

## Improved battery performance using Pd nanoparticles synthesized on the surface of LiFePO<sub>4</sub>/C with ultrasound irradiation

電池特性改善を目的とした LiFePO<sub>4</sub>/C 上へのパラジウムナノ粒子の超音波合成とその電池特性

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### 1. Introduction

Recently, LiFePO<sub>4</sub> has been the center of many studies regarding cathode materials for Li ion battery due to its high energy density, low cost and friendliness to the environment. However, the true potential of this cathode material, that has a specific capacity as high as 170 mAh/g, cannot be completely utilized because of its low Li ion diffusion and poor electrical conductivity which limit its electrochemical performance. On the basis of this, numerous solutions to overcome these weakness, such as carbon coating, doping of metal nanoparticles and minimizing the nanoparticles sizes, have been studied.<sup>1,2)</sup> Carbon coating is a method that is well known and widely applied to improve the performance of LiFePO<sub>4</sub> due to its good electrical conductivity. Metal nanoparticles are also applied using the same concept as carbon coating due to its good electrical conductivity. In this study, to investigate the effect of Pd nanoparticles on the electrochemical performance, we deposited Pd nanoparticles on the surface of LiFePO<sub>4</sub>/C. The sonochemical method of metal nanoparticles synthesis was used in this study.<sup>3)</sup> The preparation of this procedure is simple because it doesn't require any stabilizer and it has a fast reaction time. The characteristics of Pd nanoparticles, regarding their amount, size and also shape, were carried out using an X-ray diffractometer (XRD), a transmission electron microscope (TEM) and an ultraviolet-visible (UV-vis) spectrophotometer.

### 2. Experimental method

#### 2.1 Synthesis of Pd nanoparticles

A solution (50 ml) containing 0.5 mM of Pd (II) was prepared by mixing 35 ml of ion exchanged water with 10 ml of 13.18 M 2-propanol and 5 ml of 5.0 mM PdCl<sub>2</sub>·2NaCl·3H<sub>2</sub>O. All the reagents were analytical grade and purchased from Wako

corp. (Japan). Ultrasound irradiation was carried out at a frequency of 200 kHz. The calorimetric power was calculated to be 8.4 W. First, the dissolved air in the solution was purged with argon gas flow (100 ml/min) for 30 min. Next, the solution was irradiated in a water bath (the temperature of water bath was maintained at 3-5 °C). The solution was irradiated for 20 min in argon atmosphere. The color of the solution changed from yellow to dark brown during ultrasound irradiation indicates that Pd (II) were reduced into Pd. The reduction of Pd (II) was monitored using UV-vis spectrophotometer.

#### 2.2 Synthesis of Pd nanoparticles on LiFePO<sub>4</sub>/C

Experimental procedure is almost same with that of Pd nanoparticles synthesis. Before the ultrasound irradiation, 0.1 g of LiFePO<sub>4</sub>/C was added into the solution including 2-propanol and PdCl<sub>2</sub>·2NaCl·3H<sub>2</sub>O. The solution was irradiated for 20 min in argon atmosphere. The size and shape of Pd nanoparticles after the deposition on the surface of LiFePO<sub>4</sub>/C was observed using TEM. The crystalline phase of LiFePO<sub>4</sub>/C·Pd was characterized using XRD. The composite cathode material for electrochemical tests were prepared by mixing 85% of test material (LiFePO<sub>4</sub>/C or LiFePO<sub>4</sub>/C·Pd), 8% of carbon black and 7% of polyvinylidene fluoride (PVDF). The slurry was cast onto aluminum foil and then dried in a vacuum oven at 75 °C for 10 h. The dried electrode was then pressed at a pressure of 10 MPa. The cells were assembled in an argon filled glove box with lithium metal as an anode, test material as a cathode, electrolyte and separator. The electrolyte used was LiPF<sub>6</sub> (1 M) in a 1:1 volume ratio of ethylene carbonate (EC) to dimethyl carbonate (DMC). The charge and discharge of the batteries were performed at different constant current rates at 0.5, 1.0, 3.0, 5.0 and 10 C (Cut off voltage during

charge-discharge was set between 2.0-4.0 V).

