Liquid penetration as a simple detection method for structural differences in particulate films prepared from slurries

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Abstract

We have investigated the use of liquid penetration to evaluate and detect structural differences in dried thin films. Two different films were fabricated from slurries that consisted of solid particles and a polymer. Both slurries had the same composition, but were prepared using different mixing processes. Clear differences in the void distributions of the as-prepared films were observed using mercury porosimetry. No significant differences were observed after the films were compressed. However, cross-sectional scanning electron microscopy images showed clear structural differences, including segregated particles after compression. Liquid penetration times into the films were measured and explained using a modified kinetic model. The wettability of the films using solvents of low polarity was also evaluated and was found to be dependent upon the extent of segregation within the films. This result suggested that liquid penetration measurements could be used as a simple method to evaluate the structure of particulate films.

Keywords

Liquid penetration; Wettability; Kinetic model; Particulate film; Segregation

1. Introduction

Slurries are frequently used to produce electrodes and ceramics [1–7]. Mixing, casting and drying of slurries are processes that are commonly used to obtain particulate films. Additionally, compression of films by pressing is performed when the packing fraction of a film is required to be greater than the as-prepared film. All of these processes affect the final structure and properties of particulate films. In fact, Kim and Lee [8, 9] reported that the mixing sequence of raw slurries affected the performance of electrodes in lithium-ion batteries with improved mixing resulting in enhanced performance. Therefore, understanding the effects of mixing on the final structure of particulate films is critical. There are many studies that report the relationship between manufacturing processes and the properties of films [10–13]. However, to the best of our knowledge the effects of the mixing of slurries on the final structure of particulate films have not been thoroughly investigated.

Characterization methods of film structures are also important issues to evaluate particulate films. Scanning electron microscopy (SEM) [10–15] is commonly used to observe both the surface and cross-section of films. Additionally, a number of other techniques are used to characterize the structure of films, including mercury porosimetry [16], energy dispersive X-ray spectroscopy (EDS) equipped with SEM [14, 15], atomic force microscopy (AFM) [17] and Kelvin probe force microscopy [18].

These methods allow the comprehensive determination of particulate film structure.

However, both sample preparation and measurement **are** often time-consuming. Furthermore, direct observation using SEM or AFM provides information over a microscopic area of a sample, which necessitates the collection of numerous images over a large area to probe the homogeneity of a sample. Thus, a simple alternative method that gives information on the macroscopic features of a sample would be of great value. We have investigated liquid penetration into particulate films for this purpose.

When a capillary tube that is filled with liquid is placed on a dried particulate film, the spontaneous penetration of the liquid into the film occurs. Classical theory for this liquid penetration phenomenon is described by the Lucas–Washburn equation [19, 20]. Using this theory Matsumoto *et al.* [21] evaluated the contact angles of packed particles within a bed consisting only of particles. Wu *et al.* [22] analyzed the wettability of porous electrodes that were made from a mixture of particles and a polymer, using liquid penetration then compared the data with a mathematical model. However, information on the inner structures and distributions of the components within the electrodes was not provided, which means any correlations between the film structures and wettability needs further investigation.

We prepared slurries of particles and a polymer with the same composition using different mixing processes. Particulate films were prepared by casting then drying the slurries. The effects of the mixing processes on both of the slurries and the films were investigated. We then measured the liquid penetration times for the different films. The wettability of the

films was evaluated using this data and a modified kinetic model for liquid penetration.

Microscopic structures and macroscopic wettability of the films is discussed. The

applicability of this method as an evaluation technique of film structures is also discussed.

2. Experimental section

2.1. Materials

Slurries were prepared using $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ oxide particles (diameter: ca. 12 μm (Figure 1 (a)), Sakai Chemical Industry Co., Ltd.), carbon black (CB) nanoparticles (TOKABLACK #5500, primary particle size ca. 25 nm (Figure 1 (b)), Tokai Carbon Co., Ltd.), *N*-methyl-2-pyrrolidone (NMP; purity 99.5%, Nacalai Tesque, Inc.) and polyvinylidene fluoride (PVDF solution, KF polymer #1120, 12 wt% NMP solution, Kureha Co.).

