Surface-supporting method of micropad deposition onto LiCoO$_2$ epitaxial thin films to improve high C-rate performance

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High-speed rechargeable Li ion batteries are in strong demand. Two methods have been reported to improve the high-speed rechargeability of electrodes: reducing particle size and introducing a surface support. However, the effectiveness of the latter could not be directly compared among reports due to particle size differences from study to study. Our previous report revealed that Li$^+$ motion under high-speed charge-discharge conditions is accelerated around a surface-supporting material, an electrode, and an electrolyte interface. In this study, we prepared epitaxial LiCoO$_2$ thin films with micropads of various kinds of materials and evaluated the high-speed rechargeability of each.

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1. Introduction

Li ion batteries (LIBs) have been utilized in electric devices because of their high working voltages and large specific capacities. However, consumer needs call for more convenient LIBs having larger capacities, longer cycle life and, especially, faster charging. Commercialized LIBs work under the restriction of charge-discharge current to avoid capacity degradation originating from overvoltage and side reactions under the conditions of fast electrochemical reactions. To improve high-speed chargeability, two tactics have been reported: reducing particle size and introducing a surface support. The former helps to shorten the inter-diffusion length of Li$^+$ in active materials. The latter decreases the interfacial resistance of Li$^+$, resulting in an improvement of high-speed chargeability using Al$_2$O$_3$ or BaTiO$_3$ as a surface-supporting material. Unfortunately, these reports cannot be directly compared to each other due to the different particle sizes from study to study, as particle size affects high-speed rechargeability. In addition, the interface between surface-supporting materials and electrodes with bulk particles is difficult to discuss. Therefore, we prepared epitaxial thin films in order to investigate the effects of the introduction of surface-supporting materials.

We have already reported a mechanism for improving high-speed chargeability by preparing three kinds of epitaxial thin films: noncoated, fully coated, and partially coated BaTiO$_3$ onto LiCoO$_2$ films. The Li$^+$ motion could be accelerated by electric field concentrations around the interfaces between a surface-supporting material, an electrode, and an electrolyte (triplets-phase interfaces, TPI). Moreover, BaTiO$_3$ micropads with dimensions of $\sim$100 $\mu$m square deposited LiCoO$_2$ epitaxial thin film also improved high-speed chargeability, indicating that we can investigate the dependence of supporting materials by preparing micropads of various kinds of materials deposited on LiCoO$_2$ epitaxial thin films.

In this study, we focused on Al$_2$O$_3$ and BaTiO$_3$ as candidate supporting materials in light of previous reports. In addition, we utilized CeO$_2$, TiO$_2$, and SrTiO$_3$ as supporting materials because epitaxial growths on SrTiO$_3$ substrates have been reported. After preparing and evaluating micropads of supporting materials deposited on LiCoO$_2$ epitaxial thin films, we discussed the dependence of supporting materials.

2. Experimental procedure

First, LiCoO$_2$/SrRuO$_3$/(100)SrTiO$_3$ thin films were pre-
pared via pulsed laser deposition using a fourth harmonic wave of a Nd:YAG laser (266 nm wavelength). SrRuO$_3$ and LiCoO$_2$ layers were a bottom current collector and a cathode, respectively. A metal mask with 100 $\times$ 100 $\mu$m throughput holes was introduced onto LiCoO$_2$/SrRuO$_3$/SrTiO$_3$ films, and surface-supporting materials (Al$_2$O$_3$, CeO$_2$, TiO$_2$, SrTiO$_3$, and BaTiO$_3$) were deposited under the following conditions: oxygen partial pressure of 20 mTorr, substrate temperature of 580 °C, and deposition time of 1 h. Out-of-plane XRD measurements were carried out with Smartlab (Rigaku). The backside of the prepared thin film was sputter-coated with Au to make an electric contact between the SrRuO$_3$ layer and an outside current collector. The 2032-type coincell was assembled in an Ar-filled glove box using a prepared thin film as a cathode, Li metal as an anode, and 1 mol/L LiPF$_6$ in ethylene carbonate: diethyl carbonate as an electrolyte. Charge-discharge measurements were carried out with a voltage window of 3.3–4.2 V vs. Li$^+$/Li using the 580 Battery Test System (TOYO Corporation). Charge-discharge currents were shown by a C-rate definition calculated using the theoretical discharge capacity of LiCoO$_2$ (160 mAh/g) and the active material amount (the LiCoO$_2$-deposited area $\times$ the film thickness).

