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超临界二氧化碳体系中正八面体氧化钴颗粒的生长及其表征

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摘要:研究了正八面体氧化钴颗粒在超临界二氧化碳体系中的合成过程。在密闭的不锈钢高压反应釜中,1.0 g 乙酸钴和 12.0 g 干冰在 450 ℃下,反应 12 h 后合成粒径大约 10 μm 的正八面体氧化钴颗粒。通过 XRD、XPS、TEM、SEM 以及拉曼光谱的分析,氧化钴颗粒是由八个{111}面包裹着的正八面体单晶组成。条件实验显示,超临界二氧化碳体系是正八面体氧化钴颗粒合成的充分条件。其生长机理可能是:乙酸钴在超临界二氧化碳体系中的热分解;氧化钴的结晶和定向缓慢生长。在性能方面,初步研究了正八面体氧化钴颗粒在作为锂离子电池电极材料的应用。

关键词:超临界二氧化碳;正八面体氧化钴
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Growth and Characterization of Octahedral Cobalt Oxide Particles in Supercritical Carbon Dioxide System

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Abstract: The synthesis of regular octahedron cobalt oxide microcrystals for the application of battery material in supercritical carbon dioxide system was studied. Regular octahedron microcrystals of cobalt oxide with a size about 10 μm were prepared at 450 ℃ in a closed vessel consisting of 1.0 g of cobalt acetate powder and 12.0 g of dry ice. The as-obtained particles were charterized by XRD, XPS, SEM, TEM and Raman spectroscopy techniques. The XRD and Raman spectroscopy results indicate that the crystal structures of the particles (the cobalt oxide microcrystals) are inerratic. SEM and TEM results reveal that the morphology of cobalt oxide microcrystals appear to be the regular octahedron enclosed by eight {111} facets. It is found that the supercritical carbon dioxide system is a full condition to the synthesis of regular octahedron cobalt oxide. The size of cobalt oxide microcrystals increases with reaction time and the morphology is temperature dependent. The possible growth mechanism of regular octahedron cobalt oxide microcrystals was discussed based on the pyrolysis of cobalt (II) acetate, crystallization of cobalt oxide and Slowly Orientational Growth (SOG) due to anisotropy in supercritical carbon dioxide environment at reaction temperatures. The charge/discharge properties of regular octahedron microcrystals of cobalt oxide used as battery material were also characterized and discussed.

Key words: supercritical carbon dioxide; octahedral cobalt oxide

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Magnetic materials including Fe[1,2], Co[3,4], Ni[5,6] and their oxides have been studied for many years. Over the past decade there is increasing interests on the morphology and size control of magnetic materials synthesized on the microscale due to the fact that morphology and size of the particles play very important roles in determining chemical and physical properties of materials, and the particles with well-defined structures are usually associated with functionality[7~10]. Hard templates and organic compounds have been employed for chemical synthesis of special morphologies, the latter provide effective routes to objects with special morphologies. However, this synthesis strategy has some disadvantages, such as complicated reaction steps, and organic solvent is usually toxic, flammable and explosive, which increase the difficulty of the reaction process. Supercritical fluids as solvents for chemical and material processing can be advantageously exploited for new kinds of materials processing because of their unusual combination of physical properties (i.e., easy separations, variable density, low viscosity, low surface tension, and polymer plasticization)[11]. Supercritical carbon dioxide ($scCO_2$) has attracted much interest as an alternative solvent for materials synthesis and processing, and has been promoted as a sustainable and "green" solvent because it is non-toxic, non-flammable, and naturally abundant, which can be widely accepted that the advantages associated with this solvent are likely to lead to a number of new CO_2-based processes[12]. The purpose of this paper is to find a method for synthesis of crystals with well-defined structures in one-step under supercritical carbon dioxide system.

