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Ultrasonic sol-gel synthesis of $Ag_2V_4O_{11}$ from V_2O_5 gel

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For various oxidation states of silver and vanadium, silver and vanadium oxides (SVO) have been found to be practical battery material [1]. $Ag_2V_4O_{11}$ has been used in commercial lithium battery as cathode active material to power cardiac defibrillators because of its high specific capacity and high rate capability [2]. Like other vanadium-based cathode material such as $Li_{1.2}V_3O_8$, the electrochemical property of $Ag_2V_4O_{11}$ highly depends on the synthetic and processing method [3–5]. In case of the synthesis of SVO, several methods have been proposed and could be divided into two categories according to the type of chemical reaction to form SVO [1]. The first kind belongs to combination reaction. It starts with V_2O_5 and Ag_2O or $AgVO_3$ and usually requires high temperature processing. Most of the reactant is exhaused during the reaction; the other kind belongs to decomposition reaction, it starts with $AgNO_3$, V_2O_5 or NH_4VO_3 and the reaction is done under lower temperature. The product particles usually have a small size that will benefit the battery with high specific capacity and high rate capability. As $AgNO_3$ is more sensitive to light than Ag_2O, the decomposition of $AgNO_3$ is a primary contribution to the impurity phases in the final product. Moreover, the nitrogen oxide formed could cause some environmental problems.

Based on Pistoia *et al.*'s method to obtain high specific capacity for $Li_{1.2}V_3O_8$ by using sol-gel synthesis method [6], we developed a new method which is called the ultrasonic sol-gel synthesis (USGS) method for low temperature synthesis of SVO from V_2O_5 gel. By using this method, we obtained $Ag_2V_4O_{11}$ with different crystalline degree. Electrochemical tests have shown that the $Ag_2V_4O_{11}$ we obtained at lower temperature has higher specific capacity than its higher temperature counterpart.

V_2O_5 gel is an ionic layered compound made up of $V_2O_5 \cdot nH_2O$ sheets that have a microstructure resembling that of the crystalline o-V_2O_5 [7, 8]. It is expected that many vanadium-based compounds traditionally prepared from crystalline V_2O_5 may be obtained by reactions starting from V_2O_5 gel. The ultrasonic treatment presented in this paper provides an effective method to disperse the solid-state reactants such as Ag_2O powder into the ribbons of $V_2O_5 \cdot nH_2O$ layer sheets at nanometer level. This kind of nanometer level dispersion brings more sufficient contact between the reactants, thus makes the reaction easier to happen under low temperature. The V_2O_5 gel is prepared by polycondensation of vanadic acid [9]. The vanadic acid without any foreign cations is obtained by passing sodium metavanadate ($NaVO_3$) aqueous solution through a proton exchange resin. By weighing the crystalline o-V_2O_5 after heating some of the V_2O_5 gel at 360 °C in air, we could determine the concentration of V_2O_5 gel easily and precisely [8]. Some flocculation occurred when stoichiometric Ag_2O powder is added directly into V_2O_5 gel. Appropriate dispersion of the flocculation is fundamental for the synthesis. A viscous brown gel is obtained in half an hour by ultrasonic treatment. Transmission electron micrograph (TEM) of the prepared composite gel is taken on a Hitachi H-7000FA electron microscope. The gel is then dried at 50 °C under vacuum. Then heat the xerogel obtained at 150–450 °C for 10 h in air. After mild grindings, the final products of $Ag_2V_4O_{11}$ are obtained. The xerogel dried at 50 °C is used in thermogravimetry (TG) and differential thermal analysis (DTA) experiments on WCT-1A (Beijing Optical Instruments) in air. For preparing the reference material of $Ag_2V_4O_{11}$, the mixed powder of V_2O_5 and Ag_2O is heated at 500 °C in flowing O_2 for 6 h [10]. Powder X-ray diffraction (XRD) experiments are carried out using a Shimadzu XRD-6000 X-ray diffractometer with Cu K_α line. For checking the electrochemical properties of the prepared material, galvanostatic discharge experiments are conducted on Arbin BT-2000 with a current rate of 30 mA/g and cutoff potential of 2.0 V vs. Li^+/Li. The composite cathode electrode consists 40% active material, 40% acetylene black and 20% polytetrafluoethylene (PTFE) binder. A stainless steel mesh acts as the current collector. In the sandwich-type cell, the lithium disk and the cathode are separated by celgard-2400. The electrolyte is 1 M $LiClO_4$ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) solution with a volumetric ratio of EC to DMC as 1:1. All cells are assembled in

