

All-solid-state polyvinyl-alcohol-based Li-ion battery fabricated in air and its charge/discharge measurements

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Abstract

A Li-ion battery consists of two active materials, namely positive and negative electrodes, and an electrolyte in contact with both. Because they use both liquid and solid electrolytes, all-solid-state Li-ion batteries, which are composed entirely of solids, are expected to outperform electrolyte-based batteries in terms of safety, lifetime, and power output. In this paper, we propose an experimental material that enables students to fabricate an all-solid-state Li-ion battery in air and evaluate its charge/discharge characteristics using a direct-current (DC) voltage and current source/monitor. Sheets of polyvinyl alcohol (PVA) with 30 wt% Li nitrate (30%LiNO₃-PVA) were used as the Li electrolyte. Li cobaltate (LiCoO₂) and acetylene carbon black C were used as the anode and cathode, respectively. All-solid-state Li-ion batteries were constructed using 30%LiNO₃-PVA sheets and C-30%LiNO₃-PVA anodes and LiCoO₂-C-30%LiNO₃-PVA cathodes placed on either side of the sheets. Using a DC voltage and current source/monitor, good charge/discharge characteristics were obtained after constant-current charging and discharging. A constant-current charge of 5.7 mA cm⁻² was applied at room temperature in air for 10 min, achieving a voltage of 3.6 V. During the constant-current discharge of 57 μA cm⁻², the voltage was 1.4 V at the start of discharge, and a voltage drop of 2.2 V was observed. Thereafter, stable discharge continued until a voltage of 1.1 V was obtained after 20 min. Thus, a low-cost, safe, and effective all-solid-state Li-ion battery for student experiments was realized.

Key words

electrolyte, Li ionic conductor, anode, cathode, charge/discharge

1. Introduction

Among rechargeable batteries, Li-ion batteries currently have the highest energy density and output, resulting in their wide-spread use in various products, such as cellphones, personal computers, small cameras, electric and hybrid vehicles, airplanes, and energy-storage systems. Consequently, research and development for further performance improvements in Li-ion batteries are actively underway. A battery consists of two active materials, namely positive and negative electrodes, which are in contact with an electrolyte, which is usually a liquid.

In Li-ion batteries, the use of flammable nonaqueous organic solvents in the electrolyte, which can cause them to ignite, has been a pressing concern. In addition, battery assembly requires an inert gas atmosphere to prevent reactions with moisture and oxygen. Recently, the development of Li-ion conductors or Li-solid electrolytes, in which Li ions are in a solid state, has been promoted to improve battery safety. In particular, the use of inorganic materials, such as ceramics and glass, has been reported. However, non-oxide systems, such as Li₁₀GeP₂S₁₂ ceramics, which exhibit Li-ion conduction comparable to that of liquid electrolytes, require an inert gas atmosphere for battery assembly because of chemical stability issues (Kamaya et al., 2011). In addition, oxide systems, which have excellent chemical stability, are harder than nonoxide systems and have a high resistance at the junction

interface with the electrode. For example, Li_{6.25}Al_{0.25}La₃Zr₂O₁₂ ceramics, which provide high Li-ion conduction, disintegrate when left in air, and therefore, an inert gas atmosphere is required in the fabrication of Li-ion batteries (Murugan et al., 2007; Avila et al., 2021; Duan et al., 2018). Many other Li ionic conductive ceramics have been reported (Nakayama and Sadaoka, 1993; Yang and Wu, 2022).

Li-containing organic polymers have been extensively investigated as Li-solid electrolytes. Among these, Li-polyvinyl alcohol (PVA) sheets solidified at 60 °C after dissolving Li compounds, such as Li perchlorate (LiClO₄) and Li nitrate (LiNO₃), in PVA aqueous solutions have been reported to exhibit high Li-ion conductivity at room temperature (Chodankar et al., 2015; Gopalakrishnan et al., 2023). PVA is also used as a laundry glue with safe, inexpensive, and easy-handling properties.

This study aims to fabricate an all-solid-state Li-ion battery in air without the need for a glow box or other specific gas environment and to measure its charge/discharge in air during a 3-h experiment. A Li-PVA sheet, which can be easily fabricated, was used as the Li-solid electrolyte. The fabrication of the Li-ion batteries was investigated, and their charge/discharge characteristics were evaluated using a commercial direct-current (DC) voltage and current source/monitor.

2. Experimental

PVA (degree of saponification: 78-82 mol%, average degree of polymerization: 1,500-1,800) and LiNO₃ (99.9 %) were obtained from Fujifilm Wako Pure Chemicals Co. Li cobaltate (LiCoO₂) and acetylene carbon black C were purchased from

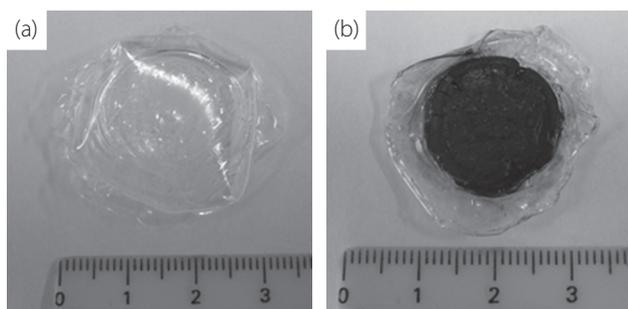


Figure 1: Photographs of (a) the 30%LiNO₃-PVA electrolyte sheet and (b) positive electrode of LiCoO₂ + C + 30%LiNO₃-PVA (black area) formed on a 30%LiNO₃-PVA electrolyte sheet

Sigma-Aldrich Co. In deionized water, a 10 % PVA solution was prepared by dissolving PVA at 80 °C. A 30 % LiNO₃-PVA solution was prepared by mixing 50 mL of 10 % PVA solution with a solution of 2.0 g LiNO₃ dissolved in 10 mL deionized water at room temperature. The solution was placed in a polyethylene Petri dish with an inner diameter of 30 mm, dried, and solidified at 60 °C on a hot plate to produce 30 % LiNO₃-PVA sheets (Figure 1 (a)). The anode was formed by thoroughly mixing 0.1 g of C with 1.0 mL of 30 % LiNO₃-PVA solution in an agate mortar, applying it to one side of the prepared 30 % LiNO₃-PVA sheet using a spatula and fixed by drying at 60 °C. Subsequently, the cathode was formed by thoroughly mixing 0.16 mg of LiCoO₂, 0.1 g of C, and 1.0 mL of 30 % LiNO₃-PVA solution were thoroughly mixed in an agate mortar, applying to the other side of the 30 % LiNO₃-PVA sheet using a spatula and fixed by drying at 60 °C. Photographs of the fabricated battery and charge/discharge characteristic apparatus are shown in Figure 1 (b).

The electrical properties of the prepared LiNO₃-PVA sheets were measured in the frequency range of 100 Hz to 10 MHz using an impedance meter (HP4194A) sandwiched at 30 MPa pressure between stainless-steel measuring fixtures (electrodes). Their ionic conductivity at room temperature was determined by complex impedance analysis. Their DC resistance was measured using a digital multimeter (7355, ADC Co.), and the charging and discharging of the all-solid-state Li-ion batteries with an anode and cathode formed on either side of the LiNO₃-PVA sheets was measured using a DC voltage and current source/monitor (6242, ADC Co.). To measure the charge and discharge characteristics, an Excel sample program (provided free of charge by ADC Co.), which enables measurement control and data capture on a PC via USB, was used.

3. Results and discussion

3.1 Properties of Li-PVA sheets

Li-PVA sheets with water-soluble LiNO₃ (solubility: 45.8 g/100 g H₂O (25 °C)), Li chloride (LiCl; solubility: 67 g/100 g H₂O (0 °C)), Li sulfate (Li₂SO₄ · H₂O; solubility: 26 g/100 g H₂O (0 °C)), Li carbonate (Li₂CO₃, solubility: 1.3 g/100 gH₂O), and Li-

ClO₄ (solubility: 60 g/100 g H₂O (25 °C)) were selected. Li-PVA sheets were prepared with 20, 30, and 40 wt% Li compounds.

Transparent soft sheets were produced using 20, 30, and 40 wt% LiNO₃; however, in sheets made with 40 wt% LiNO₃, surface wetting due to moisture absorption was observed after exposure to air for several days. Transparent sheets were obtained when LiCl was used. However, when exposed to air, these sheets immediately started absorbing moisture, resulting in severe surface wetting. Sheets using Li₂SO₄ were harder than LiNO₃-PVA sheets. Li₂CO₃ has low solubility, resulting in the difficult preparation of the Li₂CO₃-PVA solution. The use of 20 wt% LiClO₄ resulted in a transparent sheet, but it was harder than the LiNO₃-PVA sheet. Meanwhile, the use of 30 and 40 wt% LiClO₄ resulted in partially and completely cloudy sheets, respectively, with LiClO₄ crystals deposited on their surfaces. Therefore, the 30 % LiNO₃-PVA sheet was selected as the electrolyte sheet for the all-solid-state Li-ion battery, as it is flexible and does not absorb moisture when exposed to air, thereby inhibiting surface wetting.

The Nyquist plot of a 0.3-mm-thick 30 % LiNO₃-PVA sheet sandwiched between φ15 mm stainless-steel electrode dices at room temperature is shown in Figure 2. A rising arc (spike) was observed because of the electrode interface resistance between the electrolyte and electrode. The Z' value at the indicated point in the Nyquist plot indicates the bulk resistance (19 Ω) of the electrolyte (ionic conductivity at room temperature: 9.0 × 10⁻⁴ S cm⁻¹).

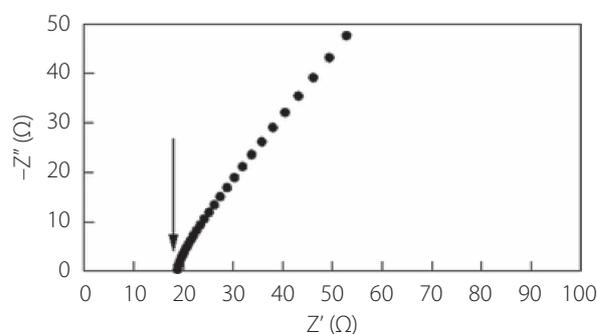


Figure 2: Nyquist plots of the 30%LiNO₃-PVA electrolyte sheet at room temperature

3.2 Charge/discharge characteristics

Figure 3 shows a schematic of the all-solid-state Li-ion battery configuration and device for the charge/discharge measurement. Figure 4 shows a photograph of the electrical measurement holder and equipment used for the charge/discharge characteristics measurements. Figure 5 shows the voltage under a constant-current charge of 5.7 mA cm⁻² immediately followed by a constant-current discharge of 57 μA cm⁻² at room temperature in air. After approximately 10 min of charging, a voltage of 3.6 V is achieved, as shown in Figure 5 (a), indicating successful charging. The results of dis-

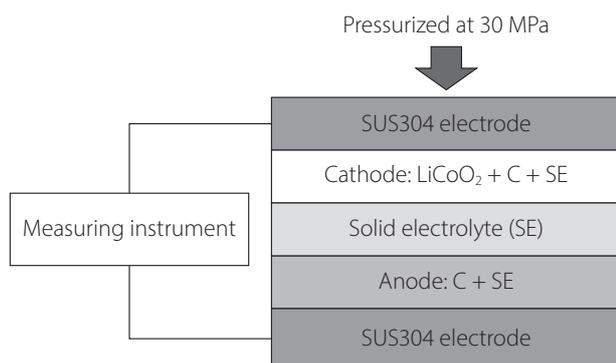


Figure 3: Schematic of the evaluation system for the charging/discharging of the all-solid-state Li-ion battery

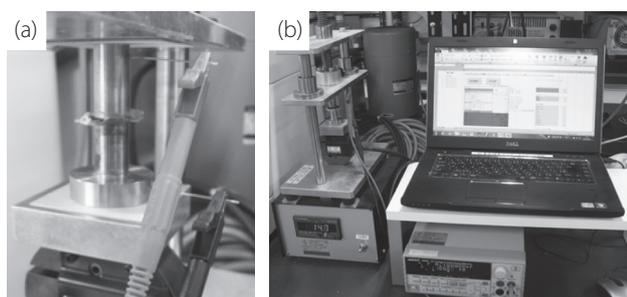


Figure 4: Photographs of the (a) electrical measurement holder and (b) charging/discharging characteristics evaluation system for the all-solid-state Li-ion batteries

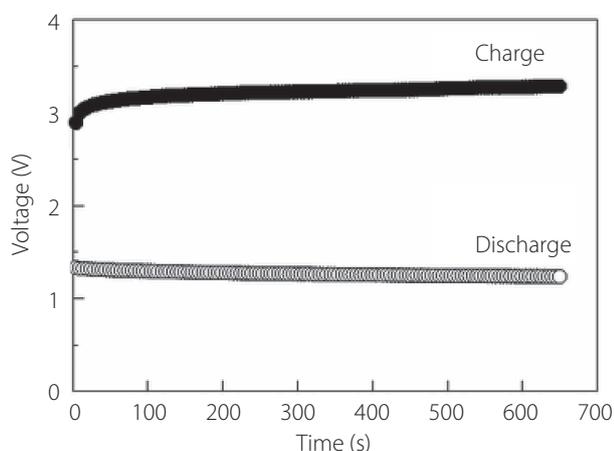


Figure 5: Voltage change when (a) charging at 5.7 mA cm^{-2} and (b) discharging at $57 \mu\text{A cm}^{-2}$ on an integrated-type battery of electrode/electrolyte/electrode sheet

charging immediately after charging are shown in Figure 5 (b). The voltage was 1.4 V at the start of the discharge, and a voltage drop of 2.2 V was observed. However, the discharge continued stably thereafter, resulting in a voltage of 1.1 V after 20 min. The expected voltage drop is 0.1 V based on the DC resistance value (1.0 k Ω) of the all-solid-state Li-ion battery used in the measurement. Therefore, the voltage drop of 2.2 V, from 3.6 V at the end of charging to 1.4 V at the start of

discharging, is approximately 20 times the expected voltage drop. This result is attributed to the increase in DC resistance due to the products at the electrolyte/electrode interface during charging or the rapid self-discharging that occurred immediately after charging. However, the explanation for this phenomenon remains unclear.

3.3 Application as instructional material

Many electrochemical topics can be used as instructional material in inorganic chemistry teaching laboratories. Examples of such experiments include the electrolysis of water, the determination of the Faraday constant from the electrolysis of a copper sulfate solution, the Volta and Daniel cells, or the observation of color changes in the positive electrode discharge reduction reaction of nickel-metal hydride batteries (Shiomi and Nakayama, 2024), among others. Nickel-metal hydride batteries are practical, and the teaching material content is designed to make a visual impact. However, until now, we have not been able to develop teaching materials on battery charging and discharging.

We propose the content reported in this study be applied as teaching material on battery charging and discharging (secondary batteries) in laboratories. In Sections 3.1 and 3.2, we report the fabrication of batteries with integrated electrolytes and electrodes. However, to save time, we also fabricated individual sheets for the anode, electrolyte, and cathode (as shown in Figure 6), each stacked (as shown in Figure 3) and sandwiched between two stainless steel measuring dies ($\phi 15 \text{ mm}$, with $\phi 1 \text{ mm}$ stainless steel lead wires). To join them, a pressure of 30 MPa was applied from above and below using a vice press (MP-001, AS ONE Co.). The set current values for measuring the charge and discharge characteristics differ owing to the differences in the fabrication of the anode, cathode, and electrolyte sheets and the sandwiching between the upper and lower dies. Figure 6 shows an example of the charge and discharge characteristics of a pressed-type battery (DC resistance 1.5 k Ω). Charging was performed at 5.7 mA cm^{-2} and discharging at $57 \mu\text{A cm}^{-2}$ for 10 min.

4. Conclusion

We studied experimental materials that enable students to fabricate their own all-solid-state Li-ion batteries, which have the highest energy density and output among secondary batteries and can be charged and discharged by the transfer of Li ions between the cathode and anode in air. We measured the charge/discharge characteristics of the battery. We focused on all-solid-state Li-ion batteries because of their superior safety. In particular, Li-PVA sheets were used as candidates for the Li electrolyte because of their safety and ease of fabrication. Based on the flexibility of the sheet and stability of the Li compound in PVA, we determined the 30%LiNO₃-PVA sheet to be the optimal Li electrolyte. This sheet was

(1) 10 % PVA solution
Dissolving 10 g of PVA in 90 mL of deionized water at 80 °C

(2) 30 % LiNO₃-PVA solution
Mixing 50 mL of (1) + solution of 2.0 g LiNO₃ dissolved in 10 mL deionized water at RT

※ (2) should be prepared before the experiment.

(3) Electrolyte sheet / 30 % LiNO₃-PVA
1 mL of (2) is placed in a PE dish and solidified on a hot plate

(4) Negative electrode sheet / C + 30 % LiNO₃-PVA
After mixing 0.1 g of C with 1.0 mL of (2) in an agate mortar, placed in a PE dish and solidified on a hot plate

(5) Positive electrode sheet / LiCoO₂ + C + 30 % LiNO₃-PVA
After mixing 0.16 mg of LiCoO₂, 0.1 g of C, and 1.0 mL of (2) in an agate mortar, placed in a PE dish and solidified on a hot plate

※ The inner diameter of the PE (polyethylene) dish is 30 mm.
The surface temperature of the hot plate is set at 80 °C.
(The temperature inside the PE dish is 60 °C.)
(3), (4), and (5) are performed simultaneously and take approximately 1-2 hours.

