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In-situ characterizations of chemo-mechanical behavior of free-standing vanadium pentoxide cathode for lithium-ion batteries during discharge-charge cycling using digital image correlation

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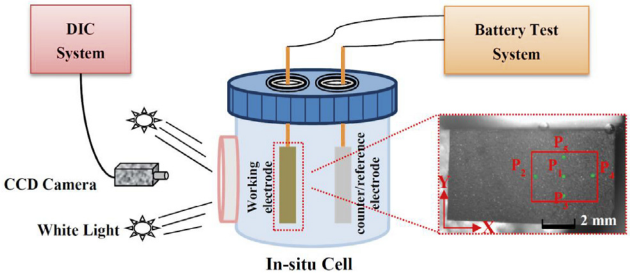
HIGHLIGHTS

- The free-standing nanobelts structure V_2O_5 cathodes were successfully synthesized.
- An in-situ and non-contact strain measurement system with digital image correlation.
- Heterogeneous strain features of V_2O_5 cathode were successfully in-situ monitored.
- The corresponding stress evolutions of V_2O_5 cathode were systematically discussed.
- The results are crucial to reveal the chemo-mechanical mechanisms of V_2O_5 cathode.

GRAPHICAL ABSTRACT



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ABSTRACT

The free-standing V_2O_5 nanobelts cathodes for lithium-ion batteries are synthesized through hydrothermal reaction followed by anneal treatments and vacuum filtration deposition. The well cycling performances of the electrode were verified by battery test system. The microstructure and surface morphologies of the V_2O_5 electrode before and after discharge-charge cycles were analyzed by X-ray diffraction and scanning electron microscope, respectively. The evolutions of strain fields of free-standing V_2O_5 electrodes are in-situ measured by digital image correlation technique. The heterogeneous features of in-plane strains of V_2O_5 electrode surface in macro-scales are characterized and systematically discussed as a function of test time (or voltage). Given the effect that the elastic modulus is dependent on the concentration and cycling number, the evolutions of in-plane stresses of V_2O_5 cathodes during discharge-charge cycling are estimated using a chemo-mechanical constitutive equation. The influences of chemical and mechanical components on in-plane stresses are extracted and discussed, respectively. The results are crucial to further reveal the chemo-mechanical coupling failure mechanism of V_2O_5 cathode and optimize the electrode structure of lithium-ion battery systems.

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1. Introduction

As an effective device for energy storage and conversion, lithium-ion batteries have been regarded as a formidable candidate in the fields of wearable electronics, electrical vehicles, hybrid electric vehicle, smart grids and household energy storage [1–5]. However, with the rapid development in the fields of energy storage and transformation, the energy and power density, rate performance and cycle life of traditional electrode materials are hard to meet those actual demands [6–8]. Therefore, many researchers have designed novel electrode materials with higher specific capacity, superior rate charge-discharge ability and longer cycle life, such as vanadium pentoxide (V_2O_5), lithium vanadium phosphate, lithium nickel cobalt manganese oxide, silicon, tin and transition metal oxides [7,9–12]. Compared with traditional cathode materials, V_2O_5 has the advantages of abundant resources, low cost, high output voltage and theoretical specific capacity (294 mA h/g) [3,13–15]. It is regarded as a promising candidate cathode material for lithium-ion batteries [16–18].

However, there are still some defects restricting the commercial applications of V_2O_5, such as low diffusion rate of lithium-ions, mild electrical conductivity and poor structural stability [19–21]. The theoretical volumetric strain of V_2O_5 can reach 15% [22]. The volume expansion and contraction can lead the collapse of material structure with the increasing of electrochemical cycles, which in turn reduces electrochemical properties [23–25]. To reveal this chemo-mechanical coupling problem, it is valuable to study the evolutions of strain/stress in V_2O_5 electrodes during charge/discharge cycling and clarify the corresponding failure mechanisms of electrochemical reactions. In recent years, to better study the evolution rule of volume swell/shrink and clarify the electrochemical reaction mechanisms, many in-situ techniques including scanning electron microscope (SEM) [26,27], transmission electron microscopy (TEM) [28,29], X-ray diffraction (XRD) [30,31], nuclear magnetic resonance (NMR) [32] have been introduced to understand the structural evolution, phase evolution, lithiation mechanisms and reaction kinetics [7,25,33,34]. In addition, digital image correlation (DIC) [35–37], Raman spectroscopy [38] and substrate curvature method [39,40] have been developed to effectively measure the strain/stress evolutions of electrodes during charge-discharge cycles. Ghodssi et al. combined in-situ Raman spectroscopy with interferometric method to characterize the microstructure and stress changes of V_2O_5 cathodes during lithiation [38]. Sheldon et al. proposed a new in-situ substrate curvature method to monitor the mechanical deformation of polymer electrolytes on $V_2O_{5\text{-}x}$ thin-film electrodes. It was useful for revealing interfacial chemistry changes during electrochemical cycling [41]. Jones et al. applied DIC to study the strains in composite graphite electrode as a function of electrochemical cycling [37]. Chen et al. used DIC technique to in-situ monitor the strain evolution of traditional graphite within a custom CR2032 coin cell LIBs [42]. However, to the best of our knowledge, less efforts have been devoted to systematically study the evolutions of strain/stress and the chemo-mechanical coupling mechanism of V_2O_5 cathodes with the aid of direct DIC measurements during electrochemical cycling.

