

# Particle size effects of carbon sources on electrochemical properties of $\text{LiFePO}_4/\text{C}$ composites

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**Abstract** Carbon-coated  $\text{LiFePO}_4$  cathode materials were prepared by a solid-state method incorporating different sizes of polystyrene (PS) spheres as carbon sources. In scanning electron microscope images, small PS spheres appear more effective at preventing aggregation of  $\text{LiFePO}_4$  particles. From transmission electron microscopy images, it was found that the  $\text{LiFePO}_4$  particles were completely uniformly coated with 5-nm carbon layer when the carbon source was 0.22  $\mu\text{m}$  PS spheres. When the size of PS sphere was increased to 2.75  $\mu\text{m}$ , a network of carbon was formed and wrapped around the  $\text{LiFePO}_4$  to create a conductive web. Raman spectroscopy and four-point probe conductivity measurement showed that using larger sizes of PS spheres as carbon sources leads to greater conductivity of  $\text{LiFePO}_4/\text{C}$ . The  $\text{LiFePO}_4$  precursor sintered with 0.22  $\mu\text{m}$  PS spheres delivered an initial discharge capacity of 145  $\text{mAh g}^{-1}$  at a 0.2 C rate, but it only sustained 289 cycles at 80% capacity. When the diameter of PS spheres was increased to 2.75  $\mu\text{m}$ , the discharge capacity of  $\text{LiFePO}_4/\text{C}$  decreased, but the cycle life reached 755 cycles, the highest number in this work probably due to the network formation of carbon wrapping around  $\text{LiFePO}_4$  particles.

**Keywords** Li-ion batteries · Cathode material ·  $\text{LiFePO}_4/\text{C}$  · Carbon structure · PS sphere · Morphology

## Introduction

$\text{LiFePO}_4$  is a popular cathode material for high-power applications in electric vehicles (EVs) or power tools because of its low raw materials cost, environmental friendliness, superior thermal safety, and long operational life. Nevertheless,  $\text{LiFePO}_4$  suffers from low tap density, poor intrinsic electronic conductivity, and slow diffusion of lithium ions across the two-phase boundary. Strategies for overcoming these intrinsic limitations include particle size reduction [1, 2], carbon coating [3–6], metal doping [7–9], the addition of small metallic particles [10], and coating an ion-conducting surface phase of  $\text{Li}_4\text{P}_2\text{O}_7$  [11].

In recent years, many researchers have applied carbon coating to overcome low electronic conductivity. Various polymeric materials such as polypyrrole [12], polyacrylamide [13], poly(styrene-methylmethacrylate-acrylic acid) [14], polyacene [15], poly(3,4-ethylenedioxythiophene) [16], polyvinylbutyral [17], polyethylene glycol [18], and polyvinyl alcohol [19] have been used to optimize the effect of carbon coating on the cell performance of  $\text{LiFePO}_4$ . Based on our previous results, the electrochemical performance depends on many carbon coating factors such as the morphology of carbon coating [20], the particle size of the active material [21], the thickness of the carbon coating layer [22], the kind of conductive carbon network [23], and the surface area of the carbon precursor [24]. Doeff [25] also reported that more graphene clusters in the structure of carbon enhanced electronic conductivity of the residual carbon.

In this paper, we employed different sizes of polystyrene (PS) spheres as carbon sources to synthesize carbon-coated

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LiFePO<sub>4</sub> and study how sphere size affects the electrochemical properties of LiFePO<sub>4</sub>/C composites.

## Experimental

### Synthesis of PS spheres

The monodisperse PS spheres were prepared by dispersion polymerization. Styrene monomer was polymerized with 2,2'-azobis isobutyronitrile (AIBN; Showa, 99 wt.%) or potassium persulfate (KPS; Merck, 99 wt.%) as an initiator and poly(vinyl pyrrolidone) (PVP; Sigma-Aldrich, M.W.=40,000) as a stabilizer dispersed in an alcohol and water solution. Quantities of solvent and polymerization temperature were varied to obtain different sizes of PS spheres. Details of the dispersion polymerization are given elsewhere [26]. The diameters of PS spheres obtained were measured by scanning electron microscopy (SEM) to be 2.75, 1.50, 0.70, and 0.22 μm.

