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Predicted Discharge Rate for γ/β-MnO_2 versus λ-MnO_2

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Contents

Figure

Recently, λ-MnO_2 has been proposed as an alternative cathode to γ/β-MnO_2 in Li/MnO_2 primary batteries [1]. One suggested advantage of λ-MnO_2 over γ/β-MnO_2 is its faster discharge rate at both room and low temperatures [1]. For the MnO_2 cathode, its discharge rate I is a function of its lithium diffusivity D and particle size d:

$$I \alpha D/d \ . \tag{1}$$

Equation (1) shows that increasing lithium diffusivity and/or decreasing the particle size leads to an increase in the discharge rate. Equation (1) also shows that if two different materials of the same particle size have a difference in discharge rates for the same experimental conditions (i.e., electrolyte), this difference must result from the difference in their D values. In this note, my goal is to determine whether a switch from a γ/β-MnO_2 cathode to a λ-MnO_2 cathode causes an increase in the discharge rate in the Li/MnO_2 system, as a result of a difference in the diffusivity D of the two materials. This comparison is made at room temperature only, since no low-temperature data for D in γ/β-MnO_2 or λ-MnO_2 currently exist.

Lithium diffusivity in γ-MnO_2 [2,3], β-MnO_2 [3], and λ-MnO_2 [4] at room temperature is plotted in figure 1. The figure includes, for λ-MnO_2, a data point at 3×10^{-11} cm^2/s (which was measured for $LiMn_2O_4$ [5]) and one at 4×10^{-11} cm^2/s (measured for $Li_{0.4}MnO_4$ [6]). These two points are plotted for λ-MnO_2 because $Li_xMn_2O_4$ has the same structure as λ-MnO_2 [7,8], and Guyomard and Tarascon [4] have shown that the diffusion coefficient of lithium in $Li_xMn_2O_4$ is independent of lithium composition x, for x from 0 to 1. Thus, the D values shown in figure 1 for $LiMn_2O_4$ ($x = 1$) and $Li_{0.4}MnO_4$ ($x = 0.4$) should correspond to lithium diffusivity in λ-MnO_2 ($x = 0$). The figure also includes lithium diffusivity values for γ-MnO_2 and β-MnO_2 produced from acid digestion of $LiMn_2O_4$ (filled symbols) [3].

Figure 1 suggests several important points. First, D in γ-MnO_2 is greater than D in β-MnO_2 (about a factor of 5 higher, if we consider only the open symbols). This is expected because the number of (2×1) channels decreases as the MnO_2 structure transforms from γ to β [8–10]. It has been suggested that lithium diffusivity is faster in the (2×1) channels than in (1×1) channels [10]. Hence, lithium diffusivity should decrease as the number of (2×1) channels decreases, which agrees with the data shown in figure 1. A similar trend is also observed in γ-MnO_2 and β-MnO_2 produced from acid digestion of $LiMn_2O_4$ (filled symbols).

A second observation from figure 1 is that two of the data points for λ-MnO_2, although from different research groups [5,6], are in excellent agreement with each other. However, there is a significant difference in D (about a factor of 25 to 30) between these data and the third data point (from Guyomard and Tarascon [4]). Reasons for this difference are not yet known. Since lithium diffusivity can be affected by impurities, it may be

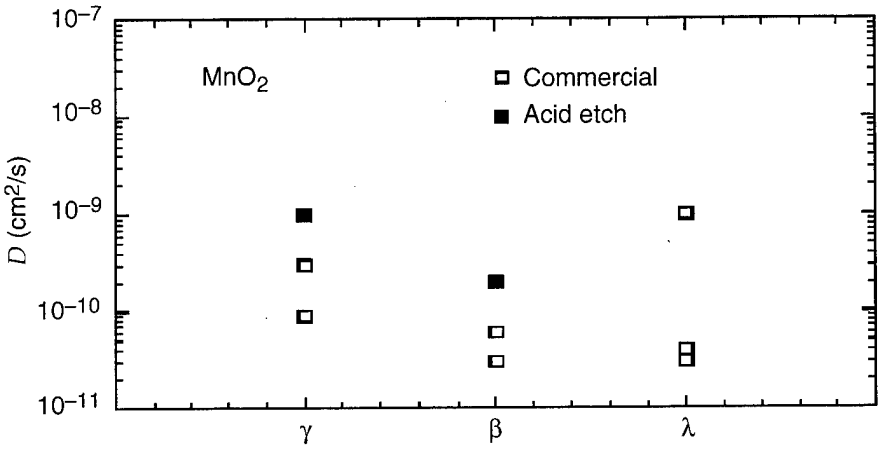

Figure 1. Lithium diffusivity in γ-MnO_2 [2,3], β-MnO_2 [3], and λ-MnO_2 [4–6] at room temperature.

that material variations account for this difference [8]. However, the impurities and concentration for the three different materials were not given, so this suggestion cannot be confirmed.