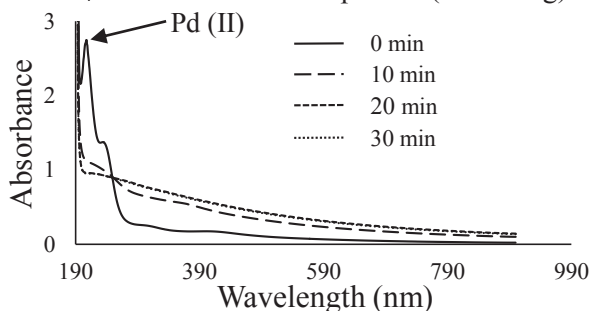
### 3. Result and discussion

#### 3.1 Synthesis of Pd nanoparticles

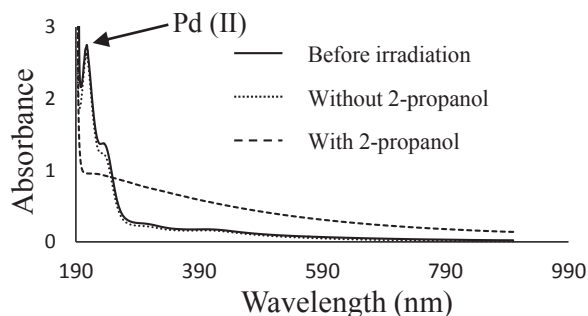
At first we investigated the effect of ultrasound irradiation time to the reduction amount of Pd (II). The solution was irradiated at different times (10, 20, 30 min) and the reduction of Pd (II) was confirmed using UV-vis spectrophotometer (Fig. 1). Result shows that at least 20 min is needed for Pd (II) to be completely reduced into Pd nanoparticles. Next, we investigated the reduction effect of alcohol during ultrasound irradiation. Synthesis of Pd nanoparticles was performed by irradiating Pd (II) in the solution with or without 2-propanol (Fig. 2). Pd (II) were greatly reduced in the solution containing 2-propanol but only slightly reduced in the solution without containing 2-propanol as shown by the disappearance of Pd (II) peak, indicating that 2-propanol enhanced the rate of formation of Pd nanoparticles.

#### 3.2 Synthesis of Pd nanoparticles on LiFePO<sub>4</sub>/C

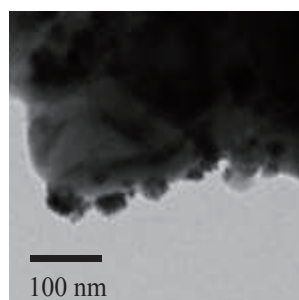
We investigated the size and shape of Pd nanoparticles synthesized on the surface of LiFePO<sub>4</sub>/C and the obtained samples were characterized using TEM (Fig. 3). The photo shows that Pd nanoparticles were agglomerated and the size of aggregate (secondary nanoparticles) was around 20-40 nm. The morphology of the secondary nanoparticles was spherical. Figure 4 shows the XRD patterns before and after the synthesized of Pd nanoparticles on the surface of LiFePO<sub>4</sub>/C. The structure of LiFePO<sub>4</sub> was kept after using ultrasound irradiation. However, after the deposition of Pd nanoparticles, the peak intensity decreases and impurity peaks were detected. The reason behind this was because during the synthesis of Pd nanoparticles, when LiFePO<sub>4</sub>/C was added into the solution containing Pd (II), LiFePO<sub>4</sub> acts as a reducing agent hence reducing the Pd (II) and as a result Fe (II) oxidizes to Fe (III) causing the formation of FePO<sub>4</sub>. The discharge capacity of LiFePO<sub>4</sub>/C-Pd at 10 C was improved (98 mAh/g).



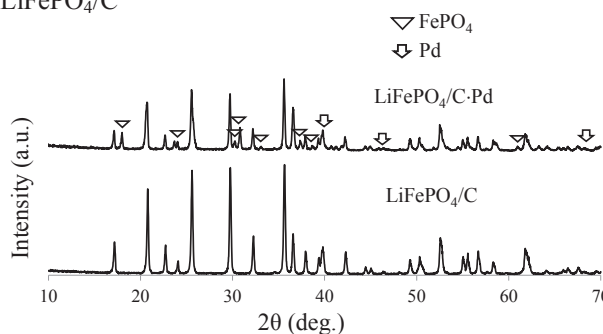
**Fig. 1** UV-vis absorption spectra of Pd (II) after ultrasound irradiation at different times (0, 10, 20, 30 min)



**Fig. 2** UV-vis absorption spectra of Pd (II) irradiated using ultrasound for 20 min with or without 2-propanol



**Fig. 3** TEM image of Pd nanoparticles on the surface of LiFePO<sub>4</sub>/C



**Fig. 4** XRD patterns of LiFePO<sub>4</sub>/C and LiFePO<sub>4</sub>/C-Pd

### 4. Conclusion

Pd nanoparticles were successfully synthesized on the surface of LiFePO<sub>4</sub>/C using ultrasound irradiation for a short time (20 min). Agglomeration of Pd nanoparticles were observed on the surface of LiFePO<sub>4</sub>/C. It is shown by TEM image that the size of the agglomerate was about 20 nm. Pd nanoparticles, that have good electrical conductivity, are effective in improving the electrochemical performance of LiFePO<sub>4</sub>.

### References

1. A. Örneç, and O. Efe: *Electrochimica Acta* **166** (2015) 338.
2. M. Chen, C. Du, B. Song, K. Xiong, G. Yin, P. Zuo, X. Cheng: *J. Of Power Sources* **223** (2013) 100.
3. K. Okitsu, A. Yue, S. Tanabe, H. Matsumoto, Y. Yobiko and Y. Yoo: *Bull. Chem. Soc. Jpn* **75** (2002) 2289.