Liquid penetration measurements were performed using *n*-hexane (purity >96.0%, Wako Pure Chemical Industries Ltd.), dimethyl carbonate (DMC; purity >98.0%, Tokyo Chemical Industry Co., Ltd.) and ethanol (purity >99.5%, Wako Pure Chemical Industries, Ltd.). All chemicals and solvents were used as received.

2.2. Sample preparation

Two raw slurries with the same final composition were prepared using different mixing protocols. The weight ratio of the three solid components, oxide particles:CB:PVDF,

was 85:10:5. The final weight fraction of the particles (oxide particles and CB), PVDF and NMP in the slurries was 51.9, 2.7 and 45.4 wt%, respectively. The slurries were prepared using a two-step process. (i) Premixing: A mixture of NMP, PVDF, oxide particles and CB was mixed using a biaxial kneading mixer (2P-06, Primix Co.) at 30 rpm for 50 min under reduced pressure to remove air bubbles. (ii) Postmixing: The slurry was mixed at 60 rpm for an additional 15 min.

The two different slurries were prepared with different weight fractions of particles in the premixing process. Slurry 1 contained a weight fraction of 51.9 wt% in both mixing steps, whereas slurry 2 contained a weight fraction of 58.9 wt% in the premixing process (less NMP was added), then this weight fraction was adjusted to 51.9 wt% in the postmixing step by adding more NMP. The viscosity of a slurry is strongly dependent on the weight fraction of particles. As such, we expected different shear stresses for these two slurries in the premixing process. Other mixing parameters, such as the mixing time and the rotation speed of the mixer, would also affect the final structures of films. However, the main focus of this work is to evaluate the relationship between particulate films with different structures and kinetics in liquid penetration. Thus we employed the solid concentration at the premixing step as the only parameter which we changed. The raw slurries were coated on 20- μ m-thick Al foil and dried at 180 °C using a commercial coater (Compact Precision Coater, Thank Metal Co., Ltd.). The dried slurries were then heated at 120 °C under vacuum to completely remove

NMP. The bulk density of the dried films was approximately 1.5 g cm^{-3} . The films were then compressed by being passed through a roll press to increase the bulk density between 2.0 g cm^{-3} and 2.7 g cm^{-3} . The different bulk densities were achieved by changing the gap between the rolls. Films prepared from Slurries 1 and 2 are denoted as Films 1 and 2, respectively.

2.3. Characterization of slurries and films

Shear stress was applied to the two slurries under a shear flow between 0 s^{-1} to 300 s^{-1} , and was measured using a parallel plate viscometer (Physica MCR 301, Anton Paar GmbH). The distance between the parallel plates was $200 \text{ }\mu\text{m}$. Direct observation and elemental distribution mapping of the films were performed using FE-SEM (JSM-6330F, JEOL Ltd.) and EDS (JED-2200F, JEOL Ltd.). Additionally, the porosity of the dried films was measured using a mercury porosimeter (Pore Sizer 9310, Micromeritics Co.). The porosity measurements were repeated twice before compression to confirm reproducibility. Film cross-sections, prepared by a cross-section polisher (SM-09010, JEOL Ltd.), were observed using FE-SEM.

2.4. Measurement of penetration time

A schematic illustration of the liquid penetration measurement is shown in Figure 2 (a). A square film ($5 \times 5 \text{ cm}^2$) was added to a glass vial and covered with a cap with a hole in

its center. The vial was filled with a solvent vapor by placing a small, open bottle of solvent in the vial for over 30 minutes prior to measurement. This minimized vaporization of the solvent during the liquid penetration measurements. A glass capillary tube (inner diameter = 0.13 mm, outer diameter = 0.5 mm, length = 120 mm) was filled with solvent to a height of 40 mm, and then slowly inserted into the vial until the wet tip contacted on the film surface. After contact, solvent spontaneously penetrated into the film and we measured the time taken for the solvent height in the capillary to drop from 30 mm (h_1) to 5 mm (h_2). Importantly, the solvents chosen had minimal effects on the film structure during the penetration measurements. Thus, solvents in which PVDF can dissolve or swell are not suitable for this experiment. We used *n*-hexane, DMC and ethanol for these measurements as, according to Hansen solubility parameters, these solvents do not dissolve or swell PVDF to any significant extent [23, 24]. Hansen solubility parameters are shown in the supporting information. The liquid penetration time was measured at 25 different positions within each film to confirm accuracy of the measurements.

