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Design of a porous cathode structure of high performance Li-ion battery

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Abstract. The cathode materials of Li-ion battery are suffering from huge loss in the specific capacity as the C-rate or cycle increases due to the unusually low diffusivity of Li-ion in specific phase. Although the porous cathode has shown the improved performance, it still has not been clearly explained whether the porosity really increases the specific capacity and how much high rate capability we can obtain. Here we report the importance of the design of porous cathode, which may provide an ultrahigh or even lower than that of the simple sphere-shaped cathode. Numerical simulations show the improved specific capacity with the porosity and the effect of porosity becomes significant as the C-rate increases. As the C-rate increases from 2.5 to 40C, the loss of specific capacity becomes only 20% with the 50% porosity, while that is about 60% with the simple sphere-shaped cathode. In addition, that decreases during total cycles from 30% to only about 2% with the 50% porosity under 40C. Interestingly, the porous cathode does not guarantee the improved specific capacity even porosity increases unless the pores are evenly distributed. The presented analysis provides important issues to design the ultrahigh performance of cathode.

1. Introduction
Although the cathode materials provide the outstanding performance of Li-ion batteries (LIBs) based on their high energy density, high capacity, simple synthesis, low cost [1-5], they are still suffering from a severe problem, such as a loss of specific capacity under the high C-rate or high cycle [6,7]. It has revealed that the loss of specific capacity originates from the various reasons, such as the structural transformation of cathode [8], the low electronic conductivity [8], and the low diffusivity of Li-ion in the cathode material [9,10]. There have been various attempts to resolve the loss of specific capacity [11]. For instance, it has been turned out that the morphology of concave or notch-like should avoid at the cathode to reduce the structural transformation of cathode [12]. In addition, the hollow structure has been proved effective to buffer the structural transformation and to reduce the loss of specific capacity. To improve the electronic conductivity, the coating of high conductive materials on the cathode has been suggested [13-15]. The improved electronic conductivity with high conductive materials have ensured the high rate capability and high cycle stability. Meanwhile, since the typical cathode materials generate the phase that has unusually low diffusivity of Li-ion during their utilization, [9-11, 13, 14], there have been many efforts in order to overcome the low diffusivity of Li-ion in the cathode materials. Especially, the various porous structures in cathode have shown the great improvement in the rate capability and the cycle stability [11,13,14]. Although it has been shown that
the porosity in cathode have the improved specific capacity, rate capability, and cycle stability than those without the porosity, however, it still has not been clearly explained whether the porosity in cathode really increases the specific capacity and how much high rate capability and high cycle stability we can obtain from a systematic analysis.

Here we report the importance of the design of porosity in cathode, which may provide an ultrahigh specific capacity with the porosity or even worsened specific capacity as the porosity increases. The specific capacity and the loss of it were systematically evaluated with various porosity, distribution of pores, C-rate, cycle. Numerical simulations show that the specific capacity can be improved as the porosity in cathode increases and the effect of porosity becomes significant as the C-rate increases. The loss of specific capacity is considerably reduced with respect to the increase of both of C-rate and cycle as the porosity in cathode increases. Interestingly, the porous cathode does not guarantee the improved specific capacity as the porosity increases unless the pores are evenly distributed.

2. Model and methods

In order to evaluate the performance of LIB with porous cathode, a three-dimensional (3D) dynamic model based on the phase field approach was developed. The phase field approach has been demonstrated its reliability and effectiveness in previous studies related to evolutions of nano- and micro-structures [16-18]. The schematic illustration of design of porous cathode are shown in Figure 1. The cathode consists of the microsphere structures, Li-ion, and electrolyte (Figure 1a). When LIB is discharged, Li-ion diffuses into the microstructure of cathode and the performance of LIB (e.g., specific capacity and rate capability) can be determined by the Li-ion concentration in the cathode. As Li-ions diffuse into the cathode, the phases of cathode material are transformed according to the concentration of Li-ion and the diffusivity of Li-ion of some phases could be considerably low, which would reduce the total amount of Li-ion in the cathode during the discharging process and induce a low specific capacity and rate capability. For instance, the cathode made with vanadium pentoxide (V2O5), which is considered in this study, has the transformation of phases from α, ε, δ to γ phases as the concentration of Li-ion increases [6]. During the discharging process, the diffusion of Li-ion into the cathode is interrupted by the ε phase because the diffusivity of Li-ion is significantly low in ε phase, which is about 10 times lower than that of other phases (i.e., α, δ, and γ). The porosity in the cathode could reduce the amount of cathode where Li-ion cannot reach due to ε phase and provide a full utilization of cathode (Figure 1b). As shown in Figure 1c, the distribution of pores also can be an important parameter in designing the microstructure of cathode.