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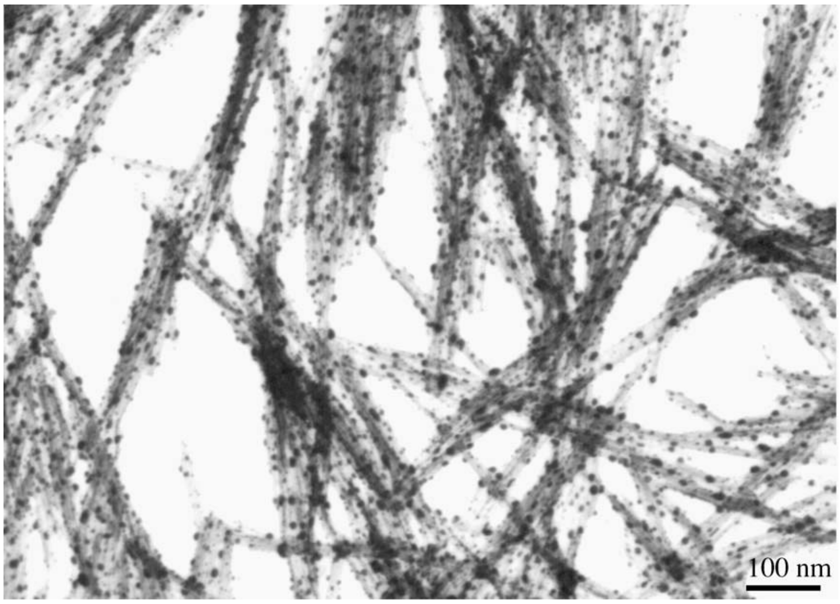

Figure 1 TEM image of the gel obtained by ultrasonically treating the V_2O_5 gel and Ag_2O.

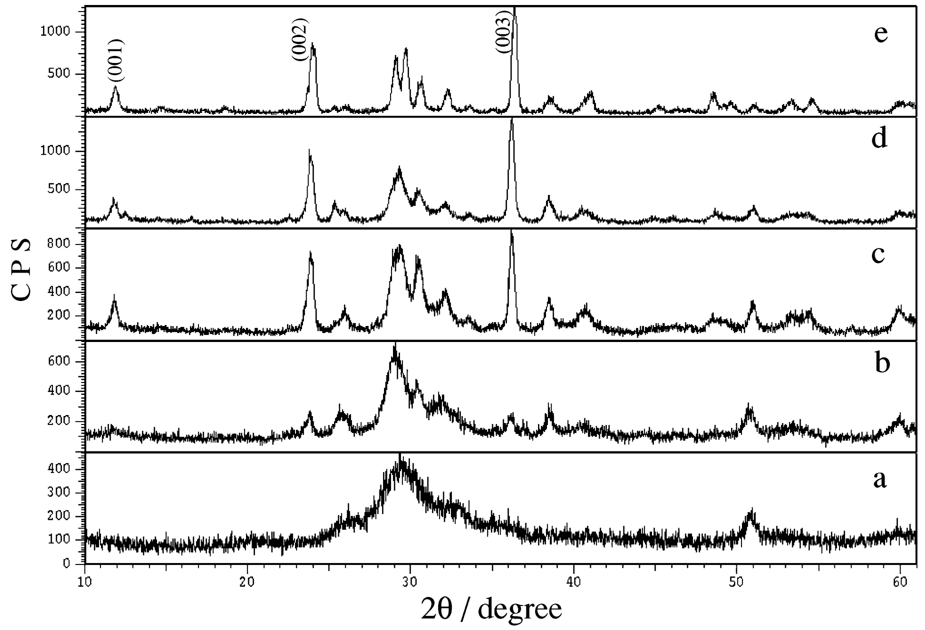

Figure 2 XRD patterns of $Ag_2V_4O_{11}$, USGS product obtained at (a) 250 °C, (b) 300 °C, (c) 350 °C, (d) 400 °C, and (e) solid-state high temperature synthesis at 500 °C.

the dry box (MECAFLEX, MECABOX 80-1s) filled with purified argon gas and are tested at 25 °C.

Fig. 1 shows the TEM photograph of the composite gel obtained by ultrasonic treating of the mixture of V_2O_5 gel and Ag_2O. The network structure is made of entangled ribbons of $V_2O_5{\cdot}nH_2O$ [7], and there are particles with the size of 5–10 nm adsorbed around these ribbons. When we set the Ag/V ratio as 1:1, a yellow crystalline precipitate of $AgVO_3$ with crystalline structure is obtained. However, brown gel is obtained when we set the ratio of Ag/V as 1:2. It is estimated that ultrasonic treatment could drive Ag_2O into nanometer scale particles that will tend to weld on the ribbons of $V_2O_5{\cdot}nH_2O$ by means of local reactions.