3. Results

The flow curves of the raw slurries are shown in Figure 3. Both slurries exhibited hysteresis. Slurry 1 showed a higher shear stress than that of Slurry 2 in both “forward” and “backward” measurements. Additionally, the hysteresis area for Slurry 1 was larger than that

of Slurry 2. These results indicated that the weight fraction of particles at the premixing step had an effect on the properties of the final slurry.

Films from the two slurries also showed different void-size distributions, as shown in Figure 4. The dried films were measured using mercury porosimetry prior to compression. There was no significant difference in the total pore volume between the two samples (Figure 4 (a)). The void-size distribution of both slurries was bimodal with almost identical peak positions. However, the peak at approximately $0.06\ \mu\text{m}$ in Film 1 was larger than that observed for Film 2, while the peak at approximately $4\ \mu\text{m}$ was larger for Film 2 than for Film 1 (Figure 4 (b)). These results clearly showed that the mixing process of the slurry affected the final film structure.

Typical FE-SEM images of the surfaces of the films prior to compression are shown in Figure 5. At low magnification (Figure 5 (a) and (b)) no differences were observed. However, at higher magnification small voids and cracks were present (white arrows, Figure 5 (c) and (d)). Cross-sectional FE-SEM images of the same samples, taken at five different positions, are shown in Figure 5 (e) and (f). Micron-sized particles (light gray) were packed together, and the surrounding areas appeared dark gray. Film 1 contained more and larger segregated “dark gray” areas than did Film 2. Elemental mapping using EDS revealed that the bright gray particles were oxide particles and the dark gray regions consisted of both CB and binder polymer (PVDF), as shown in Figure 6. PVDF contains fluorine, which enables its

position to be determined.

The compressed films were also characterized using mercury porosimetry and FE-SEM, and are shown in Figures 7 and 8. The relationship between the films bulk density and the differential void-size distribution is shown in Figure 7. The void volume and peak void size decreased because of an increase in the bulk density of the compressed films. At the highest bulk density (2.7 g cm^{-3}), the micron-sized voids virtually disappeared, leaving only nano-sized voids. There was no significant difference in the void distributions of Film 1 and Film 2 at the highest bulk density, which on its own might indicate that the inner structures of both films was same after compression. However, differences in the internal structures of the compressed films were observed using cross-sectional SEM, as shown in Figure 8 (bulk density = 2.7 g cm^{-3}). Following compression, Film 1 exhibited large, segregated areas of both CB and PVDF whereas these segregated areas were smaller in Film 2. The internal structure of Film 1 prior to compression contained these large segregations, and thus it is plausible that these remained to some extent after compression. Therefore, although the void-size distributions of Films 1 and 2 were very similar after compression, there were still differences between the structures of the films.

The penetration times (t_{penet}) for films of varying bulk densities, using different solvents, are shown in Figure 9. The t_{penet} increased with increasing bulk densities for both films for each solvent. The t_{penet} can be affected by a number of factors, including bulk

density, size of voids, wettability of films, viscosity and the air-liquid interfacial energy of the solvent. This is discussed in the following section.

4. Discussion

4.1. Effects of solid concentration at the premixing step

Slurry 1 exhibited larger shear stress **than** Slurry 2 at the same shear rates (Figure 3). Additionally, the area of the hysteresis loop of Slurry 1 was larger than that of Slurry 2. Hysteresis curves are commonly observed in rheology measurements of slurries in which the constituent particles are initially aggregated. The presence of these aggregates generally causes large shear stresses in the “forward” measurement. However, during the applied shear stress in the “forward” measurement the aggregates are re-dispersed, which lowers the shear stress experienced in the “backward” measurement. Thus, the larger shear stress observed for Slurry 1 indicated that there were a greater number of aggregates than in Slurry 2. In the premixing step, the weight fraction of oxide particles and CB was higher for Slurry 2 than for Slurry 1. Therefore, the applied shear stress to Slurry 2 was also higher than to Slurry 1. This resulted in improved dispersion in Slurry 2 compared with Slurry 1. The increased uniformity observed in the cross-sectional SEM images of Film 2 (Figures 5 and 6) also supported the idea that Slurry 2 had improved mixing.

