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A Solid-State Method for Preparing Cobalt-Doped Li_5FeO_4 Using $Fe(NO_3)_3$ as the Iron Source

Keqiang Ding[1], *Li Wang*[2,*], *Jianjun Li*[2], *Haitao Jia*[1], *Xiangming He*[2]

[1] College of Chemistry and Materials Science, Hebei Normal University, Shijiazhuang, Hebei 050016, P.R. China
[2] Institute o f Nuclear & New Energy Technology, Beijing Key Lab of Fine Ceramics, Tsinghua University, Beijing 100084, China
[*]E-mail: wang-l@tsinghua.edu.cn

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In the absence of inert gas protection, a cathode material of Co-doped Li_5FeO_4 was successfully prepared by a solid-state method, i.e., a mixture containing $Fe(NO_3)_3$•$9H_2O$, LiOH•H_2O and $Co(NO_3)_2$•$6H_2O$ was thoroughly ground leading to a powder, and then this mixture was sintered at various temperatures, generating the material of Co-doped Li_5FeO_4. The obtained samples were featured by X-ray diffraction (XRD), scanning electron microscope (SEM), and its specific capacity, cycle property and rate capabilities were also measured. A novel iron source was employed in the work though the electrochemical performance of the Co-doped Li_5FeO_4 was not very satisfactory. This method using carbon coating as protection is a very simple and useful tool to synthesize Li_5FeO_4, especially for the industrial application.

Keywords: Carbon protection, lithium battery, Li_5FeO_4, cobalt doping

1. INTRODUCTION

Although many kinds of cathode materials, such as Li_2CoO_2, $LiMn_2O_4$ and $LiFePO_4$, have been developed so far, there are still more spaces for pursuing novel cathodes since these developed cathodes materials have some obvious flaws [1]. It was reported that Li_2CoO_2 is related to a number of economic and environmental problems though it has good electrochemical performance [2]. Compared to the cobalt-based materials, Mn-based cathode raw materials are very cheap and friendly to the environment [3-5], but the capacity loss problems at elevated temperatures and an inherent lower capacity at 4 V have undermined $LiMn_2O_4$'s application as a suitable electrode [6]. Because of its relative lack of toxicity, the low cost, abundance of its raw materials, a high lithium intercalation voltage of 3.4V compared with lithium metal and a high theoretical capacity of $170mAhg^{-1}$, as a nextgeneration cathode material in lithium ion batteries, $LiFePO_4$ has been widely investigated recently. However, with the development of researching work on $LiFePO_4$, it was revealed that olivine $LiFePO_4$ has a low electronic conductivity and a low lithium diffusivity which greatly prevents its large-scale application in electric vehicles (EVs) and hybrid electric vehicles (HEVs), thus, developing novel cathode materials is still a hot topic especially in the field of electrochemistry.

To our knowledge, as far as in 1971, Demois-son et al. have developed new Lithium iron oxides, i.e., high temperature and low temperature forms of Li_5FeO_4 in the system of Li_2O and Fe_2O_3 [7, 8]. It was reported that the theoretical capacity of Li_5FeO_4 (Mr:155) is 173 $mAhg^{-1}$, and it was thought that in the relationship between ant-fluorite and fluorite structures, Li ions in anti-fluorite Li_5FeO_4 occupy the oxygen position in the fluorite type stabilized zirconia.