### Preparation of LiFePO<sub>4</sub>/C cathode materials

LiFePO<sub>4</sub> powder was prepared by a two-step solid-state reaction method. The reactants used were Li<sub>2</sub>CO<sub>3</sub> (Ferak, 99 wt.%), FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (Riedel-de Haën, 99 wt.%), and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (Showa, 99 wt.%). The starting materials were weighed in stoichiometric amounts, then mixed and ground well for 3 h using a planetary ball mill in acetone under an argon atmosphere with a rotation speed of 250 r.p.m. A quartz-tube furnace with flowing Ar/H<sub>2</sub> (vol. 95:5)

atmosphere was used to preheat the mixture. The heating rate was 4.2 K min<sup>-1</sup> and held at 593 K for 10 h. After cooling it down to room temperature at 3 K min<sup>-1</sup>, the gray LiFePO<sub>4</sub> precursor powder was obtained.

Different sizes of PS spheres were employed as carbon sources in the composite formation. Of PS spheres with different sizes, 50 wt.% were added to the LiFePO<sub>4</sub> precursor individually, mixed with a planetary ball mill for 1 h, and then the mixture was pressed into pellets. The final composite product was obtained by heating the pellets at 4.2 K min<sup>-1</sup> to 873 K for 12 h under purified Ar/H<sub>2</sub> (vol. 95:5) gas.

### Characterization

Measurements of the surface morphologies and particle sizes of PS spheres and LiFePO<sub>4</sub>/C powders were carried out on a Hitachi model S-3500 V SEM. The microstructures of the particles and the coated carbon were examined by a Hitachi, HF-2000 high-resolution transmission electron microscope (TEM) equipped with a LaB<sub>6</sub> gun. Raman spectroscopy (T64000, ISA) was used to analyze the carbon structure of the individual active materials in the range of 800–1,750 cm<sup>-1</sup>. The carbon contents in LiFePO<sub>4</sub>/C were examined by a solid total organic carbon OIA Model. The specific surface area of the samples was measured by means of the Brunauer, Emmett, Teller (BET) method (ASAP 2010 Analyzer). The conductivity was measured by four-point conductivity measurements on a Keithley Model 2400S source meter.

**Table 1** Raman spectral  $I_D/I_G$  and  $sp^3/sp^2$  ratios of LiFePO<sub>4</sub>/C synthesized with different sizes of PS spheres

Size of PS sphere (μm)	Raman					
	Peak position (cm <sup>-1</sup> )	Intensity (A.U.)	Widths (cm <sup>-1</sup> )	$I_D/I_G$ ratio	$I_{sp^3}/I_{sp^2}$ ratio	
2.75	Sp <sup>2</sup>	1,325 (D)	56,650	168	2.00	1.52
		1,592 (G)	28,354	68		
	Sp <sup>3</sup>	1,230	56,470	280	–	
		1,529	72,506	228		
1.50	Sp <sup>2</sup>	1,338 (D)	60,418	174	2.35	1.62
		1,593 (G)	25,637	63		
	Sp <sup>3</sup>	1,231	55,515	275	–	
		1,530	83,872	244		
0.70	Sp <sup>2</sup>	1,338 (D)	49,672	177	3.02	1.68
		1,593 (G)	16,471	68		
	Sp <sup>3</sup>	1,222	49,434	287	–	
		1,535	61,551	221		
0.22	Sp <sup>2</sup>	1,341 (D)	51,662	182	3.10	1.75
		1,596 (G)	16,666	68		
	Sp <sup>3</sup>	1,240	53,553	312	–	
		1,541	65,997	233		