![Figure 1](image)

**Figure 1.** Design of porous structure in the cathode for ultrahigh performance. (a) Illustration of the cathode in Li-ion battery consisting of microsphere structure, Li-ion, electrolyte. Scale bars, 500 nm. (b) Li-ion concentration and ε phase fraction in the cathode according to the design of porosity. (c) Design of porous cathode with respect to the porosity and the distribution of pores.
The diffusion flux of Li-ion into the cathode is represented by \( J_\theta = -D \nabla c \), where \( D \) and \( c \) are the diffusivity and the concentration of Li-ion, respectively. Since we assume that \( \text{V}_2\text{O}_5 \) is a cathode material, the diffusivity of Li-ion in the cathode depends on the internal phases (e.g., \( \alpha, \epsilon, \delta, \gamma \), and \( \omega \)) and the phases are determined by the Li-ion concentration in cathode. The diffusivities at each phase are defined according to the Li-ion concentration [19]. The Li-ions are supplied as a source at the cathode surface and it can be defined with current density as \( S = i_a/F \) [20], where \( F \) is Faraday constant. The governing equation with the flux and source of Li-ion is constructed by \( \partial c/\partial t = \nabla \cdot (D \nabla c) + S \), and then normalized with the characteristic time \( t_\epsilon \), length \( l_\epsilon \), and diffusivity \( D_\epsilon = l_\epsilon^2/t_\epsilon \) for computational convenience. The characteristic time and length set to be \( t_\epsilon = 0.5 \) s and \( l_\epsilon = 5.0 \) nm, respectively. The normalized diffusivity, \( D_n = D/D_\epsilon \), is defined the characteristic diffusivity. A semi-implicit Fourier spectral method is employed for high space resolution and fast computation. In the Fourier space, the periodic boundary condition is assigned in all of directions. The domain of cathode was constructed by 500 nm of diameter of the microsphere. The porosity of cathode is designed by the distribution of sphere-shaped pores. The sphere-shaped pore has 60 nm of diameter and the porosity is varied according to the total number of pores in the cathode. The simulations are performed until the completion of discharge. The fully discharged state is assumed by that the fraction of \( \omega \) phase in the cathode becomes 1% of total volume of cathode because LIB commonly stops operation when the \( \omega \) phase is generated to avoid the increase of irreversible \( \omega \) phase. The fully charged state is assumed by that the concentration of Li-ion at the surface of cathode becomes zero because the chemical reaction for charging process is terminated when Li-ion does not exit at the cathode surface.

3. Results and discussions

To analyze the performance of cathode with porosity, the difference in the porosity of cathode are systematically investigated. The numerical simulations are performed using a simulation platform for battery materials (iBat alpha; Korea Institute of Science and Technology).

Figure 2. Cross-sectional images of time-dependent Li-ion concentration and \( \epsilon \) phase fraction in the simple sphere-shaped cathode and the cathode with 50% porosity under 10C.

Figure 2 shows the cross-sectional images of time-dependent Li-ion concentrations and the fraction of \( \epsilon \) phase during the discharging process, where the simple sphere-shaped cathode and the 50% porosity of cathode are considered. The C-rate is set to be 10C. In the simple sphere-shaped cathode, Li-ion is stagnated at the out side of \( \epsilon \) phase due to its unusually low diffusivity. The \( \epsilon \) phase still
remains until the discharging process is finished. As a result, the cathode has an unutilized part and it lead to the loss of specific capacity. On the other hand, since the 50% porosity provides the significantly increased surface area of cathode and reduced diffusion pathway of Li-ion into the cathode, the cathode with porosity is less affected by the low diffusivity of ε phase. Indeed, the ε phase is transformed to the next phase that has usual diffusivity of Li-ion before the discharging process is finished and it is not observed at the final stage. Thus, the porosity in the cathode allows the full utilization of cathode.

![Cross-sectional images of time-dependent Li-ion concentration and ε phase fraction](image.png)

**Figure 3.** Cross-sectional images of time-dependent Li-ion concentration and ε phase fraction in the simple sphere-shaped cathode and the cathode with 50% porosity with C-rate 2.5 and 20C.