Cobalt oxide has a wide range of applications in battery materials, magnetic data storage, catalysis, ferrofluids and sensors, mainly due to their magnetic properties and chemical stability[13,14]. Developing new methods for the preparation of cobalt oxide with various shapes and sizes and investigating their properties are thus of considerable interest. For instance, tetrahedral cobalt oxide nanocrystals were synthesized in a hydrothermal system[15] and synthesis of hexagonal cobalt oxide nanocrystals was studied[16]. So far, however, few methods have been reported for the synthesis of regular octahedron cobalt oxide microcrystals, which is hoped to find its potential applications based on charge/discharge capacity, magnetic, gas-sensing, and catalytic properties[17~25].

In this paper, we report the synthesis and characterization of regular octahedron cobalt oxide microcrystals using a single precursor, $Co(CH_3COO)_2$ (cobalt (II) acetate) in supercritical carbon dioxide system. Compared with other methods for synthesis of cobalt oxide particles, our route is a typical single-step and template-free process. These obtained regular octahedron cobalt oxide microcrystals have been detected by a battery test system and may have potential applications in catalysis and gas-sensor fields.

1 Experimental

Typical synthetic procedures are as follows. Cobalt acetate powder and dry ice were used as reactant to synthesize microcrystals of cobalt oxide. The reaction was carried out in a stainless steel autoclave (10 mL) that is a 110-mm-long cylindrical tube with outer diameter of 85 mm and an inner diameter of 13 mm, respectively. A typical reaction used 1.0 g of cobalt acetate, 12.0 g of dry ice, which were placed in the cell at room temperature. The vessel was then immediately closed tightly and heated to 450 ℃, and kept at this temperature for 12 h. The reaction took place at an autogenic pressure depending on the amount of dry ice added. After cooling of the sample to room temperature, the black solid product was collected and was washed with distilled water and absolute ethanol several times, and dried in air at room temperature, yielding about 0.22 g of products.

XRD analysis was performed on a Rigaku (Japan) D/max-rA X-ray diffractrometer equipped with graphite monochromatized Cu Kα radiation (λ=0.154 18 nm), high voltage: 40 kV, current: 30 mA, at a scanning rate of 0.05 °·s^{-1} and in 2θ of 10 °~70 °. XPS was performed on a VG ESCALAB MKII Electron Spectrometer with the X-ray source of Mg Kα. The morphology of the samples was observed on a scanning electron microscope (SEM) (KYKY-1010B), accelerated voltage: 20 kV. The Transmission Electron Microscope (TEM) and the se-

lected area electron diffraction pattern (SAED) studies were performed on a Hitachi H-800 Transmission Electron Microscope. The Raman spectroscopy analysis was carried out on a LABRAM-HR Confocal Laser Micro-Raman spectrometer at room temperature.

The charge/discharge capacity of Li/CoO Teflon cell was used to study the charge/discharge properties of regular octahedron microcrystals of cobalt oxide. Weight fractions of regular octahedron microcrystals of cobalt oxide electrode: regular octahedron microcrystals of cobalt oxide (0.8), carbon black (0.1), PVDF (0.1), anode: Li foil, electrolyte: 1.0 mol·L^{-1} $LiPF_6$ EC-DEC (V/V, 1 1) solution, room temperature, current density= 0.2 mA·cm^{-2}. As an electroactive material, regular octahedron microcrystals of cobalt oxide would be restricted by its low electric conductivity. The addition of carbon black used as the conducting agent could promote the conductivity of the electrode and the utility of the electroactive material. The weight fractions of regular octahedron microcrystals of cobalt oxide, carbon black and polyvinylidene difluoride (PVDF)in the electrode were 0.80, 0.10 and 0.10, respectively. The studies of charge/discharge properties of crystal were performed with 0.2 mA·cm^{-2} current density on a battery test system (BTS-6V/10 mA, Newware).