## Electrochemical characterization

The cathodes for the electrochemical studies were composed of 85 wt.% LiFePO<sub>4</sub>/C powder, 10 wt.% conductive carbon black as a conductor and 5 wt.% poly(vinylidene fluoride) as a binder, in *N*-methyl-2-pyrrolidone, as the solvent for the mixture, which was then spread onto an aluminum foil current collector. After drying at 393 K for 12 h in an oven, the 1.33 cm<sup>2</sup> electrode disks were punched and weighed. Electrochemical experiments were carried out with coin type cells of the 2,032 configuration and were assembled in an argon-filled VAC MO40-1 glove box in which the oxygen and water contents were maintained below 2 ppm. Lithium metal (Foote Mineral) was used as the anode and a Celgard polypropylene membrane was used as the separator. The electrolyte was a mixture of 1 M LiPF<sub>6</sub> in ethylene carbonate/diethyl carbonate (EC/DEC; 1:1, v/v; Tomiyama

Chemicals). The cells charge–discharge cycles were performed at a 0.2 C rate over a voltage range of 2.8 and 4.0 V using a multichannel battery tester (Maccor 4000).

## Results and discussion

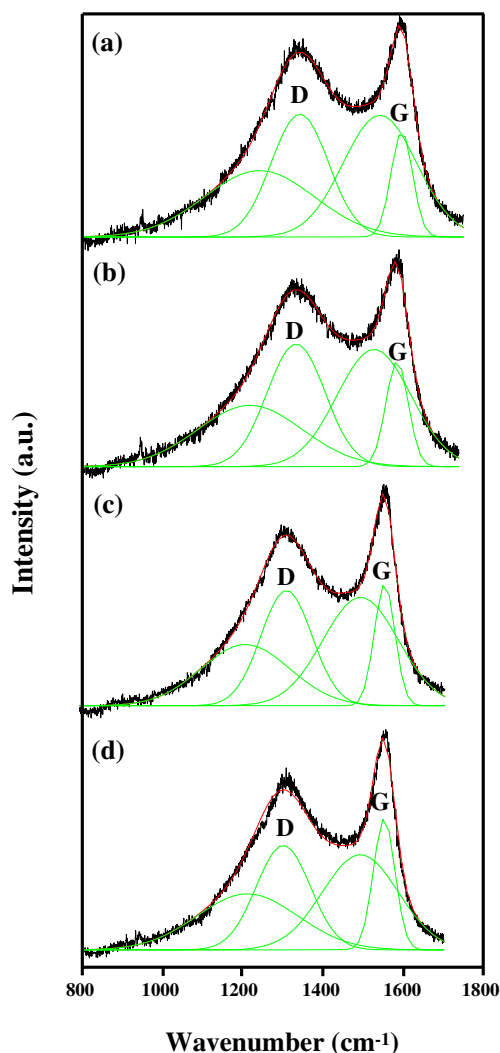
### Raman parameters/electrical conductivity

Table 1 and Fig. 1 show the results of Raman spectral analyses of LiFePO<sub>4</sub>/C composites prepared using PS spheres with different particle sizes, which confirm that carbon is present in the LiFePO<sub>4</sub> particles and forms a composite with the phosphate. The broad D and G bands of the Raman spectrum in Fig. 1 were resolved into four peaks at around 1,230, 1,325, 1,529, and 1,592 cm<sup>-1</sup> by following a standard peak deconvolution procedure. Their integrated peak intensities were calculated. The  $I_D/I_G$  ratios can be used to determine the degree of carbon disorder on the surface of LiFePO<sub>4</sub> particles, which is attributed to the number of the graphene clusters in the disordered carbon structure [25]. When the size of PS spheres was increased from 0.22 to 2.75 μm in Table 1, the  $I_D/I_G$  ratio of LiFePO<sub>4</sub>/C composites decreased from 3.10 to 2.00. A lower  $I_D/I_G$  ratio of the PS spheres with larger particle size would result in more graphene clusters in the structure of the carbon coating layer, which would improve the electronic conductivity of the residual carbon. A similar result was observed in our previous studies [24].

