

ARMY RESEARCH LABORATORY



Predicted Discharge Rate for γ/β -MnO₂ versus λ -MnO₂

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Contents

References	4
Distribution	5
Report Documentation Page	7

Figure

1. Lithium diffusivity in γ -MnO ₂ , β -MnO ₂ , and λ -MnO ₂ at room temperature	2
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Recently, λ -MnO₂ has been proposed as an alternative cathode to γ/β -MnO₂ in Li/MnO₂ primary batteries [1]. One suggested advantage of λ -MnO₂ over γ/β -MnO₂ is its faster discharge rate at both room and low temperatures [1]. For the MnO₂ cathode, its discharge rate I is a function of its lithium diffusivity D and particle size d :

$$I \propto D/d \quad (1)$$

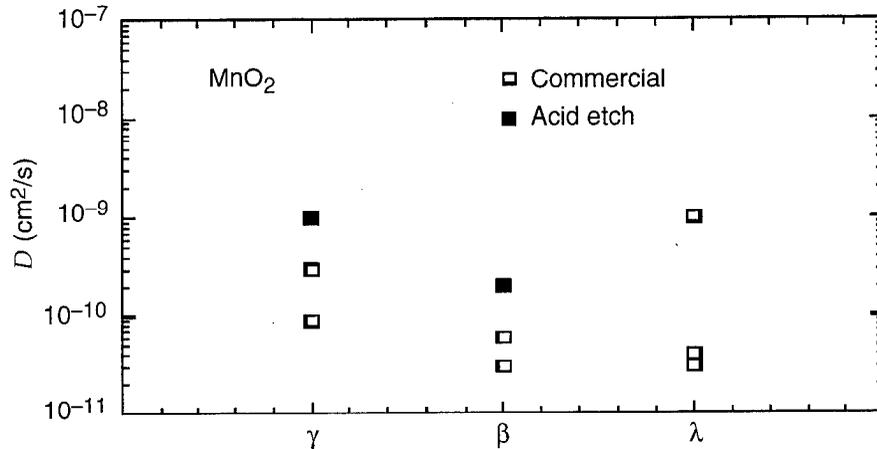
Equation (1) shows that increasing lithium diffusivity and/or decreasing the particle size leads to an increase in the discharge rate. Equation (1) also shows that if two different materials of the same particle size have a difference in discharge rates for the same experimental conditions (i.e., electrolyte), 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 -MnO₂ cathode to a λ -MnO₂ cathode causes an increase in the discharge rate in the Li/MnO₂ 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 -MnO₂ or λ -MnO₂ currently exist.

Lithium diffusivity in γ -MnO₂ [2,3], β -MnO₂ [3], and λ -MnO₂ [4] at room temperature is plotted in figure 1. The figure includes, for λ -MnO₂, a data point at 3×10^{-11} cm²/s (which was measured for LiMn₂O₄ [5]) and one at 4×10^{-11} cm²/s (measured for Li_{0.4}MnO₄ [6]). These two points are plotted for λ -MnO₂ because Li _{x} Mn₂O₄ has the same structure as λ -MnO₂ [7,8], and Guyomard and Tarascon [4] have shown that the diffusion coefficient of lithium in Li _{x} Mn₂O₄ is independent of lithium composition x , for x from 0 to 1. Thus, the D values shown in figure 1 for LiMn₂O₄ ($x = 1$) and Li_{0.4}MnO₄ ($x = 0.4$) should correspond to lithium diffusivity in λ -MnO₂ ($x = 0$). The figure also includes lithium diffusivity values for γ -MnO₂ and β -MnO₂ produced from acid digestion of LiMn₂O₄ (filled symbols) [3].

Figure 1 suggests several important points. First, D in γ -MnO₂ is greater than D in β -MnO₂ (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 MnO₂ 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 -MnO₂ and β -MnO₂ produced from acid digestion of LiMn₂O₄ (filled symbols).

A second observation from figure 1 is that two of the data points for λ -MnO₂, 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 -MnO₂ [2,3], β -MnO₂ [3], and λ -MnO₂ [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/MnO₂ batteries is likely to occur as a result of a switch from γ/β -MnO₂ to λ -MnO₂ cathodes. The currently used γ/β -MnO₂ is a combination of γ -MnO₂ and β -MnO₂. Diffusivity D for γ/β -MnO₂ (open symbols) is about 1×10^{-10} cm²/s. (This value is based on a 50 vol.% γ -MnO₂ and 50 vol.% β -MnO₂ mixture.) I compare D for γ/β -MnO₂ (1×10^{-10} cm²/s) to two values of D for λ -MnO₂: 4×10^{-10} and 1×10^{-9} cm²/s. (I choose these two values because of the discrepancy in the data for λ -MnO₂, discussed earlier.) If $D = 4 \times 10^{-10}$ cm²/s for λ -MnO₂, the value for γ/β -MnO₂ is about 2.5× higher: $D = 1 \times 10^{-10}$ cm²/s. Thus, according to equation (1), a decrease in the discharge current is predicted if λ -MnO₂ is used instead of γ/β -MnO₂ of equal particle size. If $D = 1 \times 10^{-9}$ cm²/s for λ -MnO₂, the value of D of γ/β -MnO₂ is about 10× lower: 1×10^{-10} cm²/s. In this case, according to equation (1), changing from γ/β -MnO₂ to λ -MnO₂ 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 -MnO₂, it is impossible to determine which is the correct D value for λ -MnO₂. 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 -MnO₂ to λ -MnO₂ of the same particle size is about an order of magnitude.

A third observation from figure 1 is that γ -MnO₂ and β -MnO₂ produced from acid digestion (filled symbols) have a higher lithium diffusivity than γ -MnO₂ and β -MnO₂ produced by standard commercial methods (open symbols). Figure 1 shows that for both γ -MnO₂ and β -MnO₂, 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 $10\times$ 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 $\gamma\text{-MnO}_2$ and $\beta\text{-MnO}_2$ produced by acid digestion have a higher D than commercially prepared $\gamma\text{-MnO}_2$ and $\beta\text{-MnO}_2$, acid digestion may be a method of increasing the D in MnO_2 . One could speculate that $\lambda\text{-MnO}_2$ prepared from acid digestion of LiMn_2O_4 will also exhibit a higher D than $\lambda\text{-MnO}_2$ prepared by the more common electrochemical titration of LiMn_2O_4 (the method used to prepare the $\lambda\text{-MnO}_2$ shown in figure 1 [4]). At present, no low-temperature data for D in $\gamma/\beta\text{-MnO}_2$ or $\lambda\text{-MnO}_2$ exist, and hence no comparisons can be made.

The results of the comparisons presented here suggest the following:

- (1) Switching from $\gamma/\beta\text{-MnO}_2$ to $\lambda\text{-MnO}_2$ 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 $\gamma/\beta\text{-MnO}_2$ and $\lambda\text{-MnO}_2$ before we can accurately predict whether an increase in discharge rate will occur as a result of switching from $\gamma/\beta\text{-MnO}_2$ to $\lambda\text{-MnO}_2$ in the Li/MnO_2 system.
- (3) When formed by acid digestion, $\gamma\text{-MnO}_2$ and $\beta\text{-MnO}_2$ 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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