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Short communication

Liquid permeation through cast tape of graphite particles based on non-uniform packing structure

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Abstract

In the present study, the rate of liquid permeation is measured for green and pressed tapes used as an anode film of lithium ion battery. The tape was made of graphite particles of various shapes which were modified by high-speed rotational blending. The packing structure was measured by image analysis on the cross-sections of the tape in three dimensions and was characterized by a distribution of void sizes among particles. Based on the void size distribution, the mathematical model of permeation was developed considering the tape porous structure as the bundle of parallel pipes of various sizes.

As a result, the liquid permeation data with the graphite tapes can successfully be described with the developed model, in contrast with much higher permeation rate by Kozeny–Carman's equation. The permeation rate was also confirmed to get higher for the tape made of spherical particles as a result of higher equivalent diameter due to wider void size distribution and lower tortuosity owing to more regular packing structure.

Keywords: Natural graphite; Particle shape modification; Cast tape; Liquid permeation; Tape microstructure; Lithium ion battery

1. Introduction

Modern consumer and industrial electronic devices require lithium ion batteries of large capacity with high charge–discharge capability. Such batteries utilize tape casts of graphite particles as a negative electrode. Ohzeki et al. [1] confirmed that the porous structure of the tape significantly influences on battery characteristics. Expansion of graphite crystals during charging owing to the intercalation of Li ions and subsequent constriction during discharge result in the liquid movement in and out of the tape. To estimate the degree of this phenomenon, liquid permeation through void spaces among packed graphite particles inside the tape is investigated in the present research. Then, the enhancement of liquid permeation should be useful for improving battery performances at high rate [2].

The void structure formed during casting and pressing of highly non-regular shape graphite particles is very complex [3]. Models utilizing Kozeny–Carman's equation could not successfully relate the permeation rate to the structure of porous medium due to its oversimplified representation of packing structure with an effective hydraulic diameter.

The objective of the present research is to investigate experimentally and theoretically the relationship between the liquid permeation rate and porous structure of tapes cast with graphite particles of various shapes which are modified by high-speed rotational blending.

2. Theoretical

2.1. Tape microstructure

In the present study, the structure of void space inside the packed bed of particles forming the tape is supposed to be represented as a bundle of parallel but bended tubes of various diameters. Tape microstructure was characterized by the distribution of void sizes among packed particles [4]. The distribution

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of the probability, P_2, of finding circular void of a given size, χ_2, in the packing of non-spherical particles was derived on the basis of the model of spherical particles [5] as follows:

$$P_2(\chi_2) = 3\beta \frac{\nu(1-\nu)}{1-(\nu/\nu_m)} \int_{\chi_2}^{\infty} (1+\beta\chi_3)^2 \sqrt{1-\left(\frac{\chi_2}{\chi_3}\right)^2} \times \exp\left\{-\frac{\nu}{1-(\nu/\nu_m)}[(1+\beta\chi_3)^3-1]\right\} \mathrm{d}\chi_3 \quad (1)$$

where ν is the packing density, ν_m the limiting packing density, β the shape coefficient relevant to the particle packing and χ_3 is the diameter of the spherical void normalized by the associated average particle size, respectively. The particle size distribution was measured on the volume basis and β was assumed to be equal to one in the present research. Then, the void size distribution measured by image analysis was successfully fitted to Eq. (1) with ν_m as a fitting parameter.