2 Results and discussion

The XRD pattern of a powder sample grown at 450 ℃ is shown in Fig.1. The reflections of XRD pattern can be readily indexed with a cubic phase of cobalt oxide, compatible with the literature values of a=0.426 2 nm (PDF 78-0431). An XRD pattern of the powder sample was obtained by mounting the crystal basal plane in the scattering plane, indicating high quality of the crystal. Compared with the PDF card(Fig.2), it is found that the strongest peak (200) becomes weak, while the peak (111) becomes the strongest peak in the diffraction pattern of the product, indicating possible orientated growth of the particles. The products are further examined by XPS in Fig.3(A,B). These peaks are observerd at 531 and 781 eV, corresponding to the binding energies of O1s and Co2p, respectively[26].

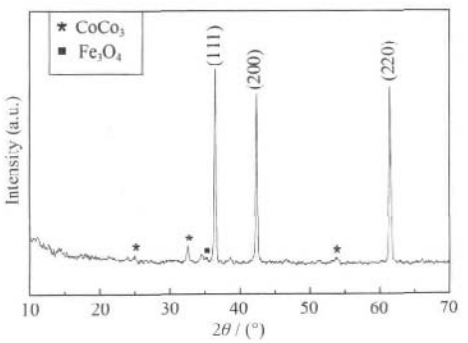


Fig.1 XRD pattern of a cobalt oxide powder sample prepared at 450 ℃

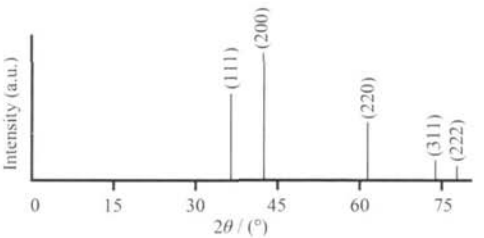


Fig.2 XRD standard pattern of cubic cobalt oxide

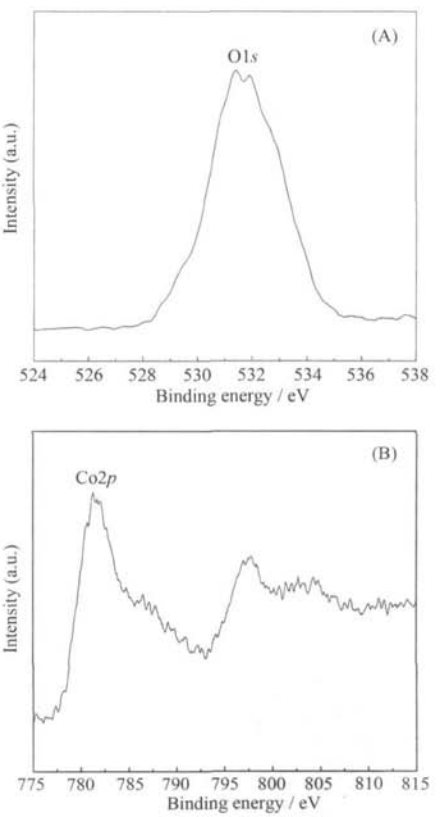
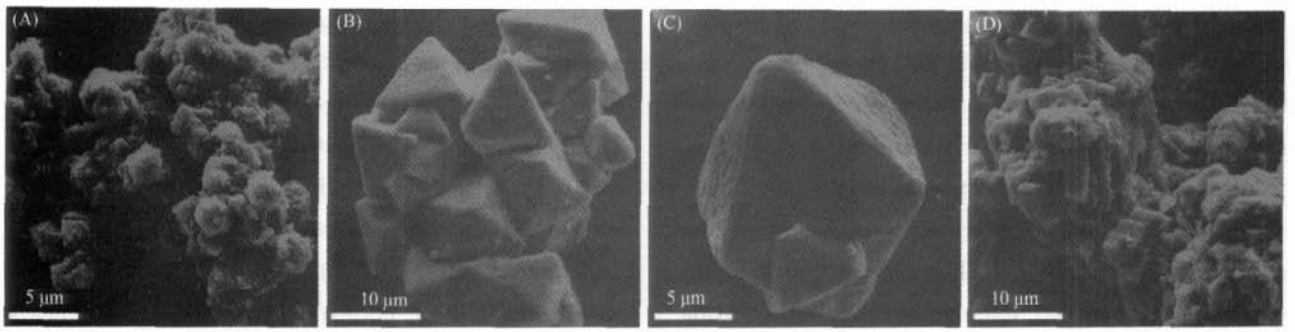