The data in figure 1 can be used to determine whether (at room temperature) an increase in the discharge rate in Li/MnO_2 batteries is likely to occur as a result of a switch from γ/β-MnO_2 to λ-MnO_2 cathodes. The currently used γ/β-MnO_2 is a combination of γ-MnO_2 and β-MnO_2. Diffusivity D for γ/β-MnO_2 (open symbols) is about 1×10^{-10} cm^2/s. (This value is based on a 50 vol.%γ-MnO_2 and 50 vol.% β-MnO_2 mixture.) I compare D for γ/β-MnO_2 (1×10^{-10} cm^2/s) to two values of D for λ-MnO_2: 4×10^{-10} and 1×10^{-9} cm^2/s. (I choose these two values because of the discrepancy in the data forλ-MnO_2, discussed earlier.) If $D = 4 \times 10^{-10}$ cm^2/s for λ-MnO_2, the value for γ/β-MnO_2 is about 2.5× higher: $D = 1 \times 10^{-10}$ cm^2/s. Thus, according to equation (1), a *decrease* in the discharge current is predicted if λ-MnO_2 is used instead of γ/β-MnO_2 of equal particle size. If $D = 1 \times 10^{-9}$ cm^2/s for λ-MnO_2, the value of D of γ/β-MnO_2 is about 10× lower: 1×10^{-10} cm^2/s. In this case, according to equation (1), changing from γ/β-MnO_2 to λ-MnO_2 of the same particle size will lead to a maximum *increase* in the discharge rate of about an order of magnitude. Unfortunately, without more experimental data for λ-MnO_2, it is impossible to determine which is the correct D value for λ-MnO_2. In any case, the results reveal that the maximum increase in discharge rate at room temperature that can be achieved by switching from γ/β-MnO_2 to λ-MnO_2 of the same particle size is about an order of magnitude.

A third observation from figure 1 is that γ-MnO_2 and β-MnO_2 produced from acid digestion (filled symbols) have a higher lithium diffusivity than γ-MnO_2 and β-MnO_2 produced by standard commercial methods (open symbols). Figure 1 shows that for both γ-MnO_2 and β-MnO_2, the D values for these materials when produced by acid digestion is higher than the D values when they are prepared by commercial methods. Among several possible explanations for this observation are differences in impurities

and in structural water content. Since the impurities and their concentrations are not given, I cannot address this possibility. However, we know that the structural water content for the materials formed by acid digestion is about a factor of 10× lower than that for the materials prepared by commercial methods [3]. It is possible that the removal of structural water leads to more sites for lithium to occupy and move to and hence a higher D. More experimental work is required to confirm this suggestion. In any case, since γ-MnO_2 and β-MnO_2 produced by acid digestion have a higher D than commercially prepared γ-MnO_2 and β-MnO_2, acid digestion may be a method of increasing the D in MnO_2. One could speculate that λ-MnO_2 prepared from acid digestion of $LiMn_2O_4$ will also exhibit a higher D than λ-MnO_2 prepared by the more common electrochemical titration of $LiMn_2O_4$ (the method used to prepare the λ-MnO_2 shown in figure 1 [4]). At present, no low-temperature data for D in γ/β-MnO_2 or λ-MnO_2 exist, and hence no comparisons can be made.

The results of the comparisons presented here suggest the following:

(1) Switching from γ/β-MnO_2 to λ-MnO_2 of equal particle size will lead to a maximum increase in the discharge rate at room temperature of about an order of magnitude.

(2) More experimental data at both room and low temperatures are needed for D in γ/β-MnO_2 and λ-MnO_2 before we can accurately predict whether an increase in discharge rate will occur as a result of switching from γ/β-MnO_2 to λ-MnO_2 in the Li/MnO_2 system.

(3) When formed by acid digestion, γ-MnO_2 and β-MnO_2 have a higher D and hence a faster discharge rate than when produced by commercial methods. This difference may be a result of the lower structural water content in materials formed by acid digestion.

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Recently, λ-MnO_2 has been proposed as an alternative cathode to γ/β-MnO_2 in Li/MnO_2 primary batteries because of its potential faster discharge rate. The results presented here suggest that (1) switching from γ/β-MnO_2 to λ-MnO_2 of equal particle size will lead to a maximum increase in the discharge rate at room temperature of about an order of magnitude and (2) when formed by acid digestion, γ-MnO_2 and β-MnO_2 have a higher lithium diffusivity and hence a faster discharge rate than when they are produced by the usual commercial means, a difference that may result from the lower structural water content in the materials produced by acid digestion.

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