In this paper, the free-standing nanobelts structure V_2O_5 cathodes were first synthesized through hydrothermal reactions followed by anneal treatments and vacuum filtration processes. XRD and SEM were applied to analyze the evolutions of crystal textures and morphologies in V_2O_5 electrode before and after discharge-charge cycling. The dynamic strain fields of free-standing electrode during electrochemical cycling were in-situ measured by using DIC technique and a customized battery device. The relationship of in-plane strain variations in V_2O_5 electrode surface and electrochemical cycles was established and discussed in detail. The elastic moduli of V_2O_5 electrodes dependent on the concentration were evaluated by nanoindentation tests at the end of different stages. The corresponding in-plane stresses were estimated with respect to the strain and electrochemical properties, which were useful for predicting the performances and life of lithium-ions batteries. Our results are helpful for better interpreting the chemo-mechanical coupling mechanism of V_2O_5 cathodes, and providing a guidance of the structure design of electrodes and batteries more reasonably.

2. Experimental

2.1. Synthesis of free-standing V_2O_5 electrode

All chemical reagents used in our work were analytical grade, and do not need any further purification. First, V_2O_5 nanobelts were synthesized by a simple hydrothermal method and followed by a anneal process in atmospheric environment. In a typical synthesis process [43,44], 4.0 mmol V_2O_5 powders were dispersed into 50 mL deionized water by magnetic stirring for 2 h, and then performed by an ultrasonic process at room temperature for about 5 min until a homogeneous mixture was got. 25 mL 30% H_2O_2 was added into this mixed solution drop by drop, and the solution color gradually turns from orange to brown. The transparent solution was transferred to a 100 mL stainless steel autoclave with a Teflon liner, and kept at 220 °C for 24 h in an electric oven. After cooling down to room temperature naturally, the resulting product was collected and washed with anhydrous ethanol and deionized water repeatedly by centrifugal separation apparatus. Finally, the product was dried at 60 °C for 12 h and then calcinated in air at 400 °C for 1 h. The brilliant yellow V_2O_5 nanobelts was achieved and used to prepare V_2O_5 electrode. To get free-standing electrode, 30 mg V_2O_5 nanobelts was dispersed into 30 mL deionized water by a magnetic stirrer. The above suspension was filtered with a mixed nylon membrane filter with 0.22 μm pore size. After the membrane with V_2O_5 nanobelts was dried at 60 °C for 12 h in a vacuum oven, a bulk free-standing electrode was obtained after the membrane was removed. Part of electrodes were cut into $10 \times 10\ \text{mm}^2$ by scalpel for in-situ cells. The mass of each V_2O_5 nanobelt specimen is about 2 mg. Other electrodes were cut into small disks with a diameter of 8 mm for coin cells.

2.2. Materials characterization

The microstructure of free-standing V_2O_5 electrodes was identified by XRD (Rigaku Ultima IV, Cu Kα radiation) and SEM (No. JSM-6610LV) before and after discharge-charge cycling. The elastic moduli of V_2O_5 electrode were measured by nanoindentation tests (Hysitron Inc., USA) in this work. All nanoindentation experiments were carried out using an indenter (Triboscope, Hysitron Inc.) equipped with a three-sided pyramidal Berkovich diamond tip and an *in-situ* scanning probe microscopy (SPM) at room temperature. The force and displacement sensitivities of the instrument are 100 nN and 0.2 nm, respectively. Indentations were performed with the maximum indentation depth of 6 μm, and each cycle was repeated 8 times to obtain reliable data.

2.3. Design, assemblage and electrochemical measurements of cells

The cycling performances of free-standing V_2O_5 cathode were evaluated before the in-situ tests. The coin cells were assembled in a glove box, using free-standing V_2O_5, lithium foil electrodes and porous polyethylene film separator, respectively. Here, the glove box was filled with high purity argon. The contents of water and oxygen were less than 0.1 ppm. The electrolyte used in coin cells was 1M $LiPF_6$ in ethylene carbonate and dimethyl carbonate with a volume ratio of 1:1. Finally, the galvanostatic discharge/charge cycling was carried out on the coin cells using an NEWWARE BTS4000 battery testing system, in the voltage range of 2.0–4.0 V vs. Li/Li^+.

To real-time measure the strain evolutions of V_2O_5 electrode surface in electrolyte during electrochemical cycling, an electrolytic cell made of high pure quartz was designed, as shown in Fig. 1. Two electrode holders were utilized to fix the V_2O_5 specimen and counter/reference electrode. To in-situ monitor the surface displacement in the working electrode by DIC, a kind of aerosol paint (SANVO) was sprayed on one