Surfactants assisted synthesis of nano-$LiFePO_4$/C composite as cathode materials for lithium-ion batteries

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Experimental section

2.1. Synthesis

All chemicals used in this article are of 99% purity. $LiFePO_4$/C was synthesized via solid state reaction between LiH_2PO_4 and FeC_2O_4 taken in stoichiometric quantities. Six types of surfactants (1.3 wt% Tween80, 2.0 wt% Tween40, 2.1 wt% Tween20 and (the weight ratios of Tween80 to Tween20 equal to 2.5, 1.5, 0.5) composites surfactants: (1.5 wt%, 1.7 wt% and 1.9 wt%) were also added into the reaction. The reaction process consisted of three steps as follow. (i) all reactants were mixed together with 50 wt% of deionized water and ball milling for 3 h at room temperature; (ii) the as-prepared precursor was dried using an oven at 80℃ for 12 h followed by disintegrate through crusher to obtain a fine solid powder, (iii) The final product was obtained by calcineing the as-obtained precursor powder at the temperature ranging from 600 to 800 ℃ under high-purity N_2 atmosphere. In order to control the amount of residual carbon in the composites, a series of samples was synthesized by calcinating amorphous $LiFePO_4$ with proper amounts of polymer at different temperatures. The final amount of residual carbon was controlled to be about 1.5 wt% for all samples. Finally, the as-prepared $LiFePO_4$/C using composites surfactants (Tween80 to Tween20 equal to 2.5, 1.5, 0.5) as carbon source were denoted as LFP-A, LFP-B and LFP-C respectively.

2.2 Characterization

The crystal structures of the as-prepared material were analyzed by X-ray diffraction (XRD: Rigaku, D/max 2500v/pc) using Cu Kα radiation. The content of carbon was examined by a 2400 Series II CHNS/O elemental analyzer (PerkinElmer, Waltham, USA). The microstructure of the powder and particle size distribution were investigated by scanning electron microscopy (SEM: Philips, FEI Quanta 200 FEG) Fourier transform infrared (FTIR) spectra were obtained on an AVATAR370 spectrometer. The carbon coating thickness was observed by transmission electron microscopy (TEM: JEM-2010, JEOL)

2.3 Electrochemical evaluation

To prepare the cathode, active material (LFP), the viscous cathode slurry composed of active material (LFP), acetylene black and polyvinylidene fluoride (PVDF) binder were mixed according to the ratio of 94:3:3 by weight in NMP solvent was cast on aluminum foil and then dried at 90 ℃ under vacuum for 12 h. After that, the cells were assembled in an argon-atmosphere-filled glove box with lithium foil as the anode, LFP as cathode,celgards2200 separator and 1 M $LiPF_6$ solution in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volumetric ratio of 1:1 as the electrolyte. Electrochemical tests were carried out using an automatic galvanostatic charge-discharge unit, with a Battery Tester between 2.5 and 4.2 V at different temperature of 25, 0 and -20℃. Electrochemical impedance spectroscopy (EIS) of the cell was carried out using IM6. The amplitude of the AC signal was 5 mV over the frequency range between 100 kHz and 0.01 Hz.