The XRD results in Fig. 2 confirm the assumption that the temperature required for the formation of $Ag_2V_4O_{11}$ is lowered when the reactants are degraded to nanometer size. The product obtained at 250 °C shows amorphous structure. When we increase treating temperature from 250 to 400 °C, the crystalline degree of the products increases gradually. There is an enthermic peak around 325 °C in DTA curve (not shown), which coincides with the crystallization temperature shown in the XRD profiles. The pattern and position of those peaks match well with the results from literature [10]. However, some differences still exist. The two strongest lines, {002} and {003} reflections in Fig. 2c, d and e, indicate a preferred orientation on $(00\,l)$ layer.

To investigate the electrochemical property of $Ag_2V_4O_{11}$, lithium batteries with $Ag_2V_4O_{11}$ as cathode active material are assembled to discharge at a current rate of 30 mA/g with a cutoff potential 2 V. Fig. 3 shows the discharge curves of $Ag_2V_4O_{11}$ prepared through sol-gel process (USGS) and high temperature process.

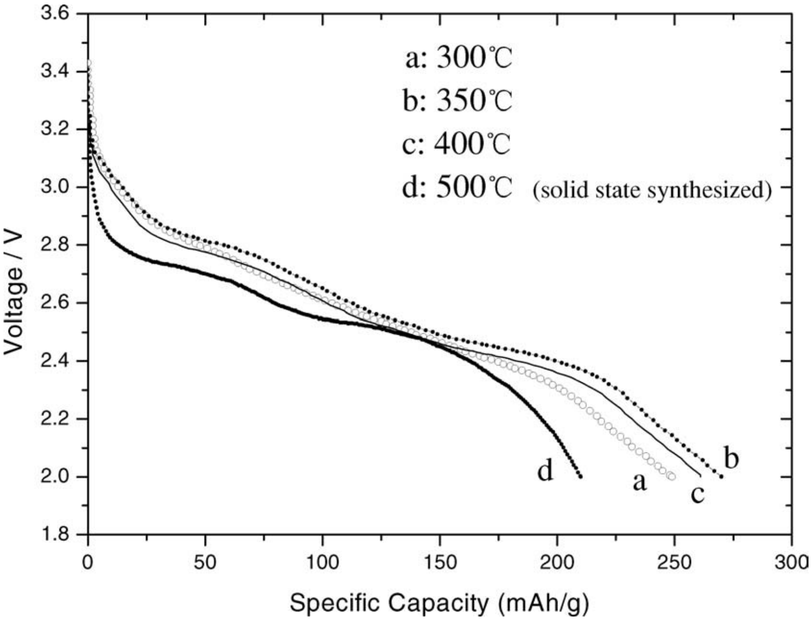

Figure 3 The discharge curves of $Ag_2V_4O_{11}$, USGS product obtained at (a) 300 °C, (b) 350 °C, (c) 400 °C, and (d) solid-state high temperature synthesis at 500 °C.

Almost all products made by using USGS method under low temperature have higher capacity and discharge potential than those made under high temperature. The product obtained at 350 °C exhibits the highest specific capacity of 270 mAh/g. The high discharge capacity and high discharge potential of the products may be ascribed to the low temperature processing involved, which makes the product particles small in size. To obtain optimistic small size particle, Crespi has invented a further heating process on DSVO (SVO obtained by decomposition reaction) to condense its lumpy topology [5]. In Fig. 2 we can see that the products are fully crystallized above 350 °C, so the size of the particles and the crystallinity increase as the heating temperature increases [4]. Thus we can explain the fact that the USGS product obtained at 400 °C has a lower capacity than the 350 °C product. It is worth noting that the 300 °C product demonstrates an attracting feature that its discharge potential declines almost linearly, and for all the USGS products the discharge curves in anaphase decline more slowly than those of the solid-state high temperature synthesis products. This kind of discharge curve is most desirable for batteries powering the importable cardiac defibrillators because it is convenient to estimate the discharge state of the battery by just measuring its potential.

This paper presents here provides a new route for the synthesis of $Ag_2V_4O_{11}$ by a USGS method from V_2O_5 gel. The reaction temperature required in this process is much lower than that conventionally used for solid-state synthesizing. The crystallinity of the products varies with processing temperature. The USGS product obtained at 350 °C delivers the highest capacity, while the 300 °C product displays an ideal discharge shape for this kind of material.

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