Raman parameters, electrical conductivity, carbon content, surface area, initial discharge capacity, and high rate performance of the as-prepared LiFePO<sub>4</sub>/C composites are listed in Table 2. More sp<sup>2</sup>-type carbon domains and less disorder in graphene planes enhanced electronic conductivity of residual carbon [25, 27]. Therefore, the electronic conductivity of these samples increased with increasing the size of PS spheres, which was attributed to the enhancement in the numbers of graphene clusters in the disordered carbon structure.

### Surface morphology

SEM images of LiFePO<sub>4</sub>/C composites synthesized using 0.22, 0.70, 1.50, and 2.75 μm PS spheres as carbon sources are shown in Fig. 2a–d, respectively. When small 0.22-μm PS sphere was used, the LiFePO<sub>4</sub>/C composite in Fig. 2a did not show significant carbon present in the interspaces between LiFePO<sub>4</sub> particles. This may make LiFePO<sub>4</sub> particles liable to lose contact from conductive carbon at high-rate application. However, the LiFePO<sub>4</sub>/C composite synthesized using small PS sphere achieved higher initial discharge capacity due to lower carbon content and less electro-inactive material. The particle size of LiFePO<sub>4</sub>/C composites with



**Fig. 1** Raman spectra of LiFePO<sub>4</sub>/C composites using PS spheres as carbon sources with different particle sizes: **a** 0.22 μm, **b** 0.70 μm, **c** 1.50 μm, **d** 2.75 μm

**Table 2** Carbon content, electronic conductivity, surface area, and cell performance data of LiFePO<sub>4</sub>/C synthesized with different sizes of PS spheres

Size of PS sphere (μm)	$I_D/I_G$	Electrical conductivity (S cm <sup>-1</sup> )	Carbon content (%)	Surface area (cm <sup>2</sup> g <sup>-1</sup> )	Discharge capacity <sup>a</sup> first D.C. <sup>b</sup> (mAh g <sup>-1</sup> )	High rate D.C. <sup>c</sup> (mAh g <sup>-1</sup> )
2.75	2.00	$4.44 \times 10^{-4}$	3.25	20.58	132	42
1.50	2.35	$4.19 \times 10^{-4}$	2.83	19.10	135	29
0.70	3.02	$1.06 \times 10^{-4}$	2.54	17.02	142	20
0.22	3.10	$9.49 \times 10^{-5}$	2.16	13.26	145	5

<sup>a</sup> Both charge and discharge rates were at a 0.2 C rate in the cutoff voltage range of 2.8–4.0 V at room temperature

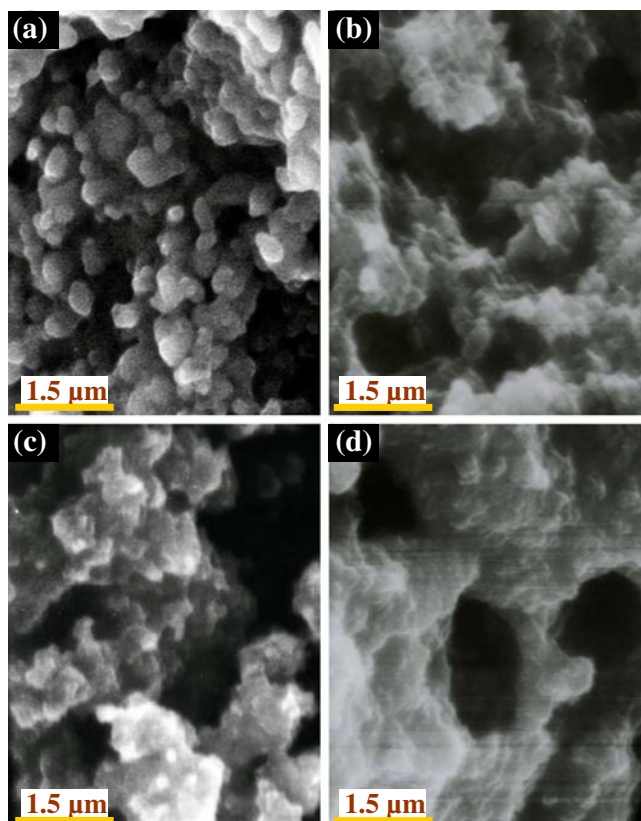
<sup>b</sup> The average standard deviation for the first discharge capacity was about 0.5 mAh g<sup>-1</sup>