Fig.3 XPS Spectra of regular octahedron particles of cobalt oxide

Fig.4 (A) shows SEM image of particles of cobalt oxide grown at 400 ℃, whose morphology is ambiguous. The regular octahedron particles of cobalt oxide prepared at 450 ℃ is displayed in Fig.4(B), which appear



(A) grown at 400 ℃; (B) regular octahedron grown at 450 ℃;
(C) the enlarged image of a regular octahedron particle in(B); (D) grown at 450 ℃ without dry ice

Fig.4 SEM images of particles of cobalt oxide

to be of distinctive shape with the sizes range about 10 μm. Fig.4(C) shows the enlarged image of a single particle in Fig.4(B). The particle with triangle shapes and a flat surface with flower pattern can be clearly seen. Fig.4(D) is the SEM image of particles of cobalt oxide grown at 450 ℃ without supercritical carbon dioxide system. It shows that the morphology of particles of cobalt oxide is irregular. TEM image of a large number of small particles grown at 450 ℃ is shown in Fig.5(A), the particles in the sample appear to be of nearly perfect regular octahedron with diameters about 10 μm. A typical regular octahedron particle with a diameter of 10 μm can be found in the product in Fig.5(B). The selected area electron diffraction pattern [Fig.5(C)] of a regular octahedron particle confirms cobalt oxide to be single crystal. Based on these characterization results, a schematic structure model with 3D shape is shown in Fig.5(D), an enclosed regular octahedron is bound by eight {111} facets. The Raman spectrum of cobalt oxide is shown in Fig.6. The spectrum shows that the sample exhibits characteristic peaks of cobalt oxide (481, 528, 688 cm^{-1})[27], and an intense peak at 688 cm^{-1}. The peak at 688 cm^{-1} corresponds to the symmetric stretching vibration. The two lower frequency bands at 481 and 528 cm^{-1} are associated with a librational motion and a translational motion of the oxygen atoms relative to the divalent cation, respectively.

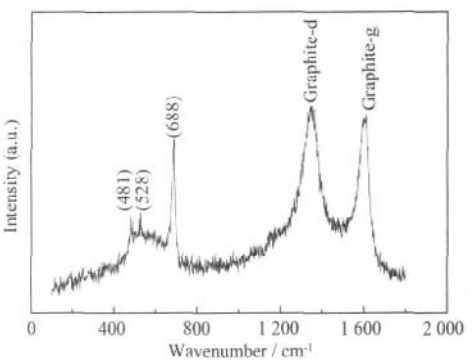
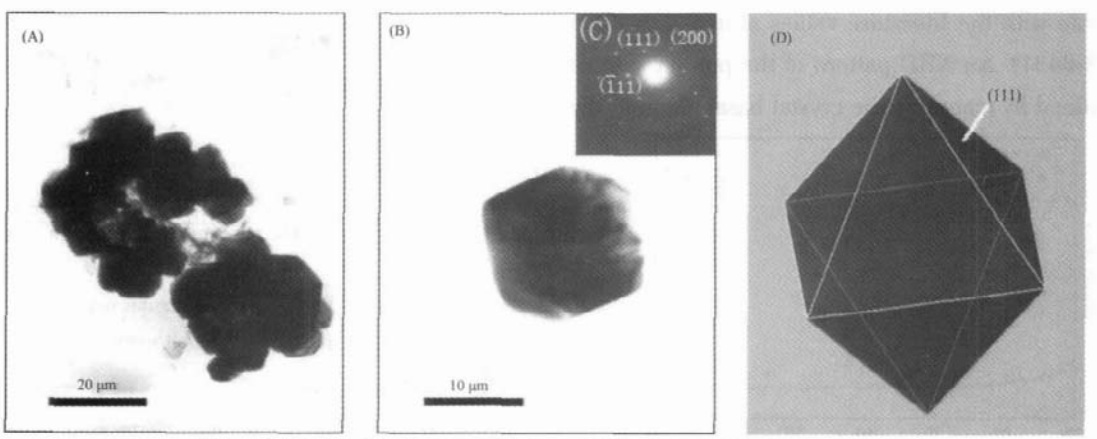


