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Sonochemical synthesis of Au/Pd nanoparticles on the surface of $LiFePO_4$/C cathode material for lithium-ion batteries
Au/Pd ナノ粒子を担持したリチウムイオン電池用正極材料 $LiFePO_4$/C のソノケミカル合成

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1. Introduction

Recently, $LiFePO_4$ (LFP) has been highly appreciated as the cathode material of lithium-ion battery for its high energy density, reasonable price, and less impact of use on the environment. LFP has relatively high theoretical capacity of 170 mAh/g. However, the electric conductivity and lithium-ion diffusivity are low. In order to solve these issues, miniaturization of LFP particles, carbon coating on LFP grains, and deposition of noble metal nanoparticles such as Au and Pd on LFP/C with dispersion have been studied[1)]. We have been studied to improve electrical conductivity of carbon coated cathode materials, LFP/C and $LiNi_{0.5}Mn_{1.5}O_4$/C, by deposition of Au nanoparticles (Au NPs) and Pd nanoparticles (Pd NPs) using sonochemical reaction[2)]. From the observation of these synthesized materials, Pd NPs are deposited on carbon coated LFP with agglomeration, Au NPs are inclined to monodisperse on the surface of carbon. Ultrasound irradiation is one of the ways to synthesize core-shell NPs in which Au has core structure and Pd has shell structure. In our best knowledge, there is no report about improvement of battery performance by deposition of Au/Pd core-shell NPs. Therefore, we tried to deposit Au/Pd core-shell NPs on carbon coated LFP. And we investigated the characteristics of Au/Pd NPs on LFP/C and evaluated the battery performance of Au/Pd NPs deposited LFP/C. Au, Pd, and Au/Pd NPs synthesized were identified using X-ray diffractometer (XRD) and an ultraviolet-visible (UV-vis) spectrometer.

2. Experimental

2.1 Synthesis of Au and Pd nanoparticles

At first, 45 mL of solution containing 35 mL of ion exchanged water and 10 mL of 13.0 M 2-propanol was prepared. And then dissolved air in the solution was purged with argon gas flow (100 mL/min) in a water bath of 5°C for 30 min. After that, 5 mL of 2.5 mM $PdCl_2 \cdot 2NaCl \cdot 3H_2O$ was added in the solution and ultrasound irradiation was carried out at a frequency of 200 kHz in argon atmosphere for 20 min. The reached power of ultrasound into the solution was calculated using calorimetric method and the values were 14.1–16.0 W. Pd(II) in the solution was monitored using UV-vis spectrometer. Experimental procedure of Au NPs synthesis was basically almost same as that of Pd. 45 mL of solution was prepared with 40 mL of ion exchanged water and 5 mL of 13.0 M 2-propanol. After the purge of dissolved air with argon gas, 5 mL of 2.5 mM $HAuCl_4 \cdot 4H_2O$ was added into the solution and ultrasonic irradiation was carried out for 20 min. Au(III) in the solution was monitored using UV-vis spectrometer.

2.2 Synthesis of Au/Pd nanoparticles

First, 40 mL of solution containing ion exchanged water and 13.0 M 2-propanol of 1 or 5 mL was prepared. And then dissolved air in the solution was purged with argon gas for 30 min. After that, 5 mL of 2.5 mM Au ion and 5 mL of 2.5 mM Pd ion were added and ultrasonic irradiation was carried out for 20 min. And then concentration of Au(III) and Pd(II) in the solution was monitored using UV-vis spectrometer. Next, acetylene black (AB) was added in the solution, and ultrasonic irradiation was carried out to confirm the deposition of Au/Pd NPs on carbon. After that, the carbon was filtered and dried under vacuum for 1 night. And the sample was heated at 300°C for 1 h in Ar atmosphere. The indentification of Au/Pd on carbon was characterized using XRD.

3. Result and Discussion

3.1 Synthesis of Au and Pd nanoparticles

At first, we investigated the appropriate time of sonication to synthesize Pd NPs. Pd (II) solution was irradiated at different times of 20 and 30 min,

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and the reduction of Pd(II) was confirmed using UV-vis spectrometer (**Fig. 1**). The result shows that all Pd(II) ion was absolutely reduced at least 20 min. Next, we monitored the change of absorbance peak of Au NPs around 563 nm under ultrasound irradiation with the lapse of time to confirm the reduction effect of ultrasound on the synthesis of Au NPs. **Fig. 2** shows that the peak around 563 nm has become largest at 30 min. As these results, we decided the sonication time of 20 to 30 min to synthesize Au/Pd NPs.