It was addressed that both the characteristics of high lithium ion mobility and easily changeable valence of the transition metal, Fe, can facilitate Li de-intercalation and subsequent Li intercalation in these oxides. In 1999, Narukawa [9] reported the synthesis of Li_5FeO_4. In his work, Li_5FeO_4 was prepared by a traditional ceramic method from Li_2O and Fe_2O_3. He addressed that the mixtures Li_2O and metal oxide were pressed into tablets (8 mm in diameter and 5-8 mm in thickness) and then were heated in an electrical furnace between 600 ℃ and 800℃ under various gas streams. He also probed the XRD patterns of $Li_{5-x}FeO_4$, and pointed that the decomposition of Li_5FeO_4 occurs with Li extraction from x=0.5, thus, he inferred that the possible reversible region may be limited between x=0 and x=0.5 in $Li_{5-x}FeO_4$.The charge and discharge curves of the Li/Li_5FeO_4 cell has revealed that the capacity loss of the first discharge is significantly large, which is more than 50%. N. Imanishi [10] and his co-workers prepared $Li_{5+x}Fe_{1-x}Co_xO_4$ and systemically probed its electrochemical performance. In his work, Li_5FeO_4 was also synthesized using traditional ceramic methods from the starting materials, i.e., Li_2O and Fe_2O_3. In his work, the mixture was heated in an electrical furnace at various temperatures under N_2 gas stream. The electrochemical test was performed under a constant current density of 0.3mA cm^{-2}. The cycle was repeated within a voltage range of 1.8-4.3V with the additional cut-off condition that the process was terminated when the capacity reached 200$mAhg^{-1}$. He thought that in the antifluorite structure the FeO_4 tetrahedral are isolated from each other, thus as lithium is removed from adjacent sites surrounding a FeO_4 tetrahedron, it is difficult to maintain the original crystal configuration like a layered host material. Also, he thought the difference between the charge and discharge potential profiles reflects an irreversible phase change, and the structural change that the host structure undergoes during the charge process may be too large to be readily recovered during the discharge process due to the fact that lithium atoms experience different surroundings when they diffuse in the crystal structure during discharge. The anti-fluorite type materials, low and high temperature forms of Li_5FeO_4 were also investigated by Hirano [11]. He reported that in the first charge, anti-fluorite type Li_5FeO_4 changed to amorphous-like phase which concerned the following discharge and charge processes. To our surprise, the published papers on the research work of Li_5FeO_4 are very limited. But the previous papers have strongly indicated that as potential anode materials, Li_5FeO_4 can be applied in the lithium battery in the near future due to its low cost and its amity to environment.

In this work, for the first time, a solid-state reaction for preparing Li_5FeO_4 was developed, in which the starting materials are LiOH and $Fe(NO_3)_3$ and no inert gas protection was employed.

2. EXPERIMENTAL

Briefly, stoichiometric amount of $LiOH•H_2O$ and $Fe(NO_3)_3•9H_2O$ were mixed to give rise to a mixture. And then this mixture was pressed into tablets (the thickness is 0.5mm and the diameter is about 4mm). The tablets were placed in a carbon-coated crucible, here the carbon used are graphite powders. And then it was heated in a furnace at a desired temperature for several hours. After cooling down to the room temperature, the resultant powder was thoroughly ground in a mortar. In this experiment, nitrogen gas such as N_2 or Ar was not involved. As a result, Li_5FeO_4 was prepared.

The particle morphology was observed by scanning electron microscope (SEM, HITACHI S-570, Japan) and X-ray diffraction (XRD, Bruker AXS, D8 ADVANCE, Germany) was used to examine the phase homogeneity. Electron dispersive X-ray analysis (EDX, PV-9900, USA) is performed by the WD-8X software established by Wuhan University.

The cathodes used for electrochemical characterization were fabricated by blending the prepared active material powders with acetylene black and polytetrafluoroethylene (PTFE) binder in a weight ratio of 85:10:5. Two-electrode electrochemical cells consisting of lithium metal foil as the negative electrode, Celgard 2400 separator, and an electrolyte of 1M $LiClO_4$ in EC:DEC:DMC (2:5:11, vol.) were assembled in an nitrogen-filled glove box. The electrochemical cycle tests were performed using a LAND series batteries testing system (CHINA, Wuhan Kinguo Electronics Co., Ltd.) at various C rates ($1C=173mAg^{-1}$) between 2.7 and 4.2 V at ambient temperature(25±2°C).

3. RESULTS AND DISCUSSION

3.1. Characterization of the Co-doped of Li_5FeO_4

As reported previously, the doping of cobalt element can greatly increase the electrochemical performance of Li_5FeO_4. Fig.1 shows the X-ray diffraction profiles of Li_5FeO_4 synthesized at 850°C with various molar ratio of Fe to Co. It can be seen that the intensities of the diffraction peaks of XRD pattern for the pure Li_5FeO_4 are too weak to be observed, indicating a poor crystal structure. While, the intensity of peaks are greatly enhanced by Co doping, suggesting an improved crystal structure. Interestingly, the XRD patterns change evidently with the molar ratio of Fe to Co. This indicated that Co content is a key factor influencing crystal structure of the samples. When the molar ratio of Fe to Co is 7:3, the peak around 65º attenuates obviously, implying that too much Co will destroy the crystal structure of Li_5FeO_4. Therefore, the sample of $Li_5Fe_{0.8}Co_{0.2}O_4$ is used in the following work.

