

Rapid Discharge Properties of Manganese Oxide Synthesized by Sol-gel Method

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In recent years, needs to the battery that rapid electric discharge lasts for a long time have been risen due to the diffusion of the hybrid electric vehicle or toward the realization of distributed power generation system. In other words, it is required that batteries both with the high energy density and the high power density are developed.

Because lithium ion batteries have enough high specific capacity, if they can acquire the ability for high power use, they can be leading candidates. For that sake, electrode that allows large discharging current must be developed. From this viewpoint, we considered following points as a manner of electrode materials choice. 1. The material can be intercalated by lithium. Thus, oxides of the transition metal were taken. 2. The material should be lightweight. Thus the fourth period transition metal oxide was taken. 3. the lithium diffusion distance should be short. To this, we need to prepare materials in the form of small particle. 4. Small internal resistance is required for battery operation under large current. To this, material itself has high electronic conductivity or can be favorably mixed with conductive additive such as acetylene black. On the ground of above, we determined to fabricate manganese oxides or their hydrate by sol-gel method and combine them properly with AB. Many manganese oxides are known well as lithium intercalation materials, for example lithium containing crystal such as spinel type LiMn_2O_4 , many types of MnO_2 such as beta, epsilon, lambda - phase and so on and still many crystalline and amorphous hydrates. As for synthesis by sol-gel method, the way where permanganate ion is reduced in their solution by appropriate reducing agents is often adopted. We also employed this method and used sodium fumarate, manganese nitrate or ethanol as a reducing agent.

Sodium permanganate monohydrate was dissolved in distilled water. Perchloric acid was portioned in that solution for keeping the pH low. Reducing reagent was added to above solution. In the case of ethanol, another route was also tried. Acetylene black (AB) was dispersed in distilled water which ethanol was beforehand added. to. The amount of AB was varied from 0.25 to 3.0 (in terms of the weight ratio of AB/active material) in order to optimize performance in rapid discharge of electrode. These two liquids, one was permanganate solution and the other AB dispersion, were mixed and kept stirring for 18 h. After filtration, thermal treatment at 120 C for 3 hours was done.

The electrodes for discharge-charge test were prepared as following: The mixture of the powder obtained as above, AB and Teflon (100:100:2, wt ratio) was ground in a mortar agate and spread on nickel mesh (100 mesh). If AB was added in the synthetic procedure, only Teflon was added without AB. The reference and counter electrodes were both lithium metal pressed on nickel mesh. 1 M lithium perchlorate of EC+DME (1:1) solution was used as an electrolyte. The discharge-charge test was performed under from 0.01 to 10 A/g. Here, the weight was based on the active material. The discharge-charge

was performed between 1.5 V and 4.3V (vs. Li^+/Li) at constant current.

Xrd patterns of all samples showed broad peaks that could be attributed to birnessite. The samples that AB was added in the synthesis had superimposed diffraction patterns of AB and birnessite. The content of sodium in each sample was below 0.05 of Na/Mn (molar ratio), typically 0.01~0.02. That is probably caused by the ion exchange of sodium ion for proton due to low pH, even if the phase containing sodium more than above generated.

Figure 1 shows the discharge curves for samples synthesized using various reducing agents under 0.1 A/g-[active material]. The weight used for standardization is, hereafter, that of active material without AB. All curves possesses regions with slow slope around 2.8 V vs. Li^+/Li , which ascribed to the reduction from Mn^{4+} to Mn^{3+} . Only the sample that synthesized using ethanol and AB (AB/active material=1/1 wt ratio) showed large capacity below 2 V and totally above 300 mAh/g.

The specific capacity of the 1st discharge against discharge current is plotted in fig. 2. The specimen synthesized using ethanol and AB has larger capacity that the others and hold 157 mAh/g even under large current of 10A/g. It was considered that such a good performance of rapid discharge resulted from the contribution of capacity appeared below 2 V and may be also due to the structure of composite in which the contact condition of constituents was favorable.

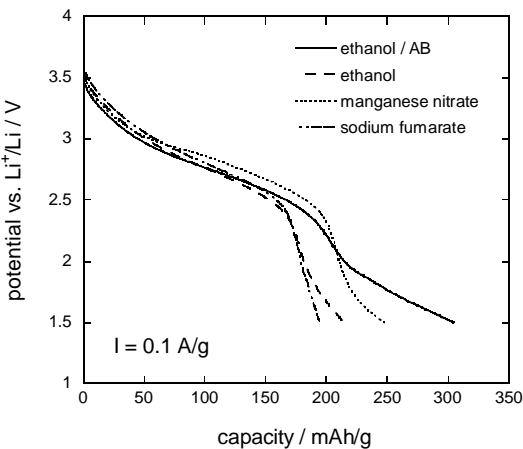


Fig. 1 Initial discharge curves for manganese oxides obtained by various reducers.

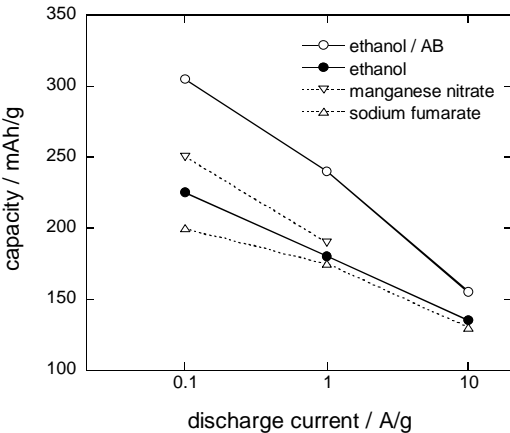


Fig. 2 Relationship between capacities and current density for manganese oxide samples.