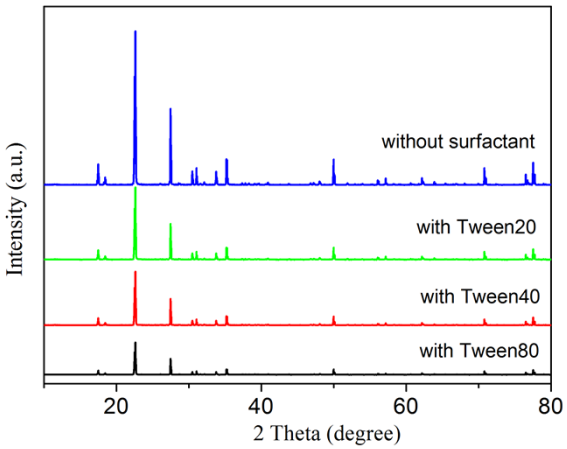
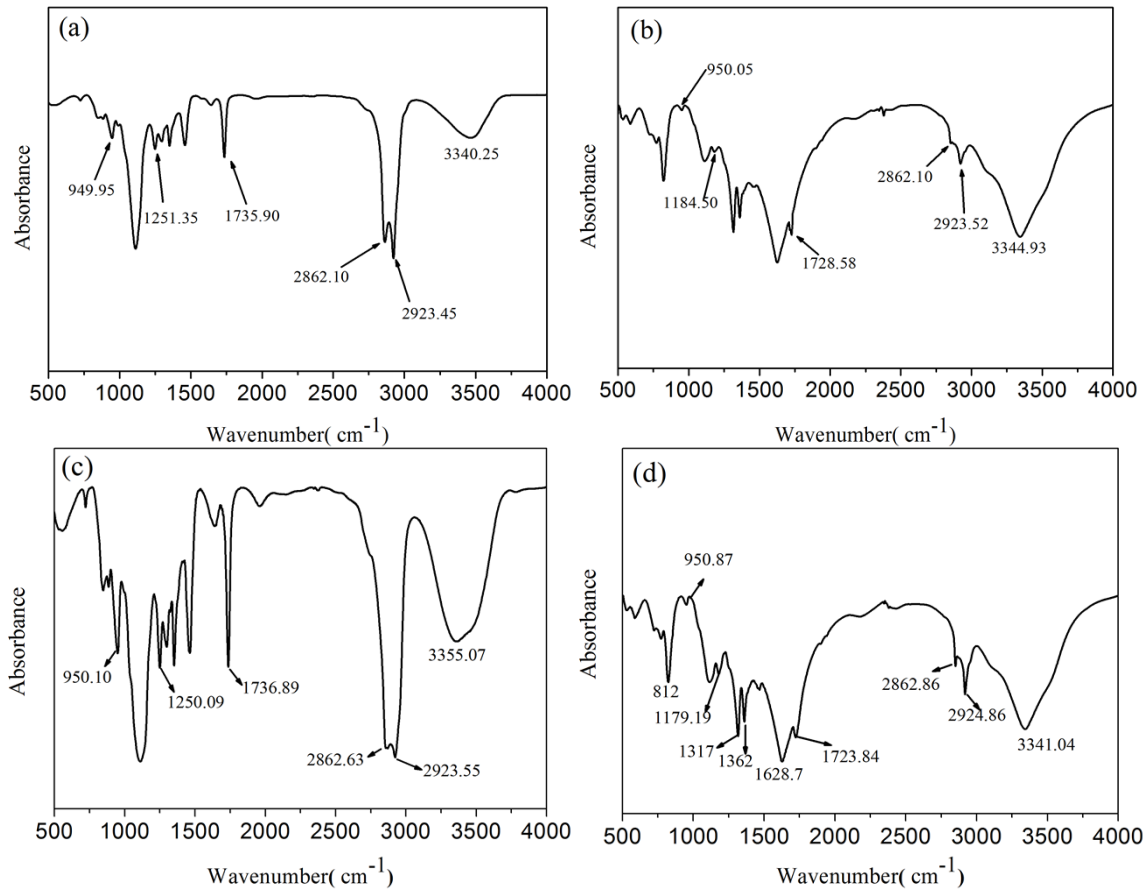


Fig. S1 XRD patterns of the LiH_2PO_4 crystals recrystallized without and with different surfactants of Tween80, Tween40 and Tween20.



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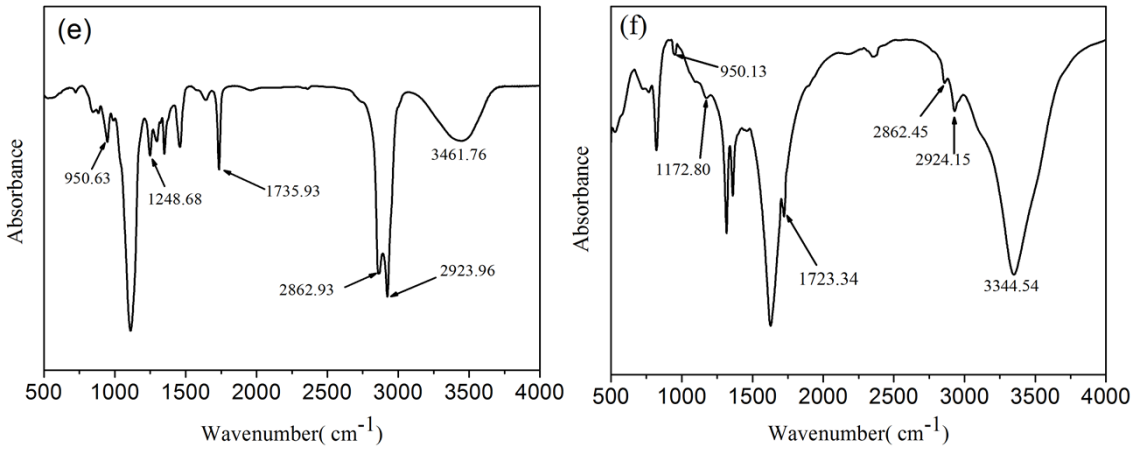

Fig. S2 Infrared spectra of pure surfactant: (a) Tween80 (c) Tween40 (e) Tween20 and the different surfactants dried with FeC_2O_4: (b) Tween80 (d) Tween40 (f) Tween20.