To determine the component of the obtained sample, EDX measurements are also carried out, as shown in Fig.2. Since lithium element cannot be detected using our present equipment, only Fe, Co, O are detected in the EDX pattern of $Li_5Fe_{0.8}Co_{0.2}O_4$, strongly indicating that the sample as-prepared have above three elements. Unfortunately, it is revealed that the molar ratio of Fe:Co:O in the as-prepared sample is 8:1:10, which does not accord with the molecular formula of $Li_5Fe_{0.8}Co_{0.2}O_4$. Considering that EDX is a semiquantitative spectrographic analysis, this indicates that some impurities may be involved in the prepared sample.

The influence of sintering temperature on crystalline structure of $Li_5Fe_{0.8}Co_{0.2}O_4$ is also investigated. As shown in Fig.3, all starting mixtures are heated for 3h, but the sintering temperatures are different.

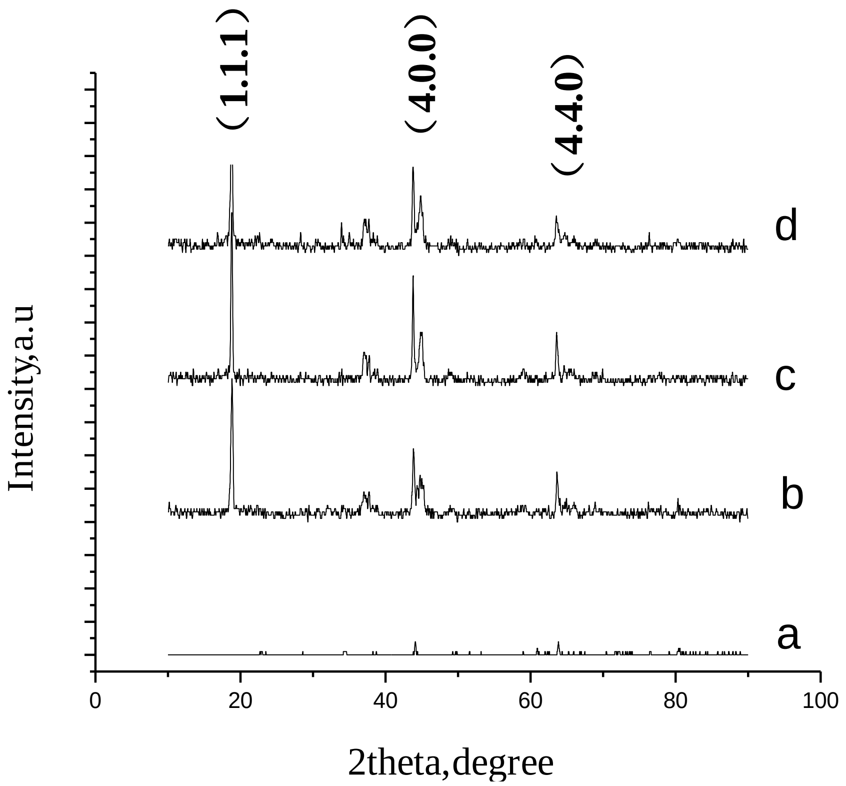

Figure 1. XRD patterns of Co-doped Li_5FeO_4 sample sintered at 850°C for 3h. **a**: Li_5FeO_4; **b**: $Li_5Fe_{0.9}Co_{0.1}O_4$; **c**: $Li_5Fe_{0.8}Co_{0.2}O_4$; **d**: $Li_5Fe_{0.7}Co_{0.3}O_4$.

