Pseudocapacitive Behavior of Ag_3PO_4 Nanospheres Prepared by a Sonochemical Process

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Ag_3PO_4 nanospheres with an average size of ~ 300 nm were synthesized via a sonochemical process. The electrochemical performances of the as-synthesized Ag_3PO_4 nanospheres in aqueous KOH electrolyte with different concentrations were investigated by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy. The measured cyclic voltammetry curves as well as charge-discharge curves reveal a good pseudocapacitive behavior of Ag_3PO_4 nanospheres. In a 1 M KOH electrolyte at a current density of 0.5 mA cm^{-2} , the specific capacitance of Ag_3PO_4 nanospheres is obtained to be 832 F g^{-1} . However, Ag_3PO_4 nanospheres exhibit an inferior charge-discharge cycling stability, which could be due to the formation of Ag_2O during the cycling process. [doi:10.2320/matertrans.M2016312]

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1. Introduction

Nowadays, there has been a great deal of interest in developing new energy sources and energy storage devices due to the ever-increasing energy demand and the depletion of non-renewable fossil fuels. Supercapacitors, also named as ultracapacitors or electrochemical capacitors, are a promising class of electrical energy storage devices, which bridge the gap between electrolytic capacitors and rechargeable batteries. They can store much more energy per unit volume or mass than electrolytic capacitors, accept and deliver charge much faster than batteries, and endure many more charge-discharge cycles than rechargeable batteries. These advantages make supercapacitors attractive for special applications such as consumer electronics, hybrid electric vehicles, memory backup systems, uninterruptible power supplies etc.^{1,2)} Electrode materials for supercapacitors can be mainly divided into carbon materials^{3,4)}, transition metal oxides^{5–12)} and conducting polymers¹³⁾. In carbon materials-based supercapacitors, the energy is stored through electric double-layer capacitance, i.e., the physical accumulation of charges at electrode/electrolyte interfaces under the action of electric field. Transition metal oxides- or conducting polymers-based supercapacitors are attributed to pseudocapacitive charge storage, which involves fast and reversible redox reaction at the surface of the electrode materials. Generally transition metal oxides-based pseudocapacitors can offer a much higher specific capacitance than electric double-layer capacitors and have been the focus of research nowadays. However, most of the transition metal oxides still have one or more deficiencies when they are used as electrode materials for supercapacitors. For example, RuO_2 can deliver a high energy density and specific capacitance with excellent cycling stability⁵⁾, but it is disadvantaged by its high cost and toxicity.

Silver orthophosphate (Ag_3PO_4) has been extensively studied as a new type of visible-light driven photocatalyst. This material has a high separation of photoexcited electrons and holes as well as a high quantum efficiency up to 90% at wavelengths above 420 nm ^{14,15)}, which makes it a powerful photo-

catalytic capability for the decomposition of organic compounds and O_2 evolution from water splitting under visible light irradiation^{14–17)}. Recently, it has been shown that Ag_3PO_4 tetrapods synthesized by a hydrothermal method can be employed as a supercapacitor electrode material¹⁸⁾. However, only double-layer capacitance was observed for Ag_3PO_4 tetrapods in KNO_3 aqueous electrolyte. In this work, we demonstrate that Ag_3PO_4 nanospheres prepared by a sonochemical process exhibit a pseudocapacitive behavior in KOH electrolyte.

2. Experimental

Spherical Ag_3PO_4 particles were synthesized via a sonochemical process as described in the literature¹⁹⁾. 0.003 mol of AgNO_3 , 0.001 mol of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and 0.002 mol of NaOH were dissolved in 20 , 10 and 10 mL of distilled water, respectively. The NaOH solution was added by drops into the NaH_2PO_4 solution to form a mixed solution, and the mixed solution was then dropped to the AgNO_3 solution slowly. Every step mentioned above was accompanied by a constant magnetic stirring to make the additives dissolve completely. The obtained mixed solution was ultrasonically irradiated at a frequency of 40 kHz and a temperature of 50°C . After reaction for 1 h , the formed precipitate was collected and washed with distilled water and absolute ethanol for 5 times, and then submitted to drying on an electrothermal constant-temperature dry box at 60°C for 12 h . The phase purity of the as-prepared sample was characterized by powder X-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation. The particle morphology and size of the sample was investigated by a field-emission scanning electron microscope (SEM).