Fig.6 Raman spectrum of regular octahedron microcrystals of cobalt oxide, using an excitation wavelength of 514 nm



(A) at 450 ℃; (B) with sizes around 10 μm; (C) The electron diffraction pattern;
(D) a schematic model showing the 3D shape of the {111} enclosed regular octahedron single crystal

Fig.5 TEM images of regular octahedron particles of cobalt oxide synthesized in supercritical carbon dioxide system

From XRD, XPS, SEM, TEM and Raman spectroscopy analysis, it is clear that the product formed by the thermal dissociation of $Co(CH_3COO)_2$ (cobalt (II) acetate) in supercritical carbon dioxide system is composed of regular octahedron microcrystals of cobalt oxide. The chemical reactions in the system can be represented as follows:

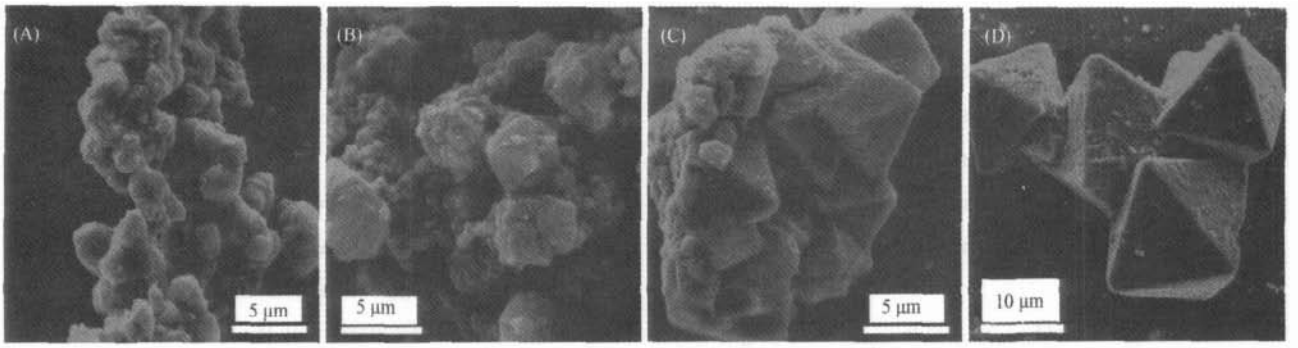
$$Co(CH_3COO)_{2(s)} \rightarrow CoO_{(microcrystals)} + 2C_{(graphite)} + 3H_2O_{(g)} \quad (1)$$

$$CoO_{(microcrystals)} + CO_{2(g)} \rightarrow CoCO_{3(s)} \quad (2)$$

One hypothesis is that the thermal decomposition of $Co(CH_3COO)_2$ takes place at a temperature between 400 **℃** and 450 **℃**: $Co(CH_3COO)_2$ forms a vapor in carbon dioxide, and then decomposes, just like the thermal dissociation of other organometallic compounds [28]. The regular octahedron crystal cores of cobalt oxide are formed by vapor nucleation under the condition of supercritical carbon dioxide and grow slowly during reaction. In reaction system, the main reaction is Reaction (1), Reaction (2) is a secondary reaction.