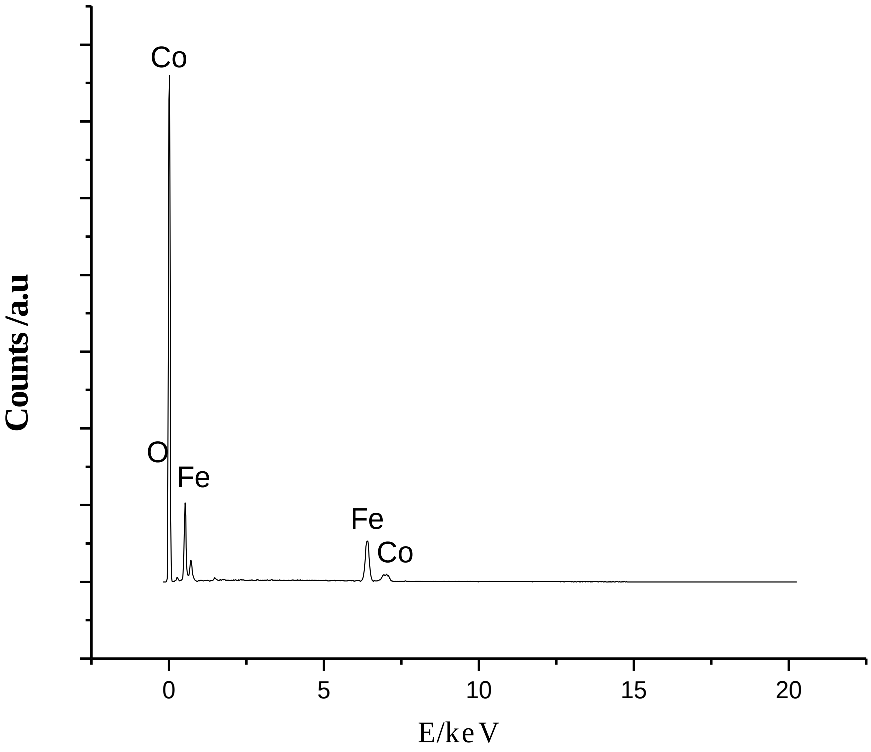

Figure 2. EDX patterns of $Li_5Fe_{0.8}Co_{0.2}O_4$.

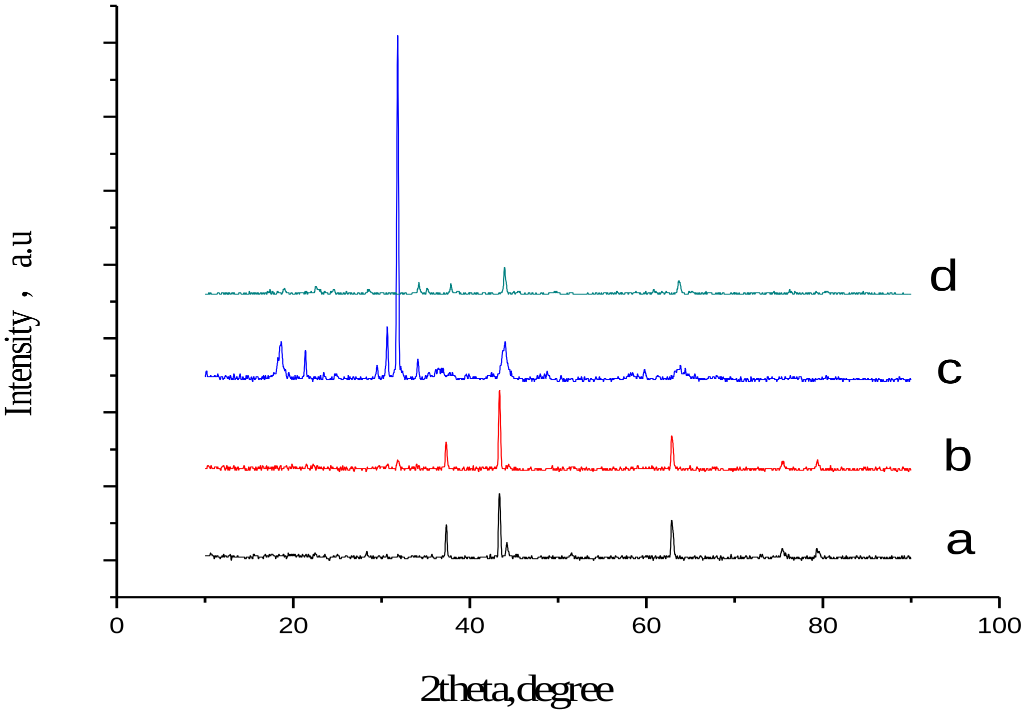

Figure 3. XRD patterns of $Li_5Fe_{0.8}Co_{0.2}O_4$ sintered for 3h at different temperatures. **a**: 650°C; **b**: 750°C; **c**: 850°C; **d**: 950°C

It can be seen that when the temperature is 950^{o}C, the diffraction peaks are significantly attenuated, indicating a poor crystal structure. Probably, when the temperature is too high, more lithium is evaporated, leading to a material with poor crystal structure. Interestingly, as the sintering temperature is 850^{o}C, more diffraction peaks similar to the standard XRD pattern of Li_5FeO_4 are displayed. Therefore, 850^{o}C is set as the optimized sintering temperature to prepare samples.