<sup>c</sup> The charge and discharge rate was at a 10 C-rate in the cut-off voltage range of 2.0–4.6 V at room temperature

0.22 μm PS spheres was roughly larger than the other samples, as shown in Fig. 2. Previous reports [2, 28, 29] indicated that the addition of carbon inhibited the particle growth during a sintering process. Dahn et al. [30] also showed that the particle size decreased with increasing the amount of carbon.

When larger PS spheres were mixed with LiFePO<sub>4</sub> precursor and sintered at 873 K for 12 h, besides the residual carbon that was left in the sample, there were many spherical hollows formed from the decomposed PS spheres, as

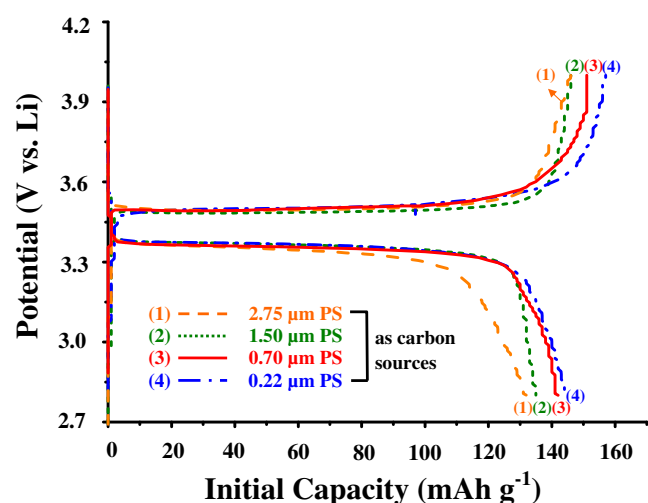
shown in Fig. 2b–d. The hollows increased the surface area of the samples, providing more contact between LiFePO<sub>4</sub> particles and better high-rate performance. The BET data of LiFePO<sub>4</sub>/C with various sizes of PS spheres are presented in Table 2. The specific area of materials was in direct proportion to the size of PS spheres. When a 2.75-μm PS sphere was applied, the sample exhibited the highest specific surface area of 20.58 m<sup>2</sup> g<sup>-1</sup>, nearly 55% greater than that of LiFePO<sub>4</sub> using a 0.22-μm PS sphere as a carbon source. The high specific surface area was attributed to the porous LiFePO<sub>4</sub> surface structure.