The distribution of void-sizes shown in Figure 4 indicated clear differences between

Films 1 and 2 before compression. These differences were significantly lowered after compression to a density of 2.7 g cm^{-3} , as shown in Figure 7. However, cross-sectional SEM images clearly showed that the segregation of CB nanoparticles remained in Film 1 after compression. Although the distribution of void-sizes in the compressed films was very similar, they still exhibited structural differences. Thus, the differences observed in t_{penet} must be caused by these differences.

4.2. Mathematical model for t_{penet} and wettability analysis of films

We have constructed a mathematical model that describes t_{penet} . Classical theory for liquid penetration into packed particles [21] was modified for our experimental system. A detailed derivation of the mathematical model is summarized in the Appendix. In this model, t_{penet} is given by eq. (1):

$$t_{\text{penet}} = \frac{\mu k^2 R^2 S_v (h_1 - h_2)}{\gamma \cos \theta} \frac{1 - \varepsilon}{h_f \varepsilon^2} \quad (1),$$

where μ is the viscosity of the liquid, k is a tortuosity constant, R is the radius of the capillary tube, S_v is specific surface area of the inner voids, γ is the air-liquid interfacial tension, θ is the contact angle, ε is the porosity, h_f is the film thickness, and h_1 and h_2 are the heights of the liquid at the beginning and the end of the measurement. In eq. (1), the value of k was reported as about 2 [25] and S_v is assumed to be $6/d$ for a packed bed of hard spherical particles with a diameter of d [26]. Thus, we expect that $\mu k^2 R^2 S_v (h_1 - h_2) / (\gamma \cos \theta)$ is constant and t_{penet} to show a

linear trend with respect to $(1-\varepsilon)/(h_f \varepsilon^2)$. These relationships are shown in Figure 10. The data were linear, except at the largest value of $(1-\varepsilon)/(h_f \varepsilon^2)$, which corresponded to a density of 2.7 g cm^{-3} . The agreement between the mathematical model and experimental data suggested the validity of our model. Possible reasons for the disagreement of the data at the largest value of $(1-\varepsilon)/(h_f \varepsilon^2)$ are discussed later. Slopes of the lines fitted to the data without the largest t_{penet} were used for the following discussion.

Of potential concern in this model is the contact angle θ , as the wettability of a film is strongly dependent on the solvent. The two parameters μ and γ in eq. (1) also depend on the solvent. Therefore, we removed these parameters from eq. (1) in order to directly compare the contact angle derived from the slopes between different solvents (Figure 10). We have re-plotted the data as $t_{\text{penet}}\gamma/\mu$ as a function of $(1-\varepsilon)/(h_f \varepsilon^2)$, as shown in Figure 11. *n-hexane exhibited the smallest slope among three solvents in both films.* As the slope of the linear function in our model is inversely proportional to $\cos\theta$, the $t_{\text{penet}}\gamma/\mu$ vs. $(1-\varepsilon)/(h_f \varepsilon^2)$ plot suggested that *n-hexane showed the best wetting to the composite films in three solvents.*

Information can also be gained from the difference in the slopes of Films 1 and 2 for DMC and *n*-hexane (Figure 10). Film 1 exhibited better wetting than Film 2, which may be caused by the structural differences between the films. As Film 1 contained large segregated areas of CB nanoparticles (Figure 8), it is plausible that these areas would act as wetting pathways for the two solvents. Conversely, we did not find any obvious differences for

ethanol penetration. This indicated that this penetration method would be a useful and simple way to evaluate the inner structure of compressed films. However, a suitable solvent must be selected in order to detect the structural differences. The polarity of ethanol may explain the fact that no significant differences observed in its penetration. This can be examined quantitatively using relative permittivity. The relative permittivity of ethanol, DMC and hexane are 25, 3.1 and 1.9 [27], respectively, which are all less polar than water (relative permittivity = 80). However, ethanol is clearly more polar than the other solvents. Thus, segregated areas containing CB nanoparticles would not act as wetting pathways for ethanol sufficiently as the polarity of CB is generally quite low.