3. Results and discussion

Figure 1 shows the out-of-plane XRD patterns of the prepared thin films. The result for the noncoated LiCoO$_2$ epitaxial thin film (Bare) indicated that LiCoO$_2$(104) and pseudo-cubic SrRuO$_3$(001)$_c$ were epitaxially grown on SrTiO$_3$(001). The (00l) related peaks of BaTiO$_3$ and SrTiO$_3$ are not distinguished in the BaTiO$_3$- or SrTiO$_3$-deposited ones because these peaks overlap with that of the substrate. We have already reported that 3 nm of BaTiO$_3$ was crystallized on a LiCoO$_2$/SrRuO$_3$/SrTiO$_3$(100) film, indicating that BaTiO$_3$ and SrTiO$_3$ would be epitaxially grown on. The XRD result of CeO$_2$-deposited LiCoO$_2$ film indicates that fluorite CeO$_2$(100) is grown along the out-of-plane direction of the substrate. On the other hand, the TiO$_2$-deposited one showed impurity phases at 18.9, 43.5, and 44.4° despite the fact that anatase TiO$_2$(100) can be grown on SrTiO$_3$(100) substrate. TiO$_2$ is known as an anode material that reacts with the cathode material of LiCoO$_2$ due to the difference in chemical potentials, resulting in the decomposition of LiCoO$_2$. In the case of Al$_2$O$_3$ deposited on SrTiO$_3$ single crystal, $\gamma$-Al$_2$O$_3$ should be crystallized on$^{21}$ However, we could see only a weak impurity diffraction observed at 30.9°. These results indicate that LiCoO$_2$ would be decomposed by introducing Al$_2$O$_3$ or TiO$_2$.

After assembling coincells using the prepared thin films, we performed charge–discharge measurements while increasing C-rates stepwise. The discharge capacities of the prepared samples are shown in Fig. 2. Micropads deposited on LiCoO$_2$ films showed lower discharge capacity at 1 C than that of Bare, indicating that LiCoO$_2$ under micropads would be inactive in charge–discharge reactions because the long inner-diffusion length prohibits electrochemical reactions. As the C-rate was gradually increased, BaTiO$_3$- or TiO$_2$-deposited LiCoO$_2$ emitted over 20 mAh/g at 50 C even when these worked at 100 C, whereas Bare could not work as a cathode at 50 C. Charge–discharge measurements at 1 C were carried out 5 times next to that at 100 C.

Figure 3 shows the fifth cycle of that at 1 C of micropad-deposited samples. The charge curves of BaTiO$_3$-, SrTiO$_3$-, and TiO$_2$-deposited LiCoO$_2$ films clearly showed a voltage plateau at 3.9 V vs. Li$^+$/Li. On the other hand, the plateau of CeO$_2$-deposited LiCoO$_2$ film was shifted to the
upper side, suggesting that the contribution of an overvoltage would increase. The Al2O3-deposited LiCoO2 film showed not a voltage plateau but a voltage slope. Results of discharge curves with SrTiO3-, BaTiO3-, TiO2-, and Al2O3-deposited LiCoO2 films showed voltage plateaus. However, the CeO2-deposited LiCoO2 film showed a voltage slope. Although the discharge capacity at 1 C of the micropad-deposited samples was 60–80 mAh/g (45–60 % of that of Bare at 1 C), the charge-discharge curves are modulated by the surface support depending on the material, indicating that supporting materials affect intercalation/de-intercalation reactions via the whole range of electrochemically active LiCoO2.

The standardized discharge capacities at each C-rate to that at 1 C are shown in Fig. 4. The discharge capacity of Bare decreased linearly as the C-rate increased, and finally Bare was unable to work at 50 C. On the other hand, the surface-supported LiCoO2 film showed a nonlinear trend of C-rate performance despite the case of CeO2 deposition, indicating the enhancement of Li⁺ motion between the cathode and electrolyte interfaces around triple-phase interfaces.13)-15) To improve the high C-rate performance, BaTiO3 and TiO2 are candidate supporting materials. Figure 5 shows the reaction voltage at each C-rate estimated from the voltage at which the differential between capacity and voltage (dQ/dV curve) is highest. Each reaction voltage of the prepared samples as a function of the C-rate had a linear relationship, suggesting that enhancement at triple-phase interfaces can be discussed using reaction voltages. Enhancements of C-rate performance by introducing triple-phase interfaces depend heavily on the supporting material; the total cell resistances calculated from the overvoltage are 570 (BaTiO3), 910 (SrTiO3), 470 (TiO2), 1300 (Al2O3), and 3100 Ω (CeO2). Although TiO2 deposition decomposes a portion of LiCoO2 due to the reaction between TiO2 and LiCoO2, TiO2 is a candidate supporting material for improving high C-rate performance. In this study, BaTiO3 is the most suitable candidate for the enhancement of high C-rate performance because BaTiO3 does not react with LiCoO2.

4. Conclusions

In this study, we prepared micropads of Al2O3-, CeO2-, TiO2-, SrTiO3-, and BaTiO3-deposited LiCoO2 epitaxial thin films and evaluated the high-speed rechargeability. In the case of Al2O3 or TiO2 deposition, a part of LiCoO2 decomposed due to the reaction between supporting materials and LiCoO2. The charge-discharge measurement as the C-rate increased stepwise revealed that high C-rate performance was enhanced by introducing surface-supporting materials without the case of CeO2. The charge–discharge curves were affected by the micropad deposition depending on the supporting material. Although TiO2 decomposed a portion of LiCoO2, the lowest total resistance of the electrochemical reaction during a charge was observed. BaTiO3 is the most suitable candidate for the enhancement of high C-rate performance without any decomposition of LiCoO2.

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