The electrochemical performances of Ag_3PO_4 particles were tested on a CST 350 electrochemical workstation using a three-electrode cell configuration which includes the working electrode, counter electrode and reference electrode. The working electrode was prepared as follows. 1 mg of Ag_3PO_4 , 0.125 mg of carbon black and 0.125 mg of PVDF (polyvinylidene fluoride) were mixed together using ethyl alcohol as solvent to form slurry. The slurry was uniformly coated onto a stainless steel foil with an area of 1 cm^2 , and was dried at

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60°C for 12 h in a thermostat drying oven. A platinum foil was employed as the counter electrode and a standard calomel electrode (SCE) was employed as the reference electrode. KOH aqueous solution with different concentrations was used as the electrolyte. The electrochemical performances of Ag₃PO₄ particles were investigated by cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS).

3. Results and Discussion

Figure 1 shows the XRD pattern of the as-synthesized Ag₃PO₄ particles, with the insert displaying the SEM image of Ag₃PO₄ particles. It is seen that all the diffraction peaks

Fig. 1 XRD pattern of the as-synthesized Ag₃PO₄ particles, with the insert displaying the SEM image of Ag₃PO₄ particles.

can be indexed to the Ag₃PO₄ cubic phase (JCPDS card no. 06-0505), and no traces of other impurity phases are detected in the XRD pattern. The SEM observation reveals that the particles are regularly shaped like spheres without any adhesive or agglomerative behaviour. The particles have a narrow diameter distribution with an average size of ~300 nm.

The electrochemical performances of Ag₃PO₄ nanospheres were investigated in KOH aqueous electrolyte at different concentrations such as 0.5, 1, 3 and 5 mol L⁻¹ (M). Figure 2 shows the CV curves of Ag₃PO₄ nanospheres in 0.5 M, 1 M, 3 M and 5 M KOH electrolytes at various scan rates. The CV curves present a reduction peak at round 0 V and a broad oxidation peak at around 0.5 V, and furthermore the reduction and oxidation potentials undergo only a slight shift toward negative and positive directions with the increase in the scan rate, respectively. The CV curves imply a fast and reversible redox reaction and a good pseudocapacitive behavior of Ag₃PO₄ nanospheres. However, at a high concentration of the KOH electrolyte (5 M), the oxidation peak becomes weak, indicating a decrease in the cycling stability of Ag₃PO₄ nanospheres. The reduction peak is due to the reduction of Ag⁺ to Ag⁰ and the oxidation peak arises from the oxidation of Ag⁰ to Ag⁺. The involved reaction process can be described as follows.

Figure 3(a) shows the charge-discharge curves at various current densities ranging from 0.5 to 3 mA cm⁻² in 1 M KOH electrolyte, which exhibit a non-linear characteristic. In particular, the discharge process undergoes an obvious potential plateau at around 0 V, which arises from the electrochemical

Fig. 2 CV curves of Ag₃PO₄ nanospheres in different KOH electrolyte concentrations at various scan rates. (a) 0.5 M KOH electrolyte; (b) 1 M KOH electrolyte; (c) 3 M KOH electrolyte; (d) 5 M KOH electrolytes.

Fig. 3 (a) Charge-discharge curves of Ag_3PO_4 nanospheres at various current densities in 1 M KOH electrolyte. (b) Calculated specific capacitance values of Ag_3PO_4 nanospheres at various current densities. (c) Charge-discharge curves in different electrolyte concentrations at a constant current density of 1 mA cm^{-2} . (d) Specific capacitance values in different electrolyte concentrations.

reaction. The non-linear characteristic of the charge-discharge curves suggests that the electrochemical reaction takes place due to the redox mechanism, and this result is concordant with the CV results shown in Fig. 2. The specific capacitance (C) of the samples can be calculated using the following equation.

