



Factors determining the packing-limitation of active materials in the composite electrode of lithium-ion batteries



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HIGHLIGHTS

- We discussed the packing-limitation in LIBs using the highly dense electrode.
- Rate-performance of LIBs depending on the electrode porosity was investigated.
- We highlight the Li⁺ transportation to the deepest part in the electrode.

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ABSTRACT

The factors limiting the capacity of highly dense electrodes are elucidated by using composite electrodes for lithium-ion batteries, which consist of active materials LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM), conductive additives and binders. Electrochemical tests of such 100- μ m-thick electrodes in 1 M LiPF₆ electrolyte indicate that a highly dense electrode (with 18% porosity) shows a capacity density significantly lower than the other sparse electrodes on 1C charging/discharging. Detailed analysis using position sensitive in situ X-ray diffraction indicates that, unlike the other sparse electrodes, NCM on the current-collector side barely functions for this dense electrode, due to the poor accessibility of Li⁺ to the inner part of the electrode. Interestingly, 2 M and 0.3 M electrolytes promote the discharge and charge reactions, respectively, over the entire area of the electrode, although they exhibit lower conductivity than the 1 M electrolyte, which indicates the importance of the initial amount of Li⁺ in the electrolyte impregnated in the electrode pores. Thus, for a high-energy-density cell, the initial amount of Li⁺ and the Li⁺ transport significantly affect the rate capability, which governs the practical capacity of the cell under constant-current operation.

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1. Introduction

The development of lithium-ion batteries (LIBs) with high-energy-density and a long cycle life will allow such batteries to be used in large-scale energy storage systems, causing a global paradigm shift in energy supply and usage [1,2]. Unmistakably, this paradigm shift has become a strong driving force in the recent commercialization of electric and hybrid electric vehicles as eco-friendly transportation methods [3,4]. Although the performance of the LIBs such as the capacity [5–7], rate capability [8] and

durability [9] has been investigated in numerous previous studies, effective designing method to fulfill the performance using given materials need to be further developed [10–14] due to the LIBs' complex structure, which consists of several components including composite electrodes (with active materials, conductive additives and binders), separators, binders, electrolytes and casings. The optimization of composition and microstructure of the composite electrodes is mandatory for designing LIBs particularly with a high specific energy (energy per weight) and a high energy density (energy per volume).

A simple solution to enhance the energy density is to increase the amount of active materials in the electrode in a fix volume, however, this way ends up in decrease of practical electrochemical capacity at high rates (insufficient rate capability), due to the

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limited utilization of the active material. The dense limit of the electrode density where the capacity density (capacity per volume, mAh cm^{-3}) reaches the maximum is hereafter referred to as “packing-limitation” in this study. With increasing the amount of the active materials, decreasing the pore volume in the composite electrode is inevitable and can influence the Li^+ transport, since the electrolyte impregnated in the pores of the electrode functions as Li^+ pathways between the active material and the outer bulk electrolyte. Actually, the Li^+ transport particularly on the current-collector side: i.e., in the deepest part of the electrode, has been a significant issue in the highly dense composite electrodes [15–18]. Recently we have established an analytical method that directly capture the inhomogeneous reaction process of a thick electrode (150 μm) using in situ energy-scanning confocal X-ray diffraction (ES-XRD) analysis [19]. These studies motivate us to investigate how the Li^+ concentration in the electrolyte impregnated in the pores, especially that in the deepest part of the composite electrode, influences the electrochemical performance and how the packing-limitation is determined.

In this study, we first report how increasing the composite electrode density affects the spatial homogeneity of the electrochemical reaction and the capacity density on constant-current discharging. The density of the composite electrode as a macroscopic measure of packing was varied by controlling the amount of active material $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) in 100- μm -thick composite electrodes, and the behavior of two electrodes near the packing-limitation were detailed by the position sensitive in situ ES-XRD analysis. The packing-limitation of the active materials is discussed on the basis of new insight into the effect of the Li^+ concentration of the electrolyte impregnated in the pores, where these Li^+ were localized away from the overall electrolyte.

