



Short communication

Lithium/water battery with lithium ion conducting glass–ceramics electrolyte

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ABSTRACT

Lithium/water batteries have attracted considerable attention as high power supply devices because they use high energy density lithium metal as an anode and water as a cathode. In this study, we investigate the use of lithium/water batteries that use a glass–ceramics plate as an electrolyte.

A lithium ion conducting glass–ceramics plate has no through-holes and does not exhibit moisture permeation. Such a plate has stable ionic conductivity in water. Lithium/water batteries that used a glass–ceramics plate as an electrolyte had a long and stable discharge for 50 days at room temperature when the lithium metal was prevented from coming into contact with water. Lithium/seawater batteries using a glass–ceramics plate as an electrolyte also operated well in the 10–70 °C temperature range.

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1. Introduction

The use of a glass–ceramics plate as an electrolyte in lithium/air and lithium/water batteries has been proposed recently [1]. Lithium/air and lithium/water batteries have the potential to achieve better discharge capacities than conventional batteries owing to the fact that they use lithium metal as an anode and oxygen and water, respectively, as a cathode. Lithium/air and lithium/water battery has a very high energy density, which consists of a cathode with humid air, ionic electrolyte and a lithium–metal anode. The theoretical capacity is about 5.8–11.4 kWh/kg [1,2]. Therefore, the lithium/air battery has attracted attention as a power supply for electric vehicles. A lithium/water battery also has a very high energy density, which consists of a cathode with water and electrolyte and a lithium–metal anode. The theoretical capacity is about 5.8–11.4 kWh/kg [1].

In particular, lithium/water batteries have potential for use as high-discharge-capacity power supplies for the long-term operation of deep-sea applications. For example, they can be employed in sensors used for geophysical observations [3].

We have developed a lithium ion conducting glass–ceramics material that has a sodium superionic conductor (NASICON)-type of structure for use as an ionic electrolyte [4,5]. The ionic conductivity of this material, which has a $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-y}\text{Ge}_y\text{PO}_4$ composition, is more than $1 \times 10^{-4} \text{ S cm}^{-1}$. This material exhibits stable ionic conduction. Further, its ionic conductivity does not decrease even

when it is soaked in a solution of Li salt in water [1,6,7]. It also does not lose weight when boiled in distilled water for 1 h. This electrolyte can protect a lithium metal anode from water and moisture in the air.

In this study, we investigated the use of the lithium ion conducting glass–ceramics material in lithium/water batteries and compared the discharge stability of the developed lithium/seawater batteries with lithium/water batteries.

2. Experimental

Glass–ceramics [4,5,8] was fabricated by crystallized $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{PO}_4-\text{GeO}_2-\text{TiO}_2$ glass system. Li_2CO_3 , $\text{Al}(\text{PO}_3)_3$, SiO_2 , H_3PO_4 , GeO_2 and TiO_2 were mixed as raw materials of glass. Glass was produced by casting the molten glass onto the preheated stainless-steel plate and quenching. The glass was heated again in the electric furnace and the glass was crystallized. After that, glass–ceramics was processed and polished to form plate. Glass–ceramics had high ionic conductivity value ($0.9-1.1 \times 10^{-4} \text{ S cm}^{-1}$ at RT).

A moisture permeation test of the glass–ceramics plate was carried out using MOCON PERMATRAN-W 3/33. The measurement cell was maintained at 1 atm and 37.8 °C with a N_2 flow rate of $10 \text{ cm}^3 \text{ min}^{-1}$. Scanning electron microscopy (SEM) was used to check the existence of through-holes in the glass–ceramics plate and to measure its density.

To evaluate the resistivity of the glass–ceramics plate when water was used as a cathode, two glass–ceramics plates were separately immersed in distilled water and synthetic seawater for comparison. After immersion for a certain duration, the plates were washed and dried. We then evaluated the ionic conductivity change

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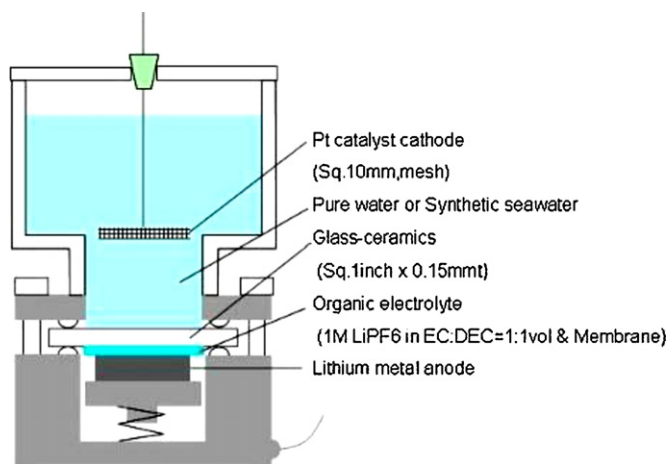


Fig. 1. Cell configuration of lithium/pure water (or seawater) battery.

