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Effect of ultrasound irradiation on deposition of Au nanoparticles on carbon coated cathode material

カーボン被覆した正極材料への金ナノ粒子担持における超音波照射の効果

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1. Introduction

Lithium ion battery is used in electeric vehicle because it has high energy density. Main cathode material used in lithium ion battery is $LiCoO_2$ which shows the high discharge voltage of 3.7 V vs Li/Li^+. Recently, cathode materials consisted of Fe, Ni and Mn have been studied as an alternative of $LiCoO_2$. However, electronical conductivity of them is lower than that of $LiCoO_2$ (1.0×10^{-3} S/cm)[1)]. Therefore, they have not been used effectively as cathode materials. Morales et al. performed that carbon or Au nano particles (Au NPs) were coated on the surface of $LiFePO_4$ (LFP) to improve the electronical conductivity[2)]. The discharge capacity of carbon coated LFP (LFP/C) was improved. Au NPs coated LFP showed the improvement of the electrical conductivity. However, the discharge capacity of Au NPs coated LFP did not show enough improvement of battery performance. It was considered that Au NPs coated on the surface of LFP interrpted the intercalation and deintercalation of lithium ion at discharge and charge. Saliman et al. reported that Pd nanoparticles (Pd NPs) deposited on the surface of carbon layer of carbon coated LFP (LFP/C·Pd) was synthesized using sonochemical reaction[3)]. Pd NPs formed agglomerations and they were deposited on the surface of carbon layer of LFP/C. Dispersion of the aggregates was even and the size of the aggregates was around 20–40 nm. This mehod does not cover the whole surface of LFP by Pd NPs. Therefore, the discharge capacity of LFP/C·Pd was drastically improved and it showed twice the capacity of LFP/C at high current rate of 10 C. In this study, we investigated effect of sonochemical reaction on the synthesis of Au NPs on the carbon layer of LFP/C and evaluated the battery performance of it.

2. Experiment

LFP/C, which is coated by 2 wt% of acetylene black carbon, was used as an active cathode material. **Fig. 1** shows experimental apparatus of ultrasound synthesis of LFP/C·Au. LFP/C (0.1 g) or acetylene black (AB) (2 mg) were added into mixed solution of ion exchange water (35 mL) and 2-propanol (5 mL, 99.7%) followed by argon (Ar) gas flow (100 mL/min) into the solution to purge air. Au (III) solution was added into the solution from the top of the reaction vessel using an injector and the solution was stirred at 500 rpm or irradiated by ultrasound (200 kHz, 200 W) for 20 min under Ar atmosphere. The solution temperature during ultrasound irradiation was controlled at 20–30°C using water bath. The size and morphology of Au NPs deposited on the surface of LFP/C were observed using TEM. Deposition ratio of Au particles was decided by measurement of Au concentration in the filtrate using an inductively coupled plasma (ICP).

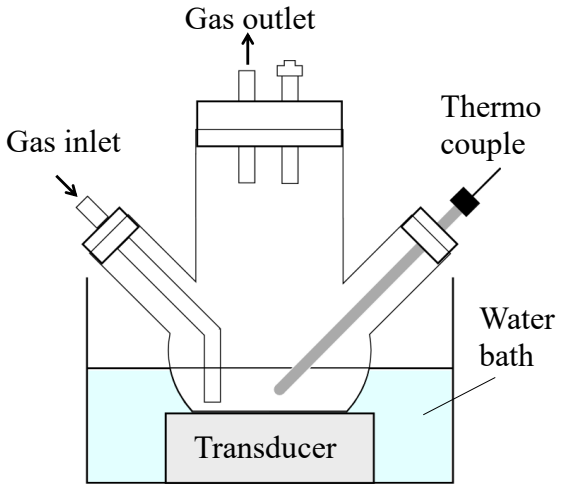

Fig.1 Schematic of the experimental apparatus

3. Results and discussions

The standard redox potential of Au, 2-propanol and LFP were given below.