2. Experimental

2.1. Sample preparation

NCM (Toda Kogyo Corp.) with an average secondary particle size of 8.9 μm was used as the active material for the cathode. NCM, acetylene black (conductive additive) and polyvinylidene fluoride (binder), which were dispersed in *N*-methyl-2-pyrrolidone, were mixed in a weight ratio of 90:5:5 to yield black slurry. This slurry was cast onto aluminum foil as a current-collector using a doctor blade (Yasuda Seiki Seisakusho, Ltd.) and subsequently dried at 80 $^{\circ}\text{C}$ for 24 h. The density of the composite electrodes was adjusted by controlling the initial amount of slurry cast onto the current-collector and the compressive force used in the secondary pressing process. Finally, four types of 100- μm -thick electrodes were prepared with densities of 2.17, 2.44, 2.96 and 3.36 g cm^{-3} based on the apparent electrode volumes. The density control for this electrode composition is substantially reflected in the amount of active materials in the electrode, as shown in Table 1. The electrode area is 25 mm (W) \times 15 mm (D).

Aluminum pouch-type three-electrode cells consisted of the composite electrode as a working electrode and lithium foils as a counter and reference electrodes and were fabricated in an Ar-

atmosphere glove box. Aluminum and nickel tabs were used as the current-collectors for the working and counter electrodes, respectively. LiPF_6 in a 3:7 (by volume) solution of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) was used as the electrolyte; the LiPF_6 concentration was 0.3 M, 1 M or 2 M. The separator used in the cell was made of a polyolefin sheet. At room temperature, all cells were conditioned by being charged/discharged between 3.0 V and 4.3 V at constant-currents of 0.2C (charge) (where a 1C rate represents a 1 h complete charge or discharge of theoretical capacity) and 0.5C (discharge) (SP-300, Biologic) to check their electrochemical performance.

2.2. Measurement and analysis

The morphology of the composite electrodes was evaluated using scanning electron microscopy (SEM) with a field-emission electron source. SEM observations of the composite electrode cross-section, which was smoothly shaped by ion milling (SM-09010, JEOL), were performed on a Hitachi S-5500 microscope (Hitachi High-Technologies Co.) operated at an acceleration voltage of 2 kV. The pore-size distribution of the electrode in the range 0.003–100 μm was determined via mercury intrusion porosimetry at 7 kPa as the maximum pressure using an Auto Pore IV 9520 (Micromeritics).

To investigate the spatially inhomogeneous electrochemical reaction in the working electrode, in situ ES-XRD measurements [19] were performed on the BL28XU beamline of SPring-8 (Hyogo, Japan). The incident beam was collimated using a pair of four-dimensional slits and adjusted to 30 μm (vertical) \times 200 μm (horizontal). The incident beam and detector angles were fixed at 7.1 and 14.2 $^{\circ}$, respectively, to yield a probe resolution of 30 μm (vertical) and 243 μm (horizontal). The composite electrode in the cell was laid on a horizontal stage, and the probe position in the electrode was controlled by manipulation of the sample stage (see Fig. 1). We set four measurement positions in the cross-section of the composite electrode; the center of each position was (a) 10, (b) 35, (c) 65 and (d) 90 μm from the electrode surface.

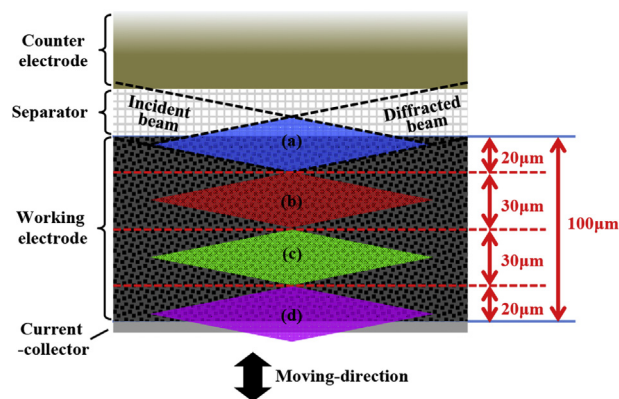


Fig. 1. Illustration of the confocal point, between the incident and diffracted beams, in the cross-section imaging generated by X-ray diffraction.

Table 1
Volume fraction and discharge capacity at a rate of 1C in electrodes with different densities.

Electrode density/ g cm^{-3}	Porosity/%	Volume fraction/%			Discharge capacity at 1C	
		Active material	Conductive additive	Binder	Specific capacity/ mAh g^{-1}	Capacity density/ mAh cm^{-3}
2.17	42	45	6	7	113	219
2.44	37	49	6	7	112	246
2.96	28	56	7	8	104	279
3.36	18	64	8	9	70	212

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