To examine the effects of the reaction temperature and other factors on the formation of microcrystals of cobalt oxide, a series of relevant experiments were carried out by altering the experimental parameters of the processes. The cobalt acetate was pyrolyzed at 100 **℃** in the air. However our pyrolysis process carried out at the temperatures lower than 400 **℃** could not initiate the reaction in the supercritical carbon dioxide system, microcrystals of cobalt oxide with a size less than 5 **μm** and irregular shape were the major products at 400 **℃**, as shown in Fig.4 (A); as the temperature was increased to 450 **℃**, microcrystals of cobalt oxide with a size up to 5 **μm** started to appear. When reaction time reached 12 h, the major product was regular octahedron microcrystals of cobalt oxide with a size about 10 **μm**, which reveals that the formation of cobalt oxide microcrystals is sensitive to the temperature of the system in the condition with enough reaction time. In our reaction system, pyrolysis process was carried out under a high pressure environment, the fact that the reaction temperature is much higher than the reaction temperature in the air may be explained by Le Châtelier's principle. At the same time, the growth of cobalt oxide microcrystals is sensitive to the supercritical carbon dioxide system. It is found that no regular octahedron cobalt oxide microcrystal is formed without dry ice in the same reaction condition [Fig.4(D)], both of which are essential factors for the growth of regular octahedron microcrystals of cobalt oxide. It was reported that Fe_3O_4 octahedra were obtained via a simple hydrothermal process, and Ostwald ripening and oriented attachment played an important role in formation of the octahedral structures[29]. In our reaction system, the carbon dioxide is in a supercritical state (31 **℃**, 7.4MPa), the system may have similar character as hydrothermal process, the reaction system maintains an equilibrium state at 450 **℃**, crystal nuclei produced appears to be regular octahedron shape due to anisotropy of cobalt oxide. At one time, the solubility of cobalt oxide increases in the supercritical carbon dioxide system and the number of crystal nuclei decreases due to supersaturation of the system, because supercritical carbon dioxide is a superior solvent; as a result the sizes of the crystals increase and the number of particles decreases[30].

To understand the formation mechanism of regular octahedron cobalt oxide, time-dependent experiments were carried out by stopping heating a stainless steel autoclave at different reaction stages. It is shown that aggregated cobalt oxide microcrystals with nearly spheroidal morphology [Fig.7(A)] emerged as the initial product after the reaction proceeds for 3 h. When prolonging the reaction time to 6 h, some flats grow out on some cobalt oxide particles, and many small particles are attached on these flats [Fig.7(B)]. This process of regular octahedron cobalt oxide microcrystals growth and morphology evolution can be described in terms of Ostwald ripening, which involves the growth of large cobalt oxide particles at the expense of the smaller ones driven by the tendency of the solid phase in the systems to adjust them to achieve a minimum total surface free energy. When increasing the reaction time to 9 h, most of the cobalt oxide particles are ready to evolve into octahedral structures [Fig.7(C)]. When the reaction time increases to 12 h, regular octahedron microcrystals of cobalt oxide, which have rough surfaces, are formed [Fig.7(D)]. Regarding the growth process, it is believed that the time plays a crucial rule in the formation of



(A) 3 h; (B) 6 h; (C) 9 h; (D) 12 h

Fig.7 SEM images of particles of cobalt oxide grown at 450 ℃ during different time

cobalt oxide octahedra. Further studies are necessary to understand the exact growth mechanism of regular octahedron cobalt oxide because it may open up new opportunities to fabricate more complex microstructur materials.

In conclusion, as a result of the effect of the supercritical carbon dioxide system, the pyrolysis of cobalt (II) acetate is carried out and the regular octahedron microcrystals of cobalt oxide are produced. However, the growth process of cobalt oxide microcrystals is not fully understood yet.