Finally, we discuss a possible reason for the discrepancy in the data from the high density films (largest value of $(1-\varepsilon)/(h_f \varepsilon^2)$) in our mathematical model. In our analysis, we assumed constant values of k and S_v , even after compression. If compression changed the tortuosity of the films, we expect the films to have more tortured inner structures because the solid components become more closely packed. This means that the tortuosity of k would increase after compression. If this is correct, the experimentally obtained values of t_{penet} should be larger than would be predicted by our model. Thus, we expect larger value of t_{penet} than a linear fit would predict (Figure 10). However, we observed smaller values of t_{penet} than the fit, which suggested that an increase in k was not the reason for the discrepancy. S_v gives the ratio of the total inner surface area of voids to the total volume of solids in the film. For a

packed bed of hard spheres, S_v is given as a constant value of $6/d$. However, a polymer was also included in our system. It is plausible that some of the small voids among the packed particles would be filled with the polymer in the compressed films. This clogging effect would be more pronounced in tightly compressed films. The voids that were filled with the polymer would not act as penetration paths for the solvent and therefore the inner surface area of voids available for liquid penetration would decrease. Provided that the solid components are not compressed during the pressing process, the clogging effect would decrease the value of S_v . This would decrease the value of t_{penet} , when compared with a theoretical value of t_{penet} with a constant S_v . It is reasonable that this change in S_v explains the discrepancies that were observed between our experiments and theory. Since multiple components are generally used in practical particulate films and values of S_v would depend not only on compression but also on composition of films, we consider that measurement of S_v is preferable for the appropriate use of our mathematical model.

The difference between the largest value of t_{penet} when using DMC was small compared with the other solvents. According to the Hansen solubility parameters shown in the supporting information, DMC is expected to show the best wetting to PVDF. Therefore, DMC could partially penetrate the clogged voids filled with PVDF, which would explain the smaller discrepancy observed (Figure 10). Thus selection of solvent is a critical factor for measurement of liquid penetration. We propose that we are able to choose an appropriate

solvent on the basis of both Hansen solubility parameters and polarity of solvents. Hansen solubility parameters are useful to find solvents in which neither dissolution nor swelling of polymers occur as described in the experimental section. Polarity of solvents should be close to that of particulate materials used in films for better wetting and liquid penetration into films. Thus we are able to evaluate the inner structures of films using a suitable solvent.

5. Conclusions

We have investigated the effects of different premixing processes on slurries and the structures of their resulting dried films. A higher concentration of solids within the slurry in the premixing step resulted in enhanced dispersion through the slurry and films with less segregation of the CB nanoparticles. We also found that any differences in the distribution of pores within the films practically vanished after compression. However, the segregated structures containing CB nanoparticles that were present in films before compression remained, even after significant compression. The liquid penetration time of solvents of varying polarity into the films was measured, which led to a proposed mathematical model. This model showed reasonable agreement with the experimental data. The wettability of the solvents towards the films varied depending on the differences in the segregated structures containing CB nanoparticles. Therefore, this work shows that liquid penetration time is a simple and useful method to evaluate the inner structures of films.

Appendix

In this Appendix, we show the derivation of a mathematical model that describes the kinetics of spontaneous penetration of a solvent into a particulate film. A schematic model for the liquid penetration phenomenon into a particulate film is shown in Figure 2 (b). The driving pressure of liquid penetration, P_t , can be expressed as eq. (A1):

$$P_t = P_f - P_c + P_g \quad (A1),$$

where P_f is the suction pressure caused by a film, P_c is the suction pressure caused by a glass capillary, and P_g is the hydrostatic pressure exerted on the film due to the weight of solvent.

P_f is caused by small pores among packed particles in the film. This capillary pressure can be expressed as eq. (A2):

$$P_f = \frac{2\gamma\cos\theta}{r_f} \quad (A2),$$

where γ is the air-liquid interfacial energy of a solvent, θ is the contact angle of solvent to the film and r_f is a mean radius of the pores between packed particles. On the basis of classical theory of a packed bed, r_f is described as eq. (A3):

$$r_f = \frac{2\varepsilon}{(1-\varepsilon)S_v} \quad (A3),$$

where ε is the porosity, and S_v is the volume-based specific surface area of the film, respectively. S_v is the ratio of the total surface area of the inner pores to the total volume of solids in the film.