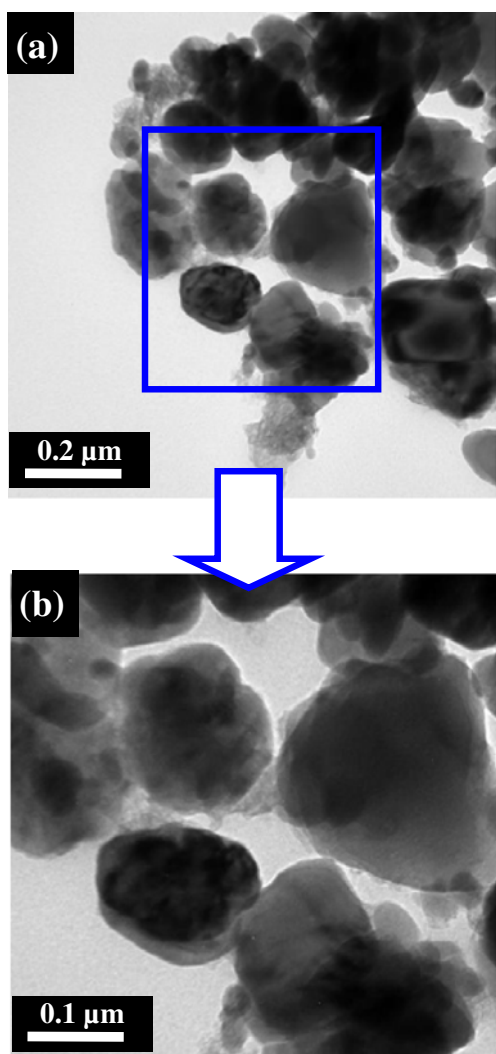
**Fig. 2** SEM images of LiFePO<sub>4</sub> powders synthesized using PS spheres as carbon sources with different particle sizes: **a** 0.22 μm, **b** 0.70 μm, **c** 1.50 μm, **d** 2.75 μm

#### Electrochemical properties analysis

Figure 3 shows the first cycle voltage profiles for LiFePO<sub>4</sub>/C samples synthesized using different sizes of PS spheres as carbon sources. All the samples displayed flat and long charge and discharge voltage plateaus around 3.5 and 3.4 V, respectively, with insignificant electrode polarization. The potential difference between the charge and discharge plateaus of



**Fig. 3** Voltage profiles of charge and discharge curves for LiFePO<sub>4</sub>/C using different sizes of PS spheres as carbon sources between 4.0 and 2.8 V at a 0.2 C rate

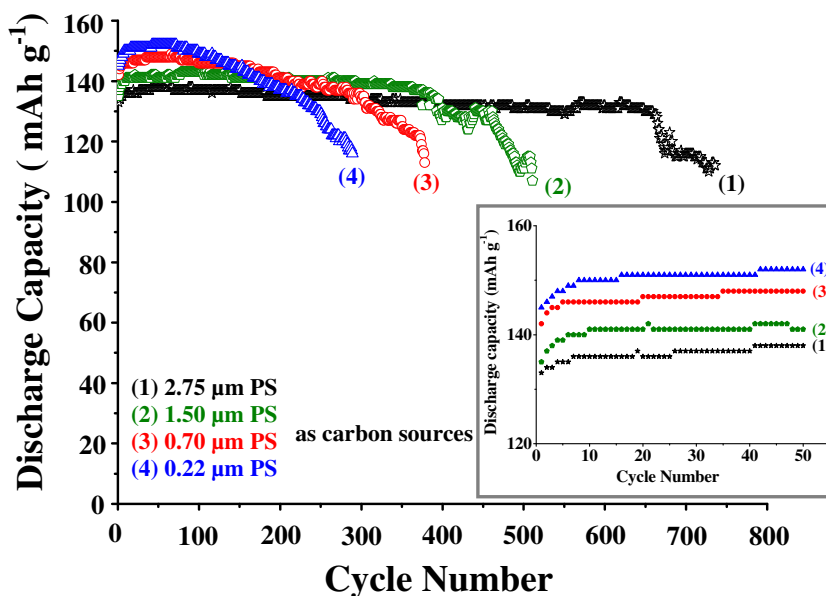


**Fig. 4** TEM micrographs of LiFePO<sub>4</sub>/C composites sintered with 2.75 μm PS spheres: **a** original, **b** enlarged