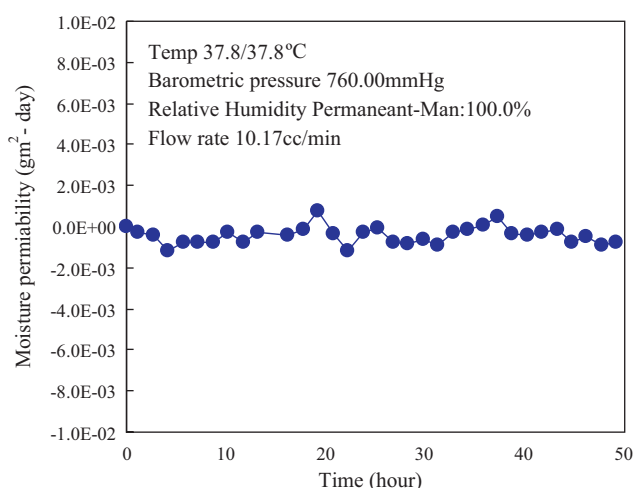


Fig. 2. Moisture permeability of glass-ceramics material.

of those plates by an AC impedance method. Au electrodes were fabricated on both surfaces of each glass-ceramics plate using a sputtering method. AC impedance measurements were carried out using Solartron 1260 for a 1 Hz–1 MHz frequency range and 0.1-V AC amplitude at room temperature (RT). Both sides of the plates used in these measurements were polished; the plates were 0.25-mm thick with 2-in. diameter.

The cell configuration of a lithium/water battery is shown in Fig. 1. To protect the polished lithium ion conducting glass-ceramics plate from lithium metal and to ensure proper measurement of ionic conductivity, a separator consisting of an organic electrolyte solution was poured between the glass-ceramics plate

Table 1

Main composition of synthetic seawater (gram per 1 L water).

NaCl	22.1 g
MgCl ₂ ·H ₂ O	9.9 g
CaCl ₂ ·H ₂ O	1.5 g
Na ₂ SO ₄	3.9 g
KCl	0.61 g
NaHCO ₃	0.19 g

and lithium metal. Both sides of the 1-square-inch and 0.15 mm² glass-ceramics polished. A mixed solvent of the organic electrolyte solution of LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC) (EC/DEC = 1/1 (v/v) Tomiyama Pure Chemical Industries) was used. The discharge capacity of the lithium metal electrode (11 mm diameter and 0.6 mm²) is 129 mAh (corresponding to Li of 0.0334 g). The discharge stability of the lithium/water battery containing the glass-ceramics plate was evaluated for a long duration at RT. Scanning electron microscopy (SEM) was used to check the change in the glass-ceramics plate surface after the discharge evaluation. The discharge characteristics were measured using ACD-01 (Asuka), an electric charge/discharge testing apparatus, under a discharge current of 0.1 mA and a cut-off voltage of 1.0 V.

The temperature dependence of the discharge stability of the lithium/seawater battery containing the glass-ceramics plate was measured under a discharge current of 0.3 mA and a cut-off voltage of 1.0 V at 10 and 70 °C. The discharge capacity of the lithium metal plate (11 mm diameter and 0.2 mm²) is 43 mAh (corresponding to Li of 0.0111 g). The seawater to be used as cathode material was synthetically prepared using Marine Art SF-1 from Tomita Pharmaceutical with distilled water and this catholyte was pH 7.8. Main composition formula of synthetic seawater is shown in Table 1.

3. Results and discussion

First, the microstructure and moisture permeation of the proposed glass-ceramics material were investigated. Fig. 2 shows the moisture permeability of a Li ion conducting glass-ceramics plate. The moisture permeability of the glass-ceramics plate was significantly low for 50 h. It can be considered, throughout the test, the moisture permeability via the through-holes in the glass-ceramics plate was almost blocked.