Assuming that the pressure loss ΔP due to a flow of liquid in a pore is approximately described by the Hagen–Poiseuille law, then the relationship between the pressure loss and the flow distance x is expressed by eq. (A4):

$$\frac{\Delta P}{x} = \frac{8\mu k u}{r_f^2} \quad (\text{A4}),$$

where μ is the viscosity of a liquid, k is a tortuosity of the pores [25] and u is an average linear flow rate of liquid in film pores. The amount of liquid that penetrates into a film must be equal to the amount of liquid lost in the glass capillary, which gives eq. (A5):

$$\pi R^2 v = 2\pi x h_f \varepsilon v_f \quad (\text{A5}),$$

where v is the rate of decrease of the liquid level in the capillary, R is the radius of the capillary, h_f is the film thickness and v_f is the rate of shift of the liquid interface in the film during penetration. Considering the tortuosity of pores in the film, v_f is equal to u/k .

Substituting eq. (A5) into eq. (A4), we obtain eq. (A6):

$$\Delta P = \frac{4\mu k^2 v}{h_f \varepsilon} \left(\frac{R}{r_f}\right)^2 \quad (\text{A6}).$$

Since $v = -dh/dt$, we obtain the following differential equation from eq. (A6), given by eq.

(A7):

$$-\frac{dh}{dt} = \frac{h_f \varepsilon \Delta P}{4\mu k^2} \left(\frac{r_f}{R}\right)^2 \quad (\text{A7}).$$

Integrating eq. (A7) with the conditions $h = h_1$ at $t = t_1$ and $h = h_2$ at $t = t_2$, we obtain eq. (A8):

$$t_2 - t_1 = \frac{4\mu k^2}{h_f \varepsilon \Delta P} \left(\frac{R}{r_f}\right)^2 (h_1 - h_2) \quad (\text{A8}).$$

In our experiments, we measured the time required for a decrease in solvent height in the

capillary from h_1 to h_2 . Therefore, the penetration time, t_{penet} , is defined as: $t_{\text{penet}} = t_2 - t_1$. ΔP is equal to P_t , the driving pressure for liquid penetration. P_c and P_g are given by eq. (A9) and (A10):

$$P_c = \frac{2\gamma \cos \theta_c}{R} \quad (\text{A9}),$$

$$P_g = \rho g h_0 \quad (\text{A10}),$$

where θ_c is the contact angle of the solvent and the glass capillary, ρ is the density of solvent and g is the gravitational constant. P_c/P_f can be approximated as r_f/R . As the typical size of r_f was 30 nm (Figure 7) and R is 65 μm , then P_c/P_f is on the order of 10^{-4} , which indicates that P_c is negligible. In the same way, assuming that ρ is typically $1 \times 10^3 \text{ kg m}^{-3}$ and h_0 is 40 mm, then P_g is approximately $3.9 \times 10^2 \text{ Pa}$. Conversely, P_f is estimated as 10^6 Pa , assuming that γ is $20 \times 10^{-3} \text{ N m}^{-1}$ and $\cos \theta \sim 1$ for a wetting liquid. Thus, P_g/P_f is on the order of 10^{-4} and P_g is also negligible. Thus, it is reasonable to consider that P_f is the main driving force for liquid penetration and we set $\Delta P = P_f$ in our model. By substituting eq. (A2) into eq. (A8), we obtain the relationship for t_{penet} as shown in eq. (1) in the main manuscript.

Acknowledgments

This study was supported by the Strategic International Cooperative Program of Japan Science and Technology Agency. S.I. is grateful for financial support by a program to disseminate tenure tracking system from the Ministry of Education, Culture, Sports, Science

and Technology (MEXT), Japan. H.M. gratefully acknowledges the support from the Program for Leading Graduate Schools of Tokyo University of Agriculture and Technology granted by MEXT, Japan.