$Au^{3+} + 3e^- = Au$ +1.52 V vs SHE (1)
$CH_3COCH_3 + 2H^+ + 2e^- = CH_3CH(OH)CH_3$ +0.33 V vs SHE (2)
$FePO_4 + Li^+ + e^- = LiFePO_4$ +0.41 V vs SHE (3)

From these values of redox potential, LFP and 2-propanol can reduce Au (III) ion to Au, in theory. 2-propanol solution containing LFP/C could reduce Au (III) ion to Au. Moreover, the deposition ratio of Au particles on LFP/C was about 100% which was higher than that of Au particles on AB, about 10%. This result indicates that the reduction rate of Au (III) ion by LFP/C and 2-propanol is higher than that by AB and 2-propanol. Next, we investigated the effect of 2-propanol on deposition of Au NPs on the carbon layer of LFP/C. The solution containing Au (III) ion and LFP/C was stirred without addition of 2-propanol. **Fig. 2** shows the TEM image of LFP/C after stirring treatment. It can be assumed that electron is released from LFP and it reduced Au (III) ion to Au NPs through carbon layer of LFP/C because carbon is a good electric conductor. The size of synthesized Au NPs was over 10 nm and the morphology was not uniform and not spherical. On the other hands, in the presence of 2-propanol, the size was 10 nm and the morphology was spherical (**Fig. 3**). The inhibition of particle growth attributed enhancement of reduction rate of Au ion by 2-propanol. According to deposition ratios of Au NPs on carbon with and without LFP in the presence of 2-propanol, it became clear that reduction rate of Au (III) ion without LFP was low even if the presence of 2-propanol. However, once Au NPs were synthesized on the carbon layer of LFP/C, autocatalytic reaction of Au NPs can help oxidation of 2-propanol. Therefore, LFP helped the generation of Au NPs by the reduction of Au (III) ion in the solution containg 2-propanol. Thus, the particle growth of Au NPs was inhibited under stirring with 2-propanol and LFP/C. Finally, we investigated the effect of ultrasound on the size and morphology of Au NPs deposited on LFP/C in the presence of 2-propanoal. TEM image of Au NPs deposited LFP/C was shown in **Fig. 4**. The particles were deposited evenly on the surface of LFP/C and the size was about 10 nm which is the almost same of the size of Au NPs synthesized by stirring with 2-propanol. Ultrasound can generate organic radical in the solution containing alcohol. This organic radical is known as a reducing agent and it can reduce Au (III) ion to Au NPs[4]. Thus, we considered that Au NPs generated under ultrasound irradition were dispersed because reduction rate of Au(III) ion was enhanced by organic radical. We will make a presentation about the effect of ultrasound on deposition of Au NPs on the various carbon particles and the evaluation of battery performance of LFP/C·Au synthesized using ultrasound or stirring in the presence of 2-propanol.

References

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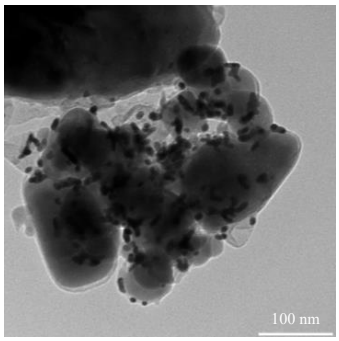

Fig.2 LFP/C·Au synthesized using stirring in the absence of 2-propanol.

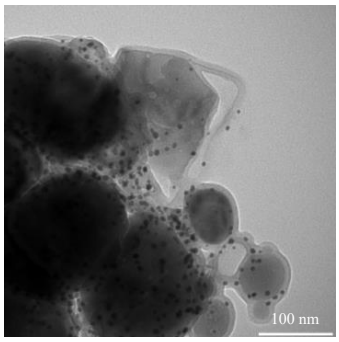

Fig.3 LFP/C·Au synthesized using stirring in the presence of 2-propanol.

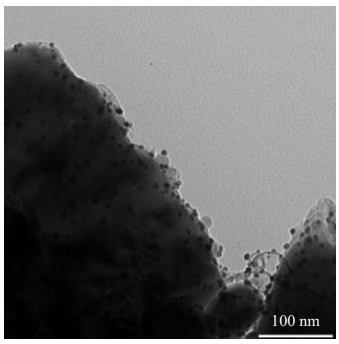

Fig.4 LFP/C·Au synthesized using ultrasound irradiation in the presence of 2-propanol.