Weight fractions of regular octahedron microcrystals of cobalt oxide electrode: regular octahedron microcrystals of cobalt oxide (0.8), carbon black (0.1), PVDF(0.1), anode: Li foil, electrolyte: 1.0 mol·L^{-1} $LiPF_6$ EC-DEC (V/V, 1 1) solution, room temperature, current density=0.2 mA·cm^{-2}

Cobalt oxide is used as a novel anodic material in the lithium ion battery due to its excellent charge/discharge capacity and the charge/discharge properties of cobalt oxide with various shapes and sizes have been studied recently [31]. The theoretical charge/discharge capacity of CoO is based on the following charge/discharge process[32].

$$CoO + 2Li^+ + 2e^- \rightleftharpoons Li_2O + Co \quad (3)$$

The charge/discharge capacity of Li/CoO Teflon cell was used to evaluate the charge/discharge properties of regular octahedron microcrystals of cobalt oxide. The capacity/cycle curves of the regular octahedron microcrystals of cobalt oxide electrode with 0.2 mA·cm^{-2} current density are given in Fig.8 (A). The discharge curve of the regular octahedron microcrystals of cobalt oxide electrode with 0.2 mA·cm^{-2} current density is observed in Fig.8 (B). The results indicate that the discharge voltage decreases sharply from OCV (2.72 V) to the discharge plateau located in the range of 1.0~0.5 V at the first discharge cycle. It was often reported that Co_3O_4 was more suitable to be electroactive material, and had a high power-output behavior with a first potential range (1.25~1.0 V)[33~35]. However our experimental results indicate that the main charge/discharge capacities of Li/CoO Teflon cell are also contributed from the redox of regular octahedron microcrystals of cobalt oxide and the formation/decomposition of gel-like polymers, respectively. Some literatures had re-

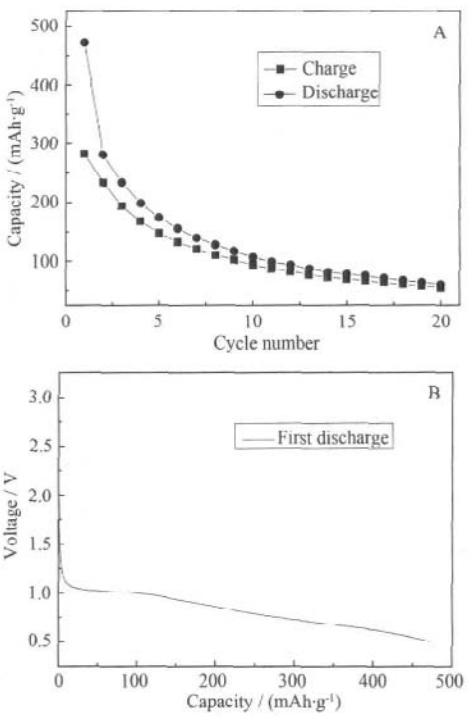


Fig.8 Effect of cycle number on the charge/discharge capacity of Li/CoO Teflon cell (A) and first discharge curve of Li/Co Teflon cell(B)

ported that CoO might be eminent electroactive material, and the first potential range might reach (1.0~0.8 V)[36,37]. It is shown that the regular octahedron microcrystals of cobalt oxide we synthesized in this work are not predominant enough to be used as electroactive material of the lithium ion battery. This may be due to the less specific surface and larger size of the regular octahedron microcrystals of cobalt oxide. Further work should be done to increase specific surface and decrease size of the crystals. At the same time, the regular octahedron microcrystals of cobalt oxide have eight {111} facets, which can have potential application as gas sensors, this will be our further subject of study.

3 Conclusions

Despite the additional cost and complexity associated with high-pressure technology, it is clear that the use of supercritical carbon dioxide as a solvent offers unique opportunities for the synthesis and processing of well-defined materials that would otherwise be difficult to obtain. The above studies illustrate regular octahedron microcrystals of cobalt oxide with a size about 10 μm can be grown at 450 ℃ in a supercritical carbon dioxide system using cobalt acetate powder as the starting material. It is suggested that cobalt oxide can form supersaturating solution in a supercritical carbon dioxide system, in which crystals of cobalt oxide can slowly grow. Some interesting aspects of supercritical carbon dioxide system are displayed in the growth of regular octahedron microcrystals of cobalt oxide. This method may provide a means to grow microcrystals of other easy pyrolysis of acetate or other microcrystals in systems where a specific limitation is imposed by the use of conventional liquid solvents.

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