References

- [1] Z. Liu, A. Yu, J.Y. Lee, Cycle life improvement of LiMn_2O_4 cathode in rechargeable lithium batteries, *J. Power Sources* 74 (1998) 228–233.
- [2] A. Ponrouch, M.R. Palacín, On the impact of the slurry mixing procedure in the electrochemical performance of composite electrodes for Li-ion batteries: A case study for mesocarbon microbeads (MCMB) graphite and Co_3O_4 , *J. Power Sources* 196 (2011) 9682–9688.
- [3] K.C. Klavetter, S.M. Wood, Y.M. Lin, J.L. Snider, N.C. Davy, A.M. Chockla, D.K. Romanovicz, B.A. Korgel, J.W. Lee, A. Heller, C.B. Mullins, A high-rate germanium-particle slurry cast Li-ion anode with high Coulombic efficiency and long cycle life, *J. Power Sources* 238 (2013) 123–136.
- [4] M. Ihara, M. Kanno, S. Inoue, Photoabsorption-enhanced dye-sensitized solar cell by using localized surface plasmon of silver nanoparticles modified with polymer, *Physica E* 42 (2010) 2867–2871.
- [5] Y. Park, W. Kim, D. Monllor-Satoca, T. Tachikawa, T. Majima, Role of interparticle charge transfers in agglomerated photocatalyst nanoparticles: Demonstration in aqueous suspension of dye-sensitized TiO_2 , *J. Phys. Chem. Lett.* 4 (2013) 189–194.
- [6] Y. Komoda, K. Okabayashi, H. Nishimura, M. Hiromitsu, T. Oboshi, H. Usui, Dependence of polymer electrolyte fuel cell performance on preparation conditions of slurry

for catalyst layers, *J. Power Sources* 193 (2009) 488–494.

[7] S. Cottrino, Y. Jorand, J. Adrien, C. Olagnon, Spray-drying of highly concentrated nano alumina dispersions, *Powder Technol.* 237 (2013) 586–593.

[8] K.M. Kim, W.S. Jeon, I.J. Chung, S.H. Chang, Effect of mixing sequences on the electrode characteristics of lithium-ion rechargeable batteries, *J. Power Sources* 83 (1999) 108–113.

[9] G.W. Lee, J.H. Ryu, W. Han, K.H. Ahn, S.M. Oh, Effect of slurry preparation process on electrochemical performances of LiCoO_2 composite electrode, *J. Power Sources* 195 (2010) 6049–6054.

[10] C.C. Li, J.T. Lee, X.W. Peng, Improvements of dispersion homogeneity and cell performance of aqueous-processed LiCoO_2 cathodes by using dispersant of PAA- NH_4 , *J. Electrochem. Soc.* 153 (2006) A809–A815.

[11] J.H. Lee, J.S. Kim, Y.C. Kim, D.S. Zang, U. Paik, Dispersion properties of aqueous-based LiFePO_4 pastes and their electrochemical performance for lithium batteries, *Ultramicroscopy* 108 (2008) 1256–1259.

[12] T.J. Patey, A. Hintennach, F.L. Mantia, P. Novák, Electrode engineering of nanoparticles for lithium-ion batteries-role of dispersion technique, *J. Power Sources* 189 (2009) 590–593.

[13] C.C. Li, X.W. Peng, J.T. Lee, F.M. Wang, Using poly(4-styrene sulfonic acid) to

improve the dispersion homogeneity of aqueous-processed LiFePO_4 cathodes, J. Electrochem. Soc. 157 (2010) A517–A520.

[14] W. Porchera, B. Lestriez, S. Jouanneau, D. Guyomard, Optimizing the surfactant for the aqueous processing of LiFePO_4 composite electrodes, J. Power Sources 195 (2010) 2835–2843.

[15] J. Li, B.L. Armstrong, J. Kiggans, C. Daniel, D.L. Wood, Optimization of LiFePO_4 nanoparticle suspensions with polyethyleneimine for aqueous processing, Langmuir 28 (2012) 3783–3790.

[16] P. R. Das, L. Komsijska, O. Osters, G. Wittstock, PEDOT:PSS as a Functional Binder for Cathodes in Lithium Ion Batteries, J. Electrochem. Soc. 162 (2015) A674–A678.

[17] M. Yoo, C.W. Frank, S. Mori, Interaction of poly(vinylidene fluoride) with graphite particles. 1. Surface morphology of a composite film and its relation to processing parameters, Chem. Mater. 15 (2003) 850–861.

[18] S.B. Lee, S.I. Pyun, Determination of the morphology of surface groups formed and PVDF-binder materials dispersed on graphite composite electrodes in terms of fractal geometry, J. Electroanal. Chem. 556 (2003) 75–82.

[19] R. Lucas, Ueber das Zeitgesetz des kapillaren Aufstiegs von Flüssigkeiten, Kolloid Z. 23 (1918) 15–22.