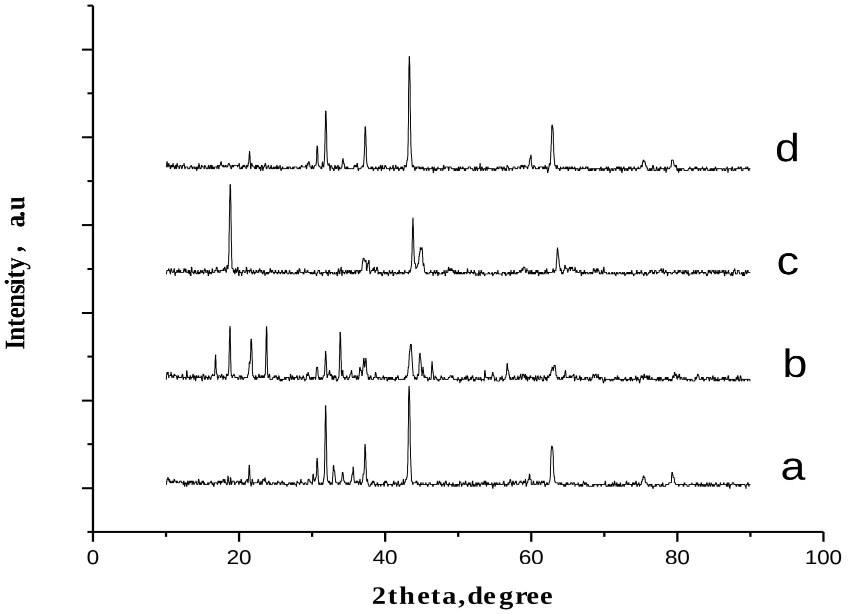

Figure 4. XRD patterns of $Li_5Fe_{0.8}Co_{0.2}O_4$ prepared at 850°C for various sintering time. **a**: 1h; **b**: 3h; **c**: 6h; **d**: 9h

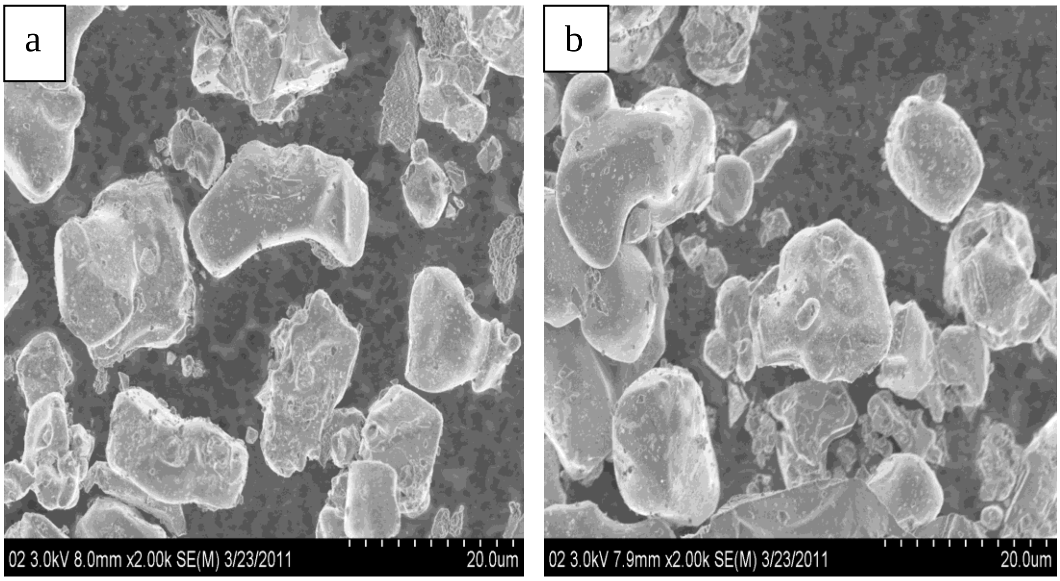

