upchurch Scientific, purchased from Techlab, Germany). For pumping the catholyte solution a peristaltic pump (ISM597D from Ismatec, Switzerland) was used with a flow rate of approx. 1 ml min^{-1} . Concentrated solutions of NaBr or NaI were used as catholyte (both $\geq 99\%$, Sigma-Aldrich). PTFE screw caps for the 100 ml glass bottle serving as external tank were purchased from Bohlender (Germany). 5 ml glass syringes with PTFE plungers (Hamilton) were purchased from Hugo-Sachs (Germany).

2.3. Physicochemical characterisation

Scanning electron microscopy (SEM) was done on a Zeiss EVO MA10 with 20 kV acceleration voltage in secondary electron detection mode. The electron diffraction (EDX) measurements were done on the same device with 10 kV acceleration voltage using the backscattered electron diffraction.

The X-ray diffraction patterns were taken on a Bruker-AXS D8 advance with $\text{Cu K}\alpha$ radiation (1.54060 Å wave length) between 10° and 85° 2θ , with 0.015° step size and 1.5 s at each step.

2.4. Electrochemical tests

Half-cell tests were done at temperatures around 100 °C in home-made polymethylpentene (TPX)-based cells in Na/Na-setup using liquid sodium (ACS reagent, dry, Sigma-Aldrich) or $\text{NaBr} + \text{Br}_2$ ($\geq 99.5\%$, Sigma-Aldrich) and $\text{NaI} + \text{I}_2$ (sublimated, p.A., Merck, Germany), respectively, and NaSICON solid electrolyte. They were performed in constant current mode at different current densities using a SP200 potentiostat/galvanostat (Biologic, France) in CP mode. Full cell measurements using liquid sodium anode and aqueous sodium halogenide/halogen cathode were done accordingly in home-made cells (polymethylpentene for the anode compartment and PCTFE for the cathode compartment). Electrochemical impedance spectroscopy was performed in the same cells using an EG&G Princeton Applied Research potentiostat/galvanostat 263 A together with SI 1287 electrochemical interface and SI 1260 impedance/gain-phase analyzer (both Solartron) for frequencies between 1 Hz and 1 MHz and a potential amplitude of 50 mV.

3. Results and Discussion

3.1. Cell development

3.1.1. Anode compartment

The anode cell body (see Figure 1) consists of polymethylpentene in which a cavity of 14 mm diameter and 8 mm depth is machined, accounting for a volume of approx. 1.25 cm^3 . A NaSICON disk is used as separator material, allowing for an accessible

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