$$C = \frac{It}{m\Delta V} \quad (3)$$

where C , I , t , m , and ΔV are the specific capacitance (F g^{-1}) of Ag_3PO_4 , discharging current (A), discharging time (s), mass of Ag_3PO_4 (g), and discharging potential range (V), respectively. The calculated specific capacitance values of Ag_3PO_4 nanospheres at various current densities are shown in Fig. 3(b). At the current density of 0.5 mA cm^{-2} , the specific capacitance of Ag_3PO_4 nanospheres is obtained to be 832 F g^{-1} . With increase in the current density, the specific capacitance exhibits a significant decrease, and decreases to 129 F g^{-1} when the current density is increased up to 3 mA cm^{-2} . This could be due to an increase in ionic resistivity and a decrease in charge diffusion to the inner active sites and redox reaction rate²⁰. Figure 3(c) shows the charge-discharge curves in different KOH electrolyte concentrations at a constant current density of 1 mA cm^{-2} . These curves present a similar non-linear characteristic. Figure 3(d) shows the specific capacitance values in different electrolyte concentrations derived from the charge-discharge curves. With increase in the electrolyte concentration, the specific capacitance increases from 321 F g^{-1} in 0.5 M KOH electrolyte to 598 F g^{-1} in 5 M KOH electrolyte. This happens due to the fact that more ions are available for participating in the redox reactions at higher electrolyte concentration.

Fig. 4 Capacitance retention of Ag_3PO_4 nanospheres as a function of the charge-discharge cycling number in different KOH electrolyte concentrations at a constant current density of 1 mA cm^{-2} .

The electrochemical cycling stability of Ag_3PO_4 nanospheres was evaluated by the repeated charge-discharge measurement at a constant current density of 1 mA cm^{-2} . Figure 4 shows the capacitance retention as a function of the charge-discharge cycling number in different KOH electrolyte concentrations. After 100 cycles, the specific capacitance of Ag_3PO_4 nanospheres in 0.5 M , 1 M , 3 M and 5 M KOH electrolytes is observed to be 133, 225, 136 and 100 F g^{-1} , maintaining 41%, 55%, 27% and 17% of the initial capacitance, respectively. This indicates that Ag_3PO_4 nanospheres exhibit an inferior charge-discharge cycling stability especially in high-concentration KOH electrolytes. The significant capacitance fading could be due to the formation of Ag_2O during the cycling process.

Fig. 5 Nyquist spectra of Ag₃PO₄ nanospheres in different KOH electrolyte concentrations, with the inset showing the equivalent circuit.

EIS measurements were carried out by the use of the sinusoidal voltage pulse with an amplitude of 5 mV and in the frequency range of 10^{-2} – 10^5 Hz. Figure 5 shows the obtained Nyquist spectra of Ag₃PO₄ nanospheres in different KOH electrolyte concentrations. It is seen that the Nyquist spectra exhibit a shape with a small semicircle at the high-frequency region and a straight line in the low-frequency region. The semicircle at the high-frequency region is ascribed to the charge-transfer resistance at the electrode/electrolyte interface (i.e., faradic resistance), and the straight line in the low-frequency region is related to the diffusion of the electrolyte ions into/from the electrode pores²¹⁾. The EIS data can be fitted by an equivalent circuit as shown by the inset in Fig. 5. The equivalent circuit includes the solution resistance (R_s), double-layer capacitance (C_d), charge-transfer resistance (R_{ct}) and Warburg impedance (W). In 0.5 M, 1 M, 3 M and 5 M KOH electrolyte, the solution resistance is obtained from the first intersection point on the real axis to be 1.5, 0.3, 0.4 and 2.2 Ω , respectively, the charge-transfer resistance is obtained by intercepting the semicircle to the real axis to be 52.0, 50.6, 33.7 and 15.3 Ω , respectively, and the double-layer capacitance is calculated to be 33×10^{-6} , 88×10^{-6} , 105×10^{-6} and 144×10^{-6} F, respectively. With increasing the KOH electrolyte concentration, the charge-transfer resistance exhibits a decreasing trend while the double-layer capacitance exhibits an increasing trend. This could be attributed to the fact that the thickness of diffusion layer becomes smaller with increasing the electrolyte concentration²²⁾. In addition, the double-layer capacitance accounts for a very small fraction of the total capacitance, indicating that Ag₃PO₄ nanospheres mainly exhibit a pseudocapacitive behavior in the present electrochemical system.

4. Conclusions

The electrochemical performances of Ag₃PO₄ nanospheres

synthesized via a sonochemical method were investigated in aqueous KOH electrolyte with different concentrations. The CV curves show a pair of reduction and oxidation peaks, and the charge-discharge curves exhibit a non-linear characteristic. These results suggest that Ag₃PO₄ nanospheres exhibit a pseudocapacitive behavior in KOH electrolyte. The specific capacitance of Ag₃PO₄ nanospheres is obtained to be 832 F g⁻¹ in 1 M KOH electrolyte at a current density of 0.5 mA cm⁻². However, the charge-discharge cycling reveals an inferior electrochemical stability of Ag₃PO₄ nanospheres.

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