[20] E.W. Washburn, The Dynamics of Capillary Flow, Phys. Rev. 17 (1921) 273–283.

- [21] K. Matsumoto, Y. Tabata, G. Hong, K. Watanabe, The Measurement of the Wettability of Hydrophilic Powder by the CST Method, *J. Soc. Powder Technol., Japan* 25 (1988) 365–370.
- [22] M.S. Wu, T.L. Liao, Y.Y. Wang, C.C. Wan, Assessment of the wettability of porous electrodes for lithium-ion batteries, *J. Appl. Electrochem.* 34 (2004) 797–805.
- [23] C.M. Hansen, *Hansen Solubility Parameters: A User's Handbook*, 2nd ed., CRC Press, Boca Raton, 2007.
- [24] Y.H. Kwon, M.M. Huie, D. Choi, M. Chang, A.C. Marschilok, K.J. Takeuchi, E.S. Takeuchi, E. Reichmanis, Toward Uniformly Dispersed Battery Electrode Composite Materials: Characteristics and Performance, *ACS Appl. Mater. Interfaces* 8 (2016) 3452–3463.
- [25] L. Carino, Kinetics of wetting of a compacted powder by aqueous solutions of surface active agents, *Colloid and Polymer Sci.* 254 (1976) 108–113.
- [26] The Society of Powder Technology, Japan, *Funtai Kogaku Binran*, 2nd ed., Nikkan Kogyo Shimbun, Ltd., Tokyo, 1998.
- [27] D.R. Lide, *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, 2002.

Figure captions

Figure 1. FE-SEM images of (a) oxide particles and (b) nanoparticles of carbon black.

Figure 2. Schematic illustrations showing the experimental apparatus for liquid penetration experiment.

Figure 3. Flow curves for the two different slurries. Arrows indicate “forward” and “backward” directions of this measurement. Solid and open symbols indicate data from Slurry 1 and Slurry 2, respectively.

Figure 4. Void-size distributions of Films 1 and 2 prior to compression. (a) Cumulative void-size distributions and (b) differential void-size distributions are shown. Blue and red lines indicate data from Film 1 and Film 2, respectively. Solid and dashed lines indicate data of the first and second measurement, respectively.

Figure 5. Typical SEM images of Films 1 and 2. (a) and (c) Surface views of Film 1 and (b) and (d) surface views of Film 2. (e) and (f) show cross-sectional images of Film 1 and Film 2, respectively. Scale bars in (e) and (f) are 30 μm .

Figure 6. Cross-sectional SEM images and the corresponding elemental mapping for (a) Film 1 and (b) Film 2.

Figure 7. Differential void-size distributions of (a) Film 1 and (b) Film 2 with different bulk densities after compression. Bulk densities of films were, 1.5 g cm^{-3} (**black, solid**), 2.0 g cm^{-3} (**green, dashed**), 2.3 g cm^{-3} for (a) or 2.4 g cm^{-3} for (b) (**red, dotted**), and 2.7 g cm^{-3} (**blue, bold**), respectively.

Figure 8. Cross-sectional SEM images of (a) Film 1 and (b) Film 2 after compression. The bulk density was 2.7 g cm^{-3} for both samples shown. Scale bars are $20 \text{ }\mu\text{m}$.

Figure 9. Measured values of t_{penet} for the composite films with variety of densities. Ethanol (triangles), DMC (circles) and *n*-hexane (diamonds) were used as solvent. Solid and open symbols indicate data from Film 1 and Film 2, respectively. Standard deviations of the experimental data of t_{penet} are shown as error bars.

Figure 10. Plots of t_{penet} using eq. (1) from the proposed kinetic model. Solid (Film 1) and dashed (Film 2) lines show linear fitting results for each set of data, excluding the largest t_{penet} value for each solvent. Ethanol (triangles), DMC (circles) and *n*-hexane (diamonds) were

used as solvent. Solid and open symbols indicate data from Film 1 and Film 2, respectively.

Error bars show standard deviations for the data.

Figure 11. Plots of $t_{\text{penet}} \gamma/\mu$ for Film 1 (a) and Film 2 (b). Ethanol (triangles), DMC (circles) and *n*-hexane (diamonds) were used as solvent. Standard deviations for data are shown as error bars.

Figure 1

(a)

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11