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Na ion- Conducting Ceramic as Solid Electrolyte for Rechargeable Seawater Batteries

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ABSTRACT

This study describes the assembly of a rechargeable seawater battery using hard carbon as the anode, seawater as the cathode, and a fast Na ion-conducting ceramic as the solid electrolyte. Two different Na ion-conducting ceramics, β″-Al_2O_3 and $Na_3Zr_2Si_2PO_{12}$ (NASICON), are used as the solid electrolytes in this study. The discharge capacity of the seawater battery with the NASICON solid electrolyte is 120 mAh g^{-1} after the first cycle and over 91% coulombic efficiency after twenty cycles. However, under the same experimental conditions, the discharge capacity of the seawater battery with a β"-Al_2O_3 electrolyte significantly drops to 10 mAh g^{-1} after one cycle. It is observed that the stability of NASICON in seawater is superior to that of β"-Al_2O_3 and impedance results of NASICON are not changed significantly compared to that of β"-Al_2O_3 after cycling tests. The stability of Na ion-conducting ceramics in seawater and their effects on the electrochemical performance of seawater batteries are presented and discussed.

1. Introduction

Environmental concerns over the use of fossil fuels and their resource constraints have motivated the development of electric and renewable energy systems for portable electronic devices, electric vehicles (EVs), and energy storage system (ESS). Rechargeable lithium-ion batteries (LIBs) have been successfully commercialized for mobile electronic devices and EVs, but have found limited use in ESSs due to their high cost. Moreover, the increasing demand for LIBs combined with possible lithium resource restrictions might lead to a prohibitive price for these batteries [1–3]. Thus, many scientists are exploring alternative battery technologies in which lithium is replaced by sodium because sodium is naturally abundant, easily accessible, and low cost [4–6].

Rechargeable seawater batteries have been recently introduced as a result of requests for new ESSs that use sodium [7–9]. These batteries are built using a fast Na ion-conducting ceramic as the solid electrolyte. A solid ceramic electrolyte is one of the key components in a seawater battery system because the sodium metal electrode can be protected from direct exposure to seawater. The feasibility of a rechargeable battery system using seawater as an electrode material has been demonstrated [9]. However, it is expected that the capacity, reliability, and coulombic efficiency of seawater batteries will depend on the stability of the solid electrolyte in seawater. Two Na ion-conducting ceramics, β″-Al_2O_3 and $Na_3Zr_2Si_2PO_{12}$ (NASICON), have been considered as solid electrolyte materials. β″-Al_2O_3 possesses a two-dimensional(2D) structure, and exhibits Na ion conductivity up to $\sim 2.0 \times 10^{-3}$ Scm^{-1} at room temperature [10]. NASICON has demonstrated an ionic conductivity of 2.5×10^{-3} Scm^{-1} [11] in a three-dimensional (3D) structure [12–14]. β″-Al_2O_3 is known to be moisture-sensitive. Will [15] reported that there is a rapid exothermic occlusion of water in the surface micropores of β″-Al_2O_3, which caused saturation of these pores in less than 1 h. This was followed by slow diffusion of H_3O^+ ions into the β″-Al_2O_3 lattice leading to ion exchange with sodium. Flor et al. [16] substantiated that β″-Al_2O_3 is unstable to moisture using thermogravimetric and X-ray techniques. Flor et al. reported that rapid penetration takes place in the first few microns near the conduction plane boundaries. Water absorption caused changes in lattice parameters a and c of β"-Al_2O_3 [16]. In contrast, NASICON-type materials are known to be stable in a moist environment. However, it was later found that the formation of hydronium NASICON [17] occurred on the surface of NASICON by ion exchange between H_3O^+ and Na^+ [18] during the reaction of NASICON in hot water. It was also reported that NASICON's instability in water could be due to the dissolution of a secondary amorphous phase, Na_3PO_4, in NASICON [19]. However, most of these studies were conducted using NASICON powders at a high temperature of 80 °C to

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accelerate its reaction with water so that comparative results could be collected in a short time. For seawater batteries operating at room temperature, dense ceramic plates are required for the electrolyte and separator, but their stability in contact with seawater and its effect on seawater battery performance have not been reported.

In this study, we used two different solid electrolytes, β″-Al_2O_3 and NASICON, in seawater batteries at room temperature. The ceramic electrolytes exposed to seawater during cycling were collected after testing, and their stability in seawater and its related seawater battery performance were compared to understand their influence on the seawater battery system.

2. Experimental

2.1. Sample preparation

A Sodium-ion conductive ceramic with nominal composition $Na_3Zr_2Si_2PO_{12}$ (NASICON) was prepared by solid state reaction of $Na_3PO_4{\cdot}12H_2O$ (Daejung, 99%), ZrO_2 (Kanto, 99.9%) and SiO_2 (Daejung, 99%). The powders were mixed and first-calcined under air at 400 °C for 5 h. The first-calcined powder was ground to make a finely-grained powder. Next, the first-calcined powder was second-calcined under air at 1100 °C for 12 h. The second-calcined powder was ground and milled in a planetary mill for 30 min. The dried powder was uniaxially pressed (5–7 MPa) into disks with about 3 mm thickness and 2.2 cm diameter. A dense ceramic plate was obtained after sintering the pressed pellet on a Pt sheet at 1280 °C for 10 h under air. Sodium β"-Al_2O_3 ceramic plates used as a solid electrolyte measuring 20 mm × 20 mm with a 1 mm thickness was purchased from Ionotec Ltd.

