

学位論文の要旨

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学位論文題目	SYNTHESIS AND ELECTROCHEMICAL ANALYSIS OF COMPOSITE ELECTRODES FOR DRY POLYMER LITHIUM ION BATTERY (英訳又は和訳 ドライポリマーリチウムイオン二次電池用複合電極の開発)					
<p>In this study, we have investigated the composite electrode for Solid Lithium Polymer Batteries (SLPBs). The report is divided in to two parts; Part1 is described the interfacial resistance between LiFePO₄/PEO-LiTFSI composite electrode and PEO-LiTFSI electrolyte. Part2 is mentioned to Graphite/PEO-LiTFSI composite electrode for SLPBs, and Si/carbon composite for liquid-type cells.</p> <p>1.1. Enhancement of electrochemical performance of lithium dry polymer battery with LiFePO₄/carbon composite cathode Interfacial resistances and the activation energies have been measured by AC impedance technique. Enhanced low-temperature performance of LiFePO₄ was achieved by modifying the interface between LiFePO₄ and polymer electrolyte. The molecular weight of the polymer and the salt concentration as the Li/O ratio were optimized at 3×10⁵ and 1/10, respectively. The reversible capacity of the laminate cell was 140 mAh g⁻¹ (C/20) and 110 mAh g⁻¹ (C/2) at 40°C, which is comparable to the performance in the liquid electrolyte system.</p> <p>1.2. Study on All Solid Lithium Polymer Batteries with the LiFePO₄/C Cathode The interfacial resistance between the PEO-Li(CF₃SO₂)₂N electrolyte and the Li_xFePO₄ cathode was examined as function of the content of Li(CF₃SO₂)₂N in PEO and x in Li_xFePO₄. The charge transfer resistance increased with increasing x. The activation energies were affected by the conductivity of polymer electrolyte. On the other hand, the molecular weight of PEO leads no significant change. These results suggest that the charge transfer resistance is dominated by the SEI near the boundary between polymer and LiFePO₄ particles.</p> <p>1.3. Interfacial properties between LiFePO₄ and poly(ethylene oxide)-Li(CF₃SO₂)₂N polymer electrolyte Four types of resistance, R0, R1, R2 and R3 were proposed according to analysis of the cell impedance using an equivalent circuit. The sum of R0 and R1 in the high frequency range is consistent with the resistance of the PEO electrolyte. R2 in the middle frequency range is related to lithium ion transport to an active point for charge transfer inside the composite electrode, and R3 in the low frequency range is considered to be the charge transfer resistance.</p>						

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The activation energy for R2 was affected by the thickness and composition of the electrode, whereas that for R3 was not.

2.1. Surface-modified meso-carbon micro-beads anode for dry polymer lithium-ion batteries

A high-anode performance for dry polymer lithium-ion batteries was obtained in the surface-modified meso-carbon micro-beads (MCMB). MCMB and polyvinylchloride (PVC) mixture was heated at 700 °C for 6 h under inert atmosphere. By this treatment, the surface of MCMB is covered with low-crystalline carbon material derived from PVC pyrolysis. The surface-modified MCMB electrode applied to dry polymer electrolytes shows a reversible capacity of 300 mAh g⁻¹, which is comparable to those obtained in the liquid electrolyte systems.

2.2. Morphology-stable silicon-based composite for Li-intercalation

Combination of high energy mechanical milling (HEMM) and twice of thermal pyrolysis reactions may provide a novel design for producing the Si/disordered carbon composite, in which multiphase Si-C cores are homogeneously distributed within the pyrolyzed carbonaceous matrix. The composite offers a large reversible capacity at ca. 900 mA h g⁻¹ within 40 cycles and a relatively high initial coulombic efficiency at ca. 80%. This research reveals that both the pyrolysis reaction and the HEMM give the important contribution to the significantly improved morphology stability. The electrochemical properties of the Si/disordered carbon composite are superior to those of Si-based hosts such as SiMg₂, Si₂Ni and SiO_{1.1}. Moreover, the thermal stability of the Si/disordered carbon composite under lithiation has been investigated to compare with that of the commercial graphite.

2.3. Electrochemical studies of the Si-based composites with large capacity and good cycling stability as anode materials for rechargeable lithium ion batteries

The Si-C and Si-M-C (C, the disordered carbon) composites prepared from pyrolysis reaction and HEMM process have a significant enhancement in the electrochemical cycling stability over pure silicon. The introduction of the hard co-milling components (M, such as TiB₂ and TiN) in the Si-C composite before pyrolysis reaction brings an improvement in the charging rate and cycling performance, but it leads to a slight loss in the reversible capacity. The full cell with the composite anodes and the LiCo_{0.2}Ni_{0.8}O₂ cathode was fabricated to show large anode capacity over 600 mAh g⁻¹ within a potential range of 2.3-3.9V that might result in a high energy density. The Si-based composites appear to be the promising anode candidates for Li-ion batteries.