Fig. 3 shows the SEM images of the glass-ceramics plate. It can be seen in Fig. 3a that the surface of the plate is nearly smooth and has regularly distributed flat plateaus. Here, we were unable to observe any traces of through-holes in the surface. Fig. 3b shows a cross-sectional view of the glass-ceramics plate, where a considerably dense configuration is seen. However, we were unable to find any through-hole in this cross section as well. From these results, it can be deduced that the glass-ceramics material has no through-holes and can therefore disallow moisture permeation.

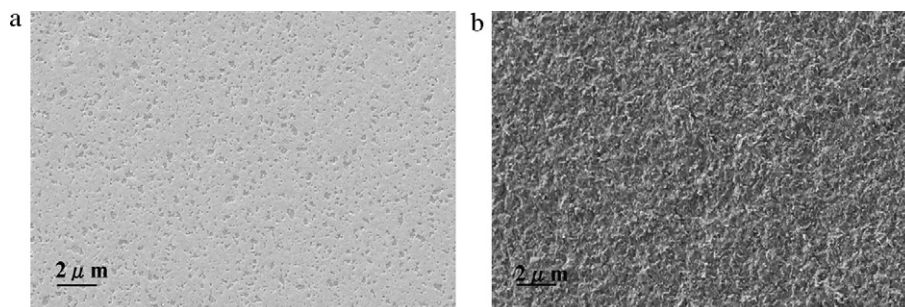


Fig. 3. SEM images of glass-ceramics plate; (a) a plane view and (b) a cross-sectional view.

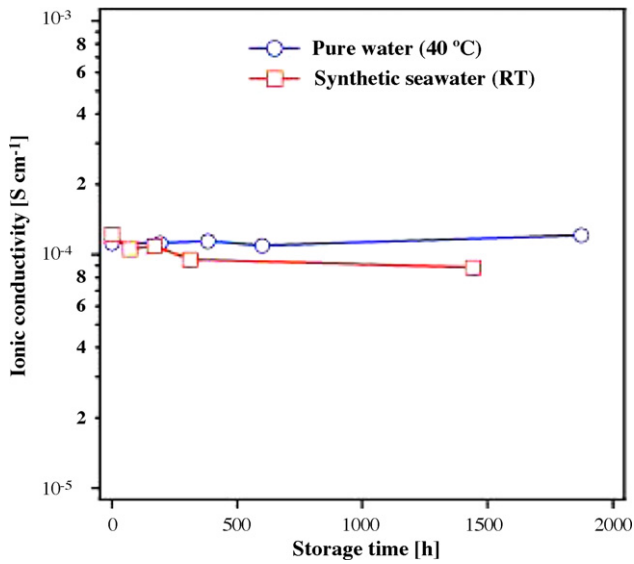


Fig. 4. Resistivity of glass-ceramics plate immersed in pure water and synthetic seawater.

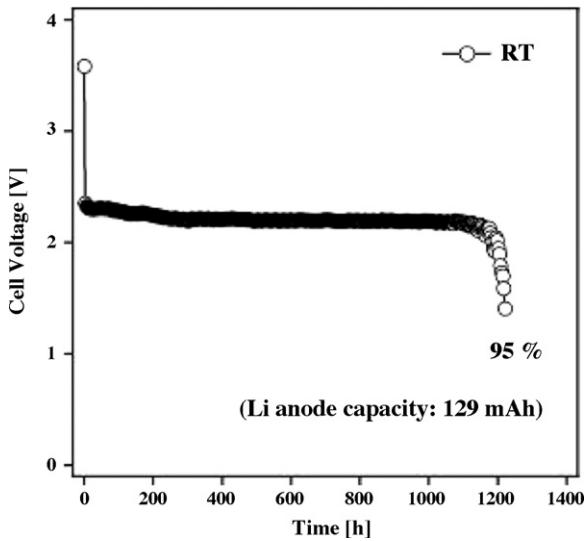


Fig. 5. Discharge curve of lithium/seawater battery with glass-ceramics plate for a prolonged duration.