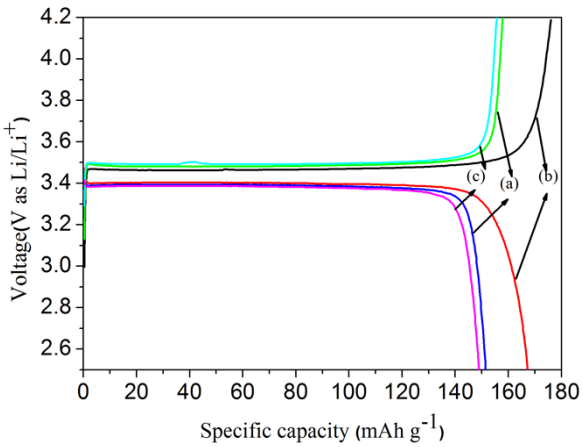

Fig. S3 The specific capacity of the $LiFePO_4$/C composites synthesized with different ratios of Tween80 to Tween20 (a) 2.5, (b) 1.5 and (c) 0.5 at 0.1 C.

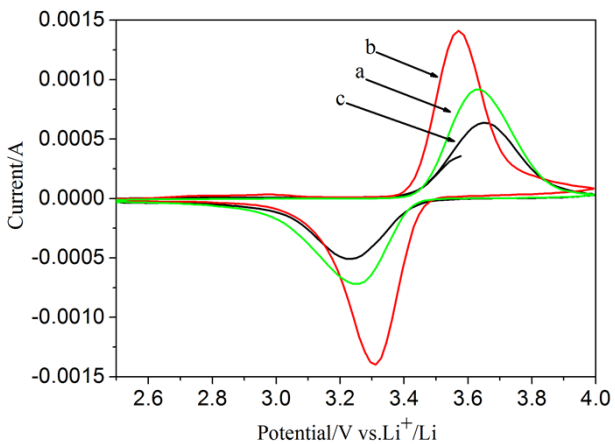

Fig. S4 The CV profiles of the $LiFePO_4$/C synthesized with different ratios of Tween80 to Tween20 (a) 2.5, (b) 1.5 and (c) 0.5 at the scan rate of $0.1 mVs^{-1}$.

Table 1 Properties of $LiFePO_4$/C prepared with different surfactants at different temperatures for 10 h

Properties Temperature	$LiFePO_4$/C prepared with Tween80 at			$LiFePO_4$/C prepared with Tween40 at			$LiFePO_4$/C prepared with Tween20 at		
	600˚C	700˚C	800˚C	600˚C	700˚C	800˚C	600˚C	700˚C	800˚C
Average crystal size (nm)	23	27	31	26	30	35	29	33	38
Particle size range (nm)	40-70	75-115	145-225	48-80	85-120	155-250	65-100	95-140	175-265
Average particle size (nm)	59	95	185	64	108	205	83	118	220

Table 2 Lattice parameters of the LiH_2PO_4 recrystallizing without and with different surfactants

Sample	a /Å	b /Å	c /Å	Crystals size
without surfactant	6.80911	7.59839	6.21861	36
with Tween80	6.77810	7.58759	6.20971	18
with Tween40	6.78021	7.58521	6.21179	23
with Tween20	6.79021	7.59121	6.21389	28

Table. 3 Parameters obtained from electrochemical impedance spectra and I_D/I_G ratios from Raman spectra for $LiFePO_4$/C samples synthesized with different surfactants.

Samples	R_Ω/Ω	R_{ct}/Ω	i_o/mA·cm^{-2}	I_D/I_G ratio
With Tween80	4.8	235	0.109	0.835
With Tween40	4.5	122.7	0.210	0.805
With Tween20	5.5	335	0.077	0.789

Table 4 Parameters obtained from electrochemical impedance spectra and I_D/I_G ratios from Raman spectra for $LiFePO_4$/C samples prepared using different weight ratios of Tween80 to Tween20.

Composite surfactants (Tween80 to Tween20)	R_Ω/Ω	R_{ct}/Ω	i_o/mA·cm^{-2}	I_D/I_G ratio
2.5	3.85	105.2	0.244	0.813
1.5	3.21	85.5	0.300	0.802
0.5	3.9	181.9	0.141	0.796