Additionally, the effect of porosity on the specific capacity was investigated with respect to the C-rates, where the C-rate increases from 2.5 to 20 (Figure 3). As shown in Figure 3, at the low C-rate (i.e., 2.5C ), Li-ion can diffuse into the cathode even without the porosity. Since the supplying rate of Li-ion at 2.5C is sufficiently small, it allows the transformation of ε phase to the next phase before the discharging process is finished. As a result, the cathode even with the simple sphere-shape can be fully utilized with the less affection of low diffusivity of ε phase. If the supplying rate of Li-ion is to be much bigger as the C-rate increases (i.e., 20C), Li-ion is rapidly stagnated at the outside of ε phase. The ε phase remains until the discharge is finished and it result in the insufficient utilization of cathode. On the other hand, Li-ion can diffuse more effectively into the cathode with 50% porosity. Due to the significantly increased surface area and reduced pathway of diffusion, the porous cathode is less affected by the ε phase than the simple sphere-shaped cathode under the same C-rate. As a result, the cathode with porosity can be fully utilized even under high C-rate condition.

A quantitative analysis on the specific capacity with different porosity in cathode was performed (data not shown). The specific capacity mostly increases as the porosity in cathode increases and the effect of porosity becomes significant as the C-rate increases. The cathode with the 50% porosity shows the 220% of improved specific capacity at the 40 C-rate condition. In addition, the high rate capability of the cathode was observed with porosity. For example, the loss of specific capacity is dramatically reduced to be only about 20 % when the porosity in cathode is 50%, while the simple sphere-shaped cathode shows about 60% loss of specific capacity. About 300% of reduction in the loss of specific capacity when the porosity is considered in the cathode means that the design of porosity in the cathode could resolve the severe loss of specific capacity of LIBs according to the increase of C-rate.
Figure 4. Effect of pore distribution on the specific capacity of cathode. (a) Maximum (triangle) and minimum (reverse triangle) specific capacities among the 15 different kinds of porous cathode at each porosity with 2.5 (red), 10 (black), and 40 (blue) C-rate condition, respectively. (b) Image of the 30% porosity in the cathode and Li-ion concentration for maximum and minimum specific capacity. Red circle, pores-concentrated region.

Next, the performance according to the distribution of pores in the cathode is investigated with 2.5, 10, and 40 C-rate conditions, respectively. 15 different kinds of porous cathode are designed for each porosity. In same porosity, 15 different kinds of cathode has the difference in only distribution of pores, not total number of pores. All of pores are randomly distributed in every porous structure. Among the specific capacities of each porous cathode, the maximum (i.e., triangle) and minimum (i.e., reverse triangle) specific capacities are presented in Figure 4a. Red, black, and red lines are the specific capacities at the 2.5, 10, and 40 C-rate, respectively. Dashed lines represent the specific capacity of simple sphere-shaped cathode at each C-rate. Simulation reveals that the porous cathode have the considerable variation of the specific capacity according to the distribution of pores, which is up to 16% of variation. Interestingly, the specific capacity can be decreased irrespective of c-rate even with the porosity in cathode unless the pores are evenly distributed. Qualitatively, the cathode with well-distributed pores has higher Li-ion concentration than the cathode with uneven distribution of pores (Figure 4b). This result can be explained by that the pores-concentrated region (i.e., red circles in the morphological image of cathode) results in the restrictive use of cathode material. Namely, Li-ion is extremely intercalated at the pores-concentrated region due to the excessively decreased pathway of diffusion into the cathode and the $\varepsilon$ phase is generated much earlier than other regions. Li-ion is increasingly stagnated where $\varepsilon$ phase is generated due to significantly low diffusivity of Li-ion.
and thus, the discharging process is terminated without full utilization of the cathode. It means that the design of porosity in cathode might become important to achieve ultrahigh performance of LIBs because the design of porosity can provide the ultrahigh specific capacity of cathode or even worsened specific capacity as the porosity increases.

4. Conclusion
In summary, we have reported the importance of the design of porosity in cathode, which may provide an ultrahigh specific capacity with the porosity or even worsened specific capacity as the porosity increases. Simulation represents that the cathode with the porous cathode can have higher specific capacity than the simple sphere-shaped cathode and the effect of porosity on specific capacity becomes great as the C-rate increases. The rate capability and the cycle stability are improved with the porosity in cathode. As the C-rate increases from 2.5 to 40, the specific capacity loss is reduced to be only about 20% with 50% porosity in the cathode, while the simple sphere-shaped cathode shows about 60% loss of specific capacity. In addition, the loss of specific capacity during total cycles is only about 2% when the porosity in cathode is 50%, while the simple sphere-shaped cathode shows about 30% loss of specific capacity. Interestingly, the porous cathode might have the degenerated specific capacity than the simple sphere-shaped cathode unless the pores are evenly distributed. We expect that the presented analysis on the structural design of cathode can provide an efficient way for the ultrahigh performance Li-ion battery as an advanced power source.

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