2.2. Characterization techniques

X-ray diffraction (XRD) was carried out with a D/Max, Rigaku apparatus equipped with a CuKα X-ray source (λ=1.5406 Å). The X'Pert HighScore Plus program (PANalytical) was used to calculate the lattice parameters. Ionic conductivity measurements were performed by dielectric spectroscopy in the frequency range of 0.1 Hz to 1 MHz using a ZIVE SP2. For impedance measurements, a Pt/NASICON/Pt cell was made by Pt sputtering. The diameter of the Pt electrode was 10 mm. SEM using high-resolution scanning electron microscopy (FEI Verios 460L) was employed to evaluate the surface of the ceramic electrolytes. The charge-discharge and cycle performance tests were carried out using an automatic galvanostatic charge-discharge unit, WBCS3000 battery cycler, at room temperature. The experiments were carried out at 0.05 $mAcm^{-2}$ current rate.

2.3. Electrochemical tests

Seawater was used as a positive electrode material. The hard carbon negative electrode was fabricated from a 80:10:10 (wt%) mixture of hard carbon (MeadWestvaco Co. U.S.A.), Super-P carbon black (TIMCAL, USA) as the conductive additive, and PVdF (Sigma–Aldrich, USA) as binder. Composition of non-aqueous electrolyte was 1.0 M $NaCF_3SO_3$ (Sigma–Aldrich, USA) salt dissolved in TEGDME (Sigma–Aldrich, USA) and NASICON or β"-Al_2O_3 ceramic plates, solid electrolytes, were used to make up the hybrid multi-layer electrolyte. Also, concentration of sodium ion in seawater is 0.46 M [9]. Carbon paper (Fuel Cell Store, Inc.) was employed as a current collector for the seawater cathode. A seawater cell was provided from 421Energy Co., Ltd. The assembled cell was exposed to seawater and connected to a testing station. A battery cell tester (WBCS3000) was employed to perform the charge and discharge tests at different current densities. The specific capacity was determined by the weight of hard carbon.

3. Results and discussion

The constitution of the seawater battery [7–9] is schematically illustrated in Fig. 1. It consists of an anode and cathode, which are separated by a dense ceramic solid electrolyte. The anode is composed of the current collector, active material, and organic liquid electrolyte ($NaCF_3SO_3$ in Triethylene glycol dimethyl ether (TEGDME)). The cathode is composed of the current collector and seawater. Seawater works as the active cathode material. The current collector is needed to provide a large surface reaction area with seawater as well as electron conductivity. Carbon paper was employed as a current collector in this study. When the seawater cell is assembled using the hard carbon anode, the redox potential of the full cell was observed to be ~3.1 V for charge and ~2.3 V for discharge, respectively. During the charging process, chlorine

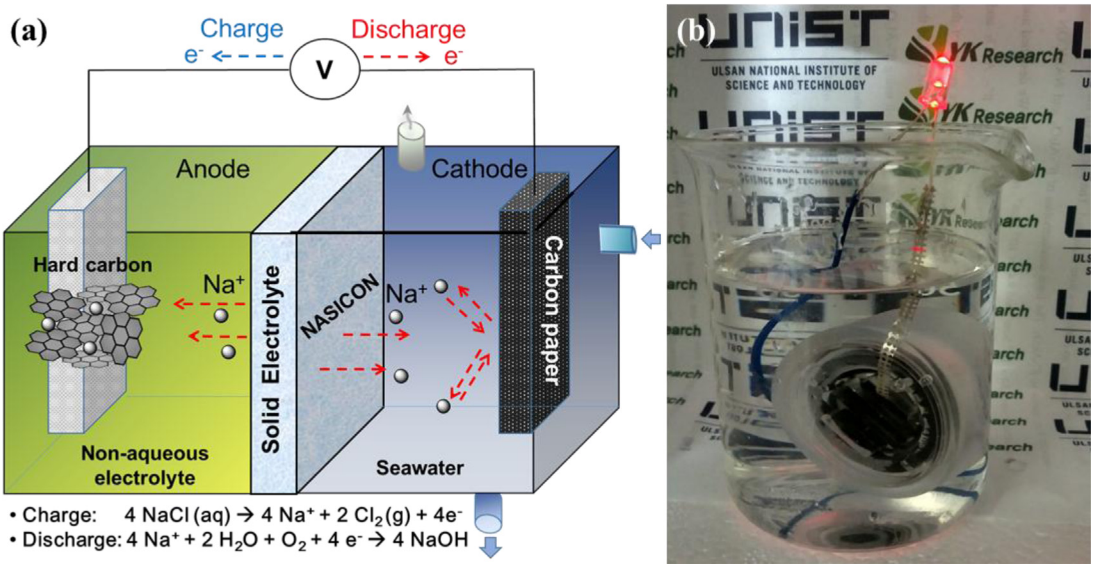

Fig. 1. (a) Schematic illustration and (b) digital picture of a seawater battery cell.