

Preparation of Carbon-coated Ramsdellite $\text{Li}_2\text{Ti}_3\text{O}_7$ and Their Charge/discharge Properties for Lithium-ion Batteries

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Introduction

Lithium-ion batteries (LIBs) are now seeing widespread use in higher-power and/or larger-size applications. The electrochemical reactions need to be maintained with high reversibility over 1000 or more cycles for 10-15 years or more if LIBs are to be used in applications such as electric-powered vehicles and stationary battery energy storage systems. To improve the cyclability and durability of LIBs, irreversible reactions, including the reductive/oxidative decomposition of electrolyte solution and a subsequent formation/growth of surface films, need to be suppressed over repeated charge/discharge cycles. The use of negative electrodes with high working potentials over 1.0 V (vs. Li/Li^+) is one of the ways for solving these issues because the reductive decomposition of EC+DMC-based electrolyte solution can be avoided in the high potential region.

Spinel $\text{Li}_{4/3}\text{Ti}_5/3\text{O}_4$ shows highly reversible charge/discharge reactions at an extremely constant working potential of about 1.56 V. However, the theoretical capacity of $\text{Li}_{4/3}\text{Ti}_5/3\text{O}_4$ is only 175 mAh g^{-1} . On the other hand, ramsdellite $\text{Li}_2\text{Ti}_3\text{O}_7$ has a theoretical capacity as high as 298 mAh g^{-1} , while the practical capacity was limited to be about 150 mAh g^{-1} [1].

In this study, we prepared carbon-coated $\text{Li}_2\text{Ti}_3\text{O}_7$ to improve the charge/discharge performance.

Experimental

A mixture of Li_2CO_3 and anatase TiO_2 (1.05:3.00, by weight) was quenched after firing in air at 1050°C for 72 h to obtain ramsdellite $\text{Li}_2\text{Ti}_3\text{O}_7$. The $\text{Li}_2\text{Ti}_3\text{O}_7$ powder was mixed with petroleum (1:0.02 and 1:0.05, by weight), and heated in Ar at 1000°C for 5 h. Composite electrodes were prepared from a slurry containing the resultant powder, Ketjenblack®, and polyvinylidene fluoride (PVdF) (8:1:1, by weight). Charge and discharge measurements were conducted at a C/6 rate between 1.2 and 2.5 V using a two-electrode cell. Li foil and 1 mol dm^{-3} $\text{LiPF}_6/\text{EC}+\text{DEC}$ (1:1, by volume) were used as a counter electrode and electrolyte, respectively. The carbon content in the carbon-coated powder was investigated by differential thermal analysis combined with thermogravimetry (TG-DTA).

Results and discussion

The carbon content in the carbon-coated powder was evaluated to be 2.42 and 4.56 wt%. Figure 1 shows the XRD patterns of the resultant powder before and after carbon-coating. The pattern of as-prepared powder indicates that single-phase ramsdellite $\text{Li}_2\text{Ti}_3\text{O}_7$ was obtained. However, new peaks at about 18.5° and 44° appeared after carbon-coating, which indicates that Li_2TiO_3 should be formed as an impurity. These peaks became apparent with an increase in the carbon content. TEM observation suggests that the surface of each powder should be covered with carbonaceous materials after carbon-coating. The thickness of the carbon layer on $\text{Li}_2\text{Ti}_3\text{O}_7$ was estimated to be 30-150 and 80-200 nm for the carbon-coated powder containing 2.42 and 4.56 wt%

carbon, respectively.

Figure 2 shows charge and discharge curves of carbon-coated powder containing 4.56 wt% carbon. The voltage plateau appeared at around 1.3 and 2.2 V after carbon-coating and the charge/discharge capacities at these voltages increased with an increase in the carbon content. These reversible capacities should be attributed to the insertion/extraction reactions of Li^+ at Li_2TiO_3 and ramsdellite TiO_2 which were detected in carbon-coated electrodes. The total reversible capacity was evaluated to be about 179 mAh g^{-1} for the 1st cycle, which is higher than those for as-prepared $\text{Li}_2\text{Ti}_3\text{O}_7$ (ca. 157 mAh g^{-1}) and carbon-coated powder containing 2.42 wt% carbon (ca. 170 mAh g^{-1}). The rate performance will be shown in our poster presentation.

Reference

[1] R. K. B. Gover *et al.*, *J. Electrochem. Soc.*, **146**, 4348 (1999).

Acknowledgment

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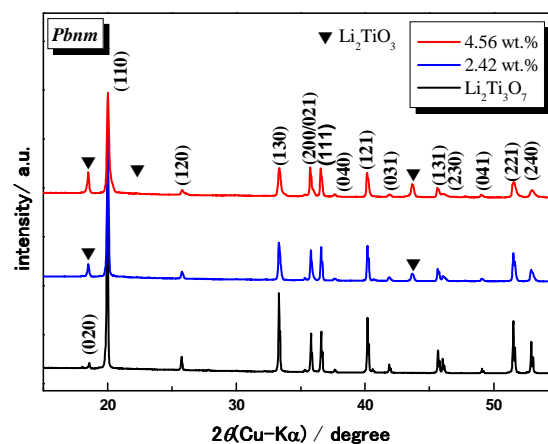


Fig.1 XRD patterns of the $\text{Li}_2\text{Ti}_3\text{O}_7$ powder before and after carbon-coating.

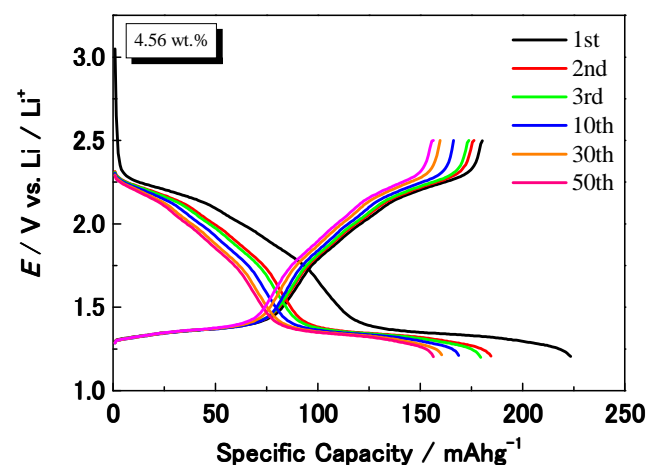


Fig.2 Charge and discharge curves of carbon-coated $\text{Li}_2\text{Ti}_3\text{O}_7$ powder containing 4.56 wt% carbon.