2.2. Liquid permeation through tape

The mean velocity, $u_{e,i}$, of streamline liquid flow through the tube of diameter, $d_{t,i}$, is given by a Hagen–Poiseuille law as:

$$u_{e,i} = \frac{\Delta p d_{t,i}^2}{32 L_{e,i}\mu} \quad (2)$$

where Δp is the pressure drop, $L_{e,i}$ the tube length and μ is the liquid viscosity. Then, the superficial velocity of liquid flowing through the bed of particles of thickness, L_b, and the total cross-sectional area, A_b, is given as:

$$u_{b,0} = \frac{\pi}{4A_b}\sum_{i=1}^{m} n_i d_{t,i}^2 \langle u_{e,i} \rangle \quad (3)$$

Here, n_i is the number of tubes of diameter $d_{t,i}$ and m is the total number of tube diameters. Introducing Eq. (2) into Eq. (3) we can obtain the following equation:

$$u_{b,0} = \frac{\pi\Delta p}{128 A_b \mu}\sum_{i=1}^{m} \frac{n_i d_{t,i}^4}{L_{e,i}} \quad (4)$$

Here, we assume that the distribution of tube diameters, f_i, can be expressed as the distribution of the void sizes among the particles [6]:

$$f_i \Delta d_{v,i} = P_i - P_{i+1} \quad (5)$$

Then, the number of tubes is as follows:

$$n_i = A_b \varepsilon \frac{f_i \Delta d_{v,i}}{\sum((\pi/4) d_{v,i}^2 f_i \Delta d_{v,i})} \quad (6)$$

Using Eq. (6) and assuming that tubes are of equal length L_e, pressure drop Δp can be deduced as:

$$\frac{\Delta p}{L_b} = 32\left(\frac{L_e}{L_b}\right)\frac{\mu u_{b,0}}{\varepsilon}\left(\sum_{i=1}^{m}\frac{f_i \Delta d_{v,i} d_{v,i}^4}{\sum\left(d_{v,i}^2 f_i \Delta d_{v,i}\right)}\right)^{-1} \quad (7)$$

Here, the equivalent diameter, D_e, can be defined as:

$$D_e = \sqrt{\sum_{i=1}^{m}\frac{f_i \Delta d_{v,i} d_{v,i}^4}{\sum\left(d_{v,i}^2 f_i \Delta d_{v,i}\right)}} \quad (8)$$

3. Experimental

3.1. Particle shape modification

Natural graphite particles of median diameter, $d_p = 45.0\,\mu m$, and of flaky shape were used as a raw material as supplied by Hitachi Powdered Metals Co. The particle size was measured by a laser diffraction method (PRO-7000, Seishin Kigyo Co.). The particle shape was modified with high-speed rotational blending machine (Hybridization System, Nara Machinery Co.) by varying peripheral velocity and treatment time [7]. The particle shape was characterized by a shape index, K, as a ratio of short to long axis of an approximate ellipse [8]. An ellipse was constructed on the basis of Fourier analysis of particle outline detected by image analysis on binarized SEM photographs. Indices averaged for at least 30 particle outlines were reported here as K_{av}. The SEM photographs of particles used for tape casting are shown in Fig. 1.

3.2. Tape casting and morphology of porous microstructure

Tape casting was performed on a laboratory casting machine (PI-1210, Tester Sangyo Co.) with a blade with a gap of 200 μm moving at constant speed over the slurry, which was prepared by mixing particles with binders, styrene-butadiene rubber emulsion and carboxyl methyl cellulose, in distilled water. Green tapes thus obtained were dried at 393 K for 10 min. Green tapes were pressed with a roller press to yield pressed tapes of constant thickness of 70 μm and bulk density of $1.5\,g\,cm^{-3}$.

The tape cross-sections were observed by SEM in three different directions on tape samples mounted into resin separately for each surfaces. Here, the tape surface parallel to the casting direction is denoted as X surface, while Y surface is perpendicular to the cast one and Z is the top surface. The distribution of void sizes among packed particles in the cross-section was measured by randomly placing void circles of various sizes all over the binary image as described in detail elsewhere [6].

3.3. Measurements of liquid permeation

Liquid permeation through the tape was measured with a device manufactured by Jacom Co., as shown in Fig. 2. Liquid was supplied to the cell at desired flow rate by a custom-made syringe pump. The pressure difference was measured with a pressure gauge during flow in Z direction across the tape fixed inside the permeation cell. In the beginning of the experiment air trapped inside the tape was removed with vacuum pump and liquid was filled inside the cell.