3.2 Synthesis of Au/Pd nanoparticles

At first, we investigated the most appropriate time to synthesize Au/Pd NPs. 50 mL of solution containing each of 0.25 mM Au(III) and 0.25 mM Pd(II), and 5 mL of 2-propanol was irradiated for 20 and 30 min. And Au(III) and Pd(II) in the solution were monitored using UV-vis spectrometer. **Fig. 3** shows that the peak around 563 nm which indicates the existence of Au NPs is confirmed at 20 min. However, the peak intensity became very low at 30 min. This result referred that Au/Pd NPs that have core-shell structure could be successfully synthesized. Next, we reduced the amount of 2-propanol from 5 mL to 1 mL and utilized ultrasound to synthesize Au/Pd NPs (**Fig. 4**). In this case, a peak of Au(III) was also low. Therefore, the most appropriate condition to synthesize Au/Pd NPs is that 1 mL of 2-propanol addition and 20 min of ultrasonic irradiation. While ultrasonic irradiation, the color of solution turned from yellow to red and changed to dark brown at the end. **Fig. 5** shows XRD patterns of Au/Pd NPs deposited carbon before and after heating at 300°C for 1h in Ar atmosphere. The result shows that the peak at 38.2°, which comes from Au, shifted to 39°. This shift indicates that Au/Pd NPs of core-shell structure changes to the random alloy. This peak shift supports that our synthesized Au/Pd NPs have core-shell structure.

4. Conclution

We have investigated the synthesis of Au/Pd NPs on carbon. And we have confirmed the most appropriate conditions to synthesize Au/Pd nanoparticles that could have core-shell structure.

References

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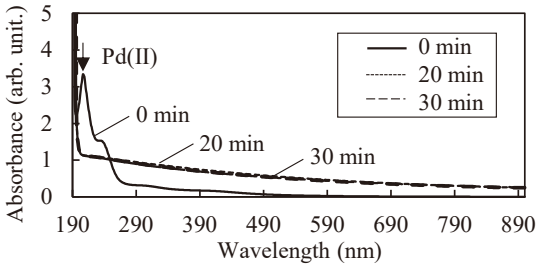

Fig. 1 UV-vis absorption spectra of Pd(II) after ultrasound irradiation for 0, 20 and 30 min.

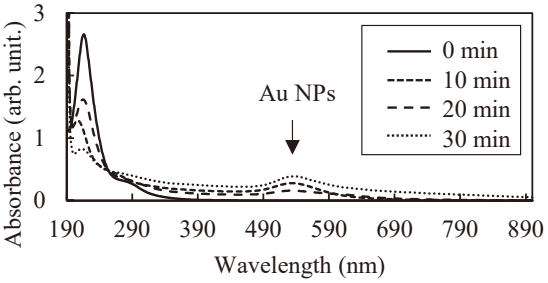

Fig. 2 UV-vis absorption spectra of Au(III) solutions after ultrasound irradiation for 0, 10, 20 and 30 min.

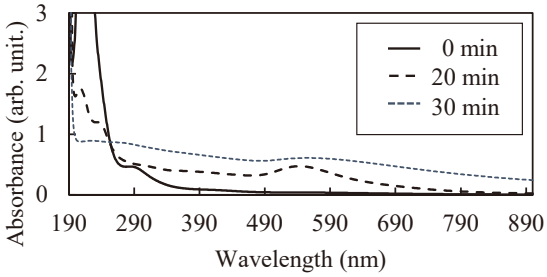

Fig. 3 UV-vis absorption spectra of Au(III)-Pd(II) solutions after ultrasound irradiation for 0, 20 and 30 min.

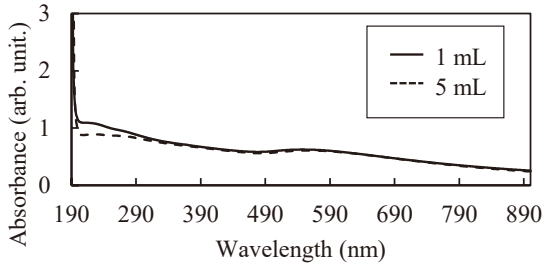

Fig. 4 UV-vis absorption spectra of Au(III)-Pd(II) solutions after ultrasound irradiation for 20 min with different amount of 2-propanol (1, 5 mL).

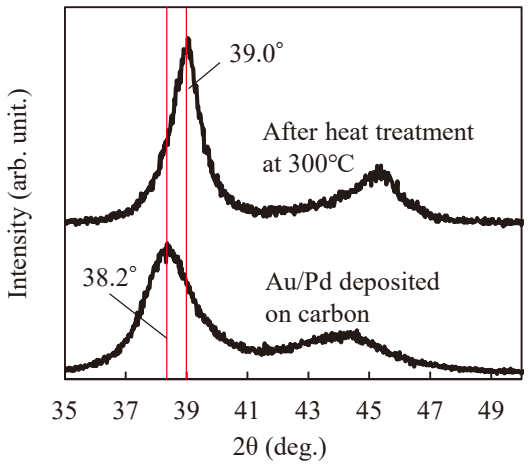

Fig. 5 XRD patterns of Au/Pd deposited carbon, before and after heating at 300ºC for 1h in Ar.