LiFePO<sub>4</sub>/C composites was only 0.1 V, exhibiting weak electrode polarization between lithium extraction and insertion. The plateau voltages were almost the same for all samples. It indicates that the diameters of PS spheres did not affect the potential of the LiFePO<sub>4</sub>/C electrochemical reaction. Table 2 displays that the initial discharge capacities of LiFePO<sub>4</sub>/C composites synthesized using 0.22, 0.70, 1.50, and 2.75-μm PS spheres as carbon sources were 145, 142, 135, and 132 mAh g<sup>-1</sup>, respectively. Clearly, the initial capacity of the materials decreased when the size of PS sphere increased. As the size of PS spheres increased from 0.22 to 2.75 μm, both electronic conductivity and carbon content increased significantly. The LiFePO<sub>4</sub>/C composite prepared using the largest size PS spheres has a higher electronic conductivity, and showed the best discharge capacity of 42 mAh g<sup>-1</sup> at a 10 C high rate between 4.6 and 2.0 V, which was probably due to the compact carbon network wrapping around LiFePO<sub>4</sub> particles, as confirmed by the TEM images (see Fig. 4). However, high residual carbon content did not seem to improve the discharge capacity since it was a low 0.2 C rate, probably due to a large amount of electro-inactive material. Sun et al. [31] reported the effects of different structural features on carbon coating, and showed that the conductive carbon network and optimum carbon content are the keys to better electrochemical performance of LiFePO<sub>4</sub>/C composites.

The cycling behavior of LiFePO<sub>4</sub>/C samples synthesized using different sizes of PS spheres as carbon sources is plotted in Fig. 5. The cycle tests were performed between 4.0 and 2.8 V at a 0.2 C rate. The sample associated with the large 2.75-μm diameter PS sphere in Fig. 3 had the lowest initial discharge capacity, which could be attributed to particle agglomeration and relatively high carbon content, as

**Fig. 5** Cyclability of LiFePO<sub>4</sub>/C composites using different sizes of PS spheres as carbon sources between 4.0 and 2.8 V at a 0.2 C rate



displayed in Fig. 2d and Table 2, respectively. As the PS sphere diameter was reduced to 1.5, 0.7, or 0.22  $\mu\text{m}$ , discharge capacity increased progressively. For the  $\text{LiFePO}_4/\text{C}$  sample that used 0.22  $\mu\text{m}$  PS spheres as a carbon source, the discharge capacity was elevated to 152  $\text{mAh g}^{-1}$  after the first 40 cycles, showing the highest capacity in the series. The initial increase in discharge capacity during the early cycles was common for all samples. This behavior may be due to the electrolyte slowly penetrating into the porous carbon structure on the  $\text{LiFePO}_4/\text{C}$  surfaces and reacting with the electrode materials. Moreover, the volume change during lithium insertion and extraction will partially crack the carbon layer, which promotes further penetration of the electrolyte [32, 33].

The  $\text{LiFePO}_4$  sample sintered with large PS spheres (2.75  $\mu\text{m}$ ) demonstrated higher cycle stability than the sample sintered with small PS ones (0.22  $\mu\text{m}$ ). In fact, the  $\text{LiFePO}_4/\text{C}$  samples that used 2.75  $\mu\text{m}$  PS spheres as carbon sources achieved 755 cycles, the highest number of cycles in the series.

## Conclusions

In this work, carbon-coated  $\text{LiFePO}_4$  cathode materials were prepared successfully by a solid-state method incorporating different sizes of PS spheres as carbon sources. The  $\text{LiFePO}_4$  precursor sintered with small 0.22  $\mu\text{m}$  PS spheres delivered a greater first discharge capacity of 145  $\text{mAh g}^{-1}$  at a 0.2 C rate, even though it only sustained 289 cycles at 80% capacity retention. However, when larger 2.75  $\mu\text{m}$  PS spheres were used, the first cycle discharge capacity was lower at 132  $\text{mAh g}^{-1}$ , but achieved 755 cycles. Therefore, a small particle carbon source of the PS sphere was conducive to achieving higher capacity, while a large particle carbon source of the PS sphere resulted in longer cycle life.

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