Next, the resistivity of the glass-ceramics material in water was investigated. Fig. 4 shows the change in the ionic conductivity of the glass-ceramics plate with time in water and synthetic seawater. The ionic conductivity of the plate remained constant with not even a slight decrease for 1872 h when it was immersed in dis-

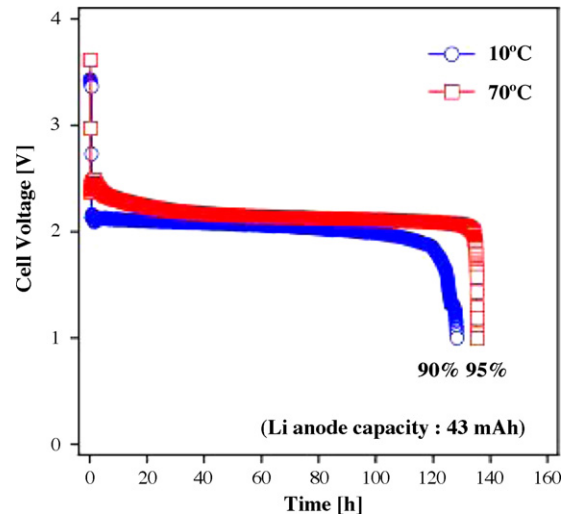


Fig. 7. Discharge curves of lithium/seawater battery with glass-ceramics plate at 10 and 70 °C.

tilled water at 40 °C. On the other hand, the ionic conductivity of the plate decreased by 20% after its immersion for 1440 h in synthetic seawater at RT. Nevertheless, it was established that the glass-ceramics plate was stable in water as well as in synthetic seawater, because the plate did not become porous or break down even after prolonged immersion.

Finally, for use in practical applications such as power supplies for marine sensing devices, the electrochemical behavior of the lithium/seawater battery containing a lithium ion conducting glass-ceramics plate was evaluated. Fig. 5 shows the long-term discharge characteristics of the lithium/seawater battery at RT. The discharge voltage remained constant at 2.2 V, and the battery could operate for 1220 h at 0.1 mA. From this result, we can conclude that the battery discharged 122 mAh to the designed capacity 129 mAh and could discharge at a capacity of 95% when lithium metal was used as an anode. Fig. 6 shows the SEM images of the glass-ceramics plate after the discharge test for a long duration. It can be seen in Fig. 6a and b that the surface of the plate is nearly smooth and has regularly distributed flat plateaus as before discharge test. We were unable to observe any change in the surface. It was found that the lithium ion conducting glass-ceramics material is effective and stable even in the lithium/seawater battery. Fig. 7 shows the temperature dependence of the discharge capacity of the lithium/seawater battery measured at 70 and 10 °C. At 70 °C, the discharge voltage remained constant at 2.14 V, and the battery discharged for 135 h at 0.3 mA. It could operate 40.5 mAh and a 95% discharge capacity of the lithium metal anode with the designed capacity 43 mAh. On the other hand, at 10 °C, the discharge voltage remained constant at 2.05 V and the battery discharged for 128 h

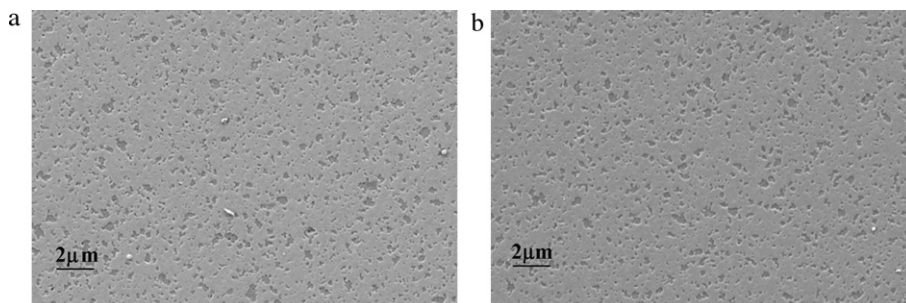


Fig. 6. SEM images of glass-ceramics plate after discharge test for a long duration at RT; (a) synthetic seawater side view and (b) organic electrolyte side view.

at 0.3 mA. It could operate 38.4 mAh and a 90% discharge capacity of the lithium metal anode to the designed capacity 43 mAh. It should be noted that the differences in discharge voltage and discharge capacity were derived from the ionic conductivity of the glass–ceramics material at each temperature value.

4. Conclusions

Lithium ion conducting glass–ceramics plates do not have through-holes and do not exhibit moisture permeation. Such plates have stable ionic conductivity in water. Lithium/seawater batteries containing a glass–ceramics plate showed a long and stable discharge for 50 days at RT when the lithium metal anode was prevented from coming into contact with water. The lithium/seawater battery with the glass–ceramics plate operated well in the 10–70 °C temperature range. On the basis of the above results, it can be concluded that the lithium-ion-conducting glass–ceramics material can be suitably used as a solid electrolyte in lithium/water batteries.

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