HYDROTHERMAL SYNTHESIS OF SILVER EMBEDDED LIFEPo4/C

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ABSTRACT

Silver embedded LiFePO4/C were prepared by direct hydrothermal synthesis of Li2CO3, FeSO4 and H3PO4 in mixed solution of Glucose and Ag(NH)2·OH. Samples were characterized by XRD, SEM and galvanostatic charge-discharge test. Results show that silver particles are located in the inner part of synthesized diamond-like and rectangular particles. The reversible capacities of prepared samples are 141.3 mAh g-1 and no capacity loss is detected after 800 cycles at 1C.

Key words: Li-ion batteries; LiFePO4; Hydrothermal; Silver carbonate(DMC)(1:1 by volume). The cells were galvanostatically charged and discharged in the voltage range of 2.7-4.2V versus Li/Li+ counter electrode.

RESULTS AND DISCUSSION

Most of the reported papers about hydrothermal method took LiOH as Lithium resource and using Li2CO3 as starting materials was seldom. Reactions using Li2CO3 as starting materials in this paper could be described as follows:

\[ \begin{align*}
1.5\text{Li}_2\text{CO}_3 + \text{H}_3\text{PO}_4 & \rightarrow \text{Li}_4\text{PO}_4 + 1.5\text{H}_2\text{O} + 1.5\text{CO}_2 \uparrow \\
1.5\text{Li}_2\text{CO}_3 + 3\text{Fe}\text{SO}_4 & \rightarrow 3\text{Li}_2\text{PO}_4 + 1.5\text{H}_2\text{O} + 1.5\text{CO}_2 \uparrow \\
1.5\text{Li}_2\text{CO}_3 + 3\text{H}_2\text{PO}_4 & \rightarrow 3\text{Li}_2\text{PO}_4 + 1.5\text{H}_2\text{O} + 1.5\text{CO}_2 \uparrow
\end{align*} \]

Reaction (1) was difficult and not complete because partial products were LiH2PO4 and LiPO4. NH3·H2O was added to mixed solution until pH value was 7 in reaction (2) in order to get LiFePO4 grain easier. Obtained sample from reaction (1) was called sample 1 and the other one was sample 2. XRD patterns of samples and residue of samples were shown in Fig.1 and 2. We performed a cell refinement to samples using MGI Jade 5.1 software. Samples were indexed in the orthorhombic system with space group Pnmb and cell parameters of sample 1 was, a = 6.017(1) Å, b = 10.34(57) Å, c = 4.709(8) Å and V = 293.1(6) Å3, sample 2 was, a = 6.010(2) Å, b = 10.350(5) Å, c = 4.70(45) Å and V = 292.6(7) Å3. Fig.2 showed XRD patterns of residue of samples. Ag and AgCl were detected and AgCl should be come from the reaction of HCl and minor silver salt contained in samples.

EXPERIMENTAL

Silver embedded LiFePO4/C were prepared by direct hydrothermal synthesis of Li2CO3, FeSO4 and H3PO4 in the stoichiometric ratio of 1.5 : 1.0 : 1.0 and 1.5 : 1.0 : 3.0. First, Glucose was added into Ag(NH)2·OH solution to obtain silver particle along with stirring and Ag : LiFePO4 = 1 : 99(wt%). Second, FeSO4 was mixed with Ascorbic acid in order to avoid Fe3+ was oxidized to Fe2+. Third, Li2CO3 and H3PO4 were mixed with different molar ratio. At last, all solutions were quickly transferred to Parr reactor for up to 10h at 180 °C, and all the reactions are under the protection of N2 (99.9% purity). After the samples were cooled, the precipitates were filtered and dried at 65 °C for 8h in vacuum oven. Dried samples were fired at 750 °C for 5h to decompose residual glucose and ascorbic acid.

In order to testify the existence of conducting silver particles, prepared samples were dissolved in 11.6 mol/L HCl solution, stirred and filtered, residue of samples were obtained separately.

Samples and residue were characterized by X-ray diffraction using a PANalytical X Pert PRO diffractometer with Cu Kα radiation. SEM observation of samples were performed on a JEOL scanning electron microscope(JSM-5610LV).

Electrodes were made by dispersing 85wt.% active materials, 8wt.% carbon black and 7wt.% polyvinilidenefluoride(PVDF) binder in 1-Methyl-2-pyrroldione solvent to form a slurry. The slurry was then spread uniformly on a electrode slice and dried in the vacuum oven at 65°C for at least 12h. the cells were assembled in an argon filled glove-box(MBraun, Unilab, USA). The electrolyte was 1M LiPF6 in a mixture of ethylene carbonate(EC) and dimethyl carbonate(DMC)(1:1 by volume). The cells were galvanostatically charged and discharged in the voltage range of 2.7-4.2V versus Li/Li+ counter electrode.

Fig.1 XRD patterns of sample 1 (a) and sample 2 (b).
Fig. 2 XRD patterns of residue of sample 1 (a) and sample 2 (b).

Morphology for prepared samples were observed on SEM, as shown in Fig. 3, samples were uniformly distributed. Sample 1 was composed of diamond and slightly agglomerated particles, particle size was 1-5 μm. Particles of sample 2 were rectangular and agglomerated, grain size was 1-8 μm.

Fig. 3 Particle morphology of LiFePO4/C+Ag prepared by reaction (1) and (2).

Electrochemical performance of prepared samples were shown in Fig. 4. Cycle performance of sample 1 are better than that of sample 2. After 1, 400, 500 and 800 cycles, the specific capacity of sample 1 are 111.1, 122.5, 133.2 and 141.3 mAh g⁻¹ separately at 1C (1C=150 mA g⁻¹); after 1, 400 and 800 cycles, the specific capacity are 87.4, 89.6 and 80.7 mAh g⁻¹ separately at 15C. The specific capacity of sample 2 are 129.5, 130.6 and 126.3 mAh g⁻¹ separately at 1C after 1, 200 and 300 cycles. Good cycle performance were achieved and it might because that LiFePO4 grain grow up on the surface of reduced silver particles since Ag(NH3)2⁺ ions were firstly reduced to Ag under stirring and Wrapped silver particles enhance the conductivity of LiFePO4.
Fig 4. Cycle performance of prepared samples at the current density of 750mA g⁻¹.

CONCLUSIONS

Diamond-like and rectangular particles of silver embedded LiFePO₄/C were successfully synthesized through hydrothermal reactions. At ambient temperature, the discharge capacities of sample 1 are 141.3 mAh g⁻¹, and no capacity loss were detected after 800 cycles at 1C. Good electrochemical performance could be correlated with wrapped silver particles which might lead to the enhancement of conductivity of individual particle.

REFERENCES