Figure 6: Preparation procedure of each sheet of 30 % LiNO₃-PVA electrolyte, C-30%LiNO₃-PVA negative electrode, and LiCoO₂-C-30% LiNO₃-PVA positive electrode

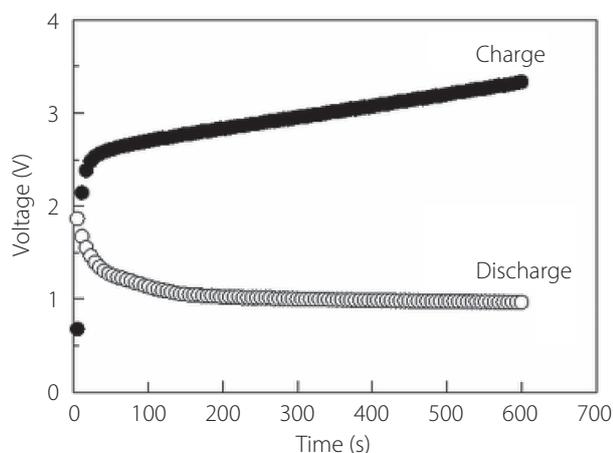


Figure 7: Voltage change when (a) charging at 5.7 mA cm⁻² and (b) discharging at 57 μA cm⁻² on a pressed-type battery of electrode sheet + electrolyte sheet + electrode sheet

used to form a C-30%LiNO₃-PVA anode and LiCoO₂-C-30% LiNO₃-PVA cathode on each side of the sheet to form an all-solid-state Li-ion battery. Using a commercial DC voltage and current source/monitor, constant-current charging and discharging were tested. The results show that the material exhibits good charge/discharge characteristics. In future works, the mechanism for the charging/discharging behavior of the material will be elucidated.

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References

- Avila, V., Yoon, B., Ghose, S., Raj, R., and Jesus L. M. (2021). Phase evolution during reactive flash sintering of Li_{6.25}Al_{0.25}La₃Zr₂O₁₂ starting from a chemically prepared powder. *Journal of the European Ceramic Society*, Vol. 41, 4552-4557.
- Chodankar, N. R., Dubal, D. P., Lokhande, A. C., and Lokhande, C. D. (2015), Ionically conducting PVA-LiClO₄ gel electrolyte for high performance flexible solid state supercapacitors. *Journal of Colloid and Interface Science*, Vol. 460, 370-376.
- Duan, H., Zheng, H., Zhou, Y., Xu, B., and Liu H. (2018). Stability of garnet-type Li ion conductors: An overview. *Solid State Ionics*, Vol. 318, 45-53.
- Gopalakrishnan, N., Mohamed M., Ali, N., Karthikeyan, S., Venkatesh, K., Jenova, I., Madeswaran, S., Kumar, R., Nayak, P. K., and Boopathi, D. (2023). Facile synthesis of PVA-formamide based solid state electrolyte membrane: A combined experimental and computational studies. *Solid State Ionics*, Vol. 402, 116378.
- Kamaya, N., Homma, K., Yamakawa, Y., Hirayama, M., Kanno, R., M. Yonemura, M., Kamiyama, T., Kato, Y., Hama, S., Kawamoto, K., and Mitsui, A. (2011). A lithium superionic conductor. *Nature Materials*, Vol. 10, 649-650.
- Murugan, R., Thangadurai, V., and Weppner, W. (2007). Fast lithium ion conduction in garnet-type Li₇La₃Zr₂O₁₂. *Angewandte Chemie International Edition*, Vol. 46, 7778-7781.
- Nakayama, S. and Sadaoka Y. (1993). Ionic conductivity of ceramics prepared by sintering of M₂O-Ln₂O₃-2SiO₂ mixtures (M = Li, Na, K, Rb, Cs; Ln = La, Nd, Sm, Gd, Dy, Y, Ho, Er, Yb). *Journal of Materials Chemistry*, Vol. 3, 1251-1257.
- Shiomi, M. and Nakayama, S. (2024). Observation experiment of color change on discharge reduction reaction of cathode nickel oxyhydroxide. *Journal of JSEE*, Vol. 72, No. 4 in press. (in Japanese)
- Yang, H. and Wu, N. (2022). Ionic conductivity and ion transport mechanisms of solid-state lithium-ion battery electrolytes: A review. *Energy Science & Engineering*, Vol. 10, 1643-1671.

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