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Numerical Simulation of Thin-Film-All-Solid-State-Lithium Battery

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Abstract

This paper reports the simulated results on charge/discharge curves of thin-film-all-solid-state-Li battery. One-coordinate system in the direction normal to the electrode/electrolyte interface is assumed for the simplicity. The cathode and anode are $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) and Li metal, respectively. The solid-state electrolyte is assumed to be glass electrolyte such as lithium phosphorous oxynitride (LiPON). The chemical diffusion and ionic conduction are only considered for the mass transport mechanisms of Li in NCM and Li ions in the electrolyte, respectively. The potential distribution in the electrolyte between cathode and anode is calculated by the Poisson equation. Eventually, the simulated discharge curves well fit the experimental results at 0.2 C, especially when the Li composition of NCM is smaller than 0.7. On the other hand, the experimental discharge curves exhibit much larger overpotentials than the simulated results. This means that our simulation still lacks in taking into account certain critical overpotential terms, which is suspected to be involved with the space charge layer.

1. Introduction

All-solid-state-Li batteries using oxide-based-solid-state electrolytes have attracted much attention due to the high safety and high energy density. Still, the charge/discharge performance at higher C rates must be improved for practical applications. Hence, it is necessary to understand the rate-limiting processes involved in charge-transfer reactions at electrode active material/solid-state electrolyte interfaces where the space charge layer develops in the vicinity. In this study, we fabricate thin-film-all-solid-state-Li batteries using glass electrolytes and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathode to compare experimental and simulated results.

2. Experimental

An NCM film was deposited on the Pt/Ti/Si substrate by a pulsed laser deposition (PLD) method. LPO, LiPON, and Li films were deposited by RF-magnetron sputtering and vacuum evaporation deposition on the NCM surface to fabricate a thin-film-all-solid-state-Li battery with the Li/LiPON/LPO/NCM structure. OCV and charge/discharge curves were measured by CCCV and GITT measurements, respectively. The charge transfer resistance (R_{ct}) was measured by electrochemical impedance spectroscopy (EIS).

3. Simulation Scheme

One-dimensional-coordinate system (x) was considered with an assumption that NCM and Li were the cathode and anode, respectively, for the simulation. The Fick's second law was applied to analyze the Li diffusion in NCM, but the chemical diffusion coefficient of Li ($\widetilde{D}_{Li}$) was assumed to vary depending on the composition of NCM (y of $Li_yNi_{1/3}Co_{1/3}Mn_{1/3}O_2$). $\widetilde{D}_{Li}$ increased from 8.8×10^{-11} cm^2 s^{-1} to 4.1×10^{-10} cm^2 s^{-1} with increasing the y from 0.4 to 1.0 in the simulation [1]. Only the Li^+ conduction was considered in the solid-state electrolyte. The electric potential distribution in the solid-state electrolyte was calculated by the Poisson equation. A ninth-order function was used to approximate the dependency of experimentally obtained Rct values on y. Substituting this regression function into the Butler-Volmer equation enables the estimation of the activation overpotential for the solid-state electrolyte/NCM interface at a giving y. Eventually, the overall overpotential is calculated as the sum of the activation overpotential, ohmic loss, and concen-

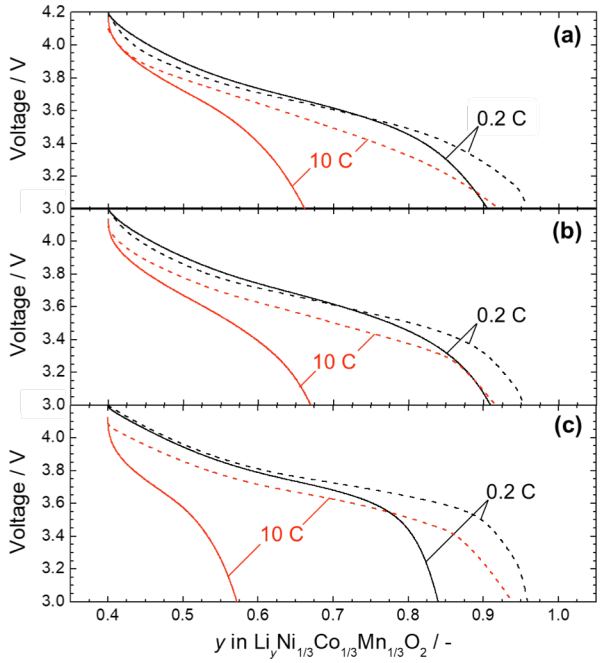

Figure 1. Experimental (solid line) and simulated (dashed line) discharge curves with (a) 130 nm-, (b) 260 nm-, (c) 390nm-thick-NCM-cathode films.

tration overpotential in NCM. The discharge voltage was calculated by subtracting the overall overpotential from the OCV value.

3. Results & Discussion

Figure 1 shows the experimental (solid line) and simulated (dashed line) results for discharge curves at 0.2 C and 10 C. In the simulated results, the overpotential is much smaller than that in the experimental results, especially when the discharge rate is 10 C. This means that our simulation does not yet take into account some critical overpotential terms. We will present simulated results taking into consideration the effect of Li^+ diffusion in solid-state electrolyte.

4. Conclusions

The simulated discharge curves fit the experimental results at 0.2 C, especially when the Li composition of NCM is smaller than 0.7. On the other hand, the experimental discharge curves exhibit much larger overpotential than the simulated results. This means that our simulation still lacks in taking into account certain critical overpotential terms, which is suspected to be involved with the space charge layer.

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References

[1] R. Amin et al., *J. Electrochem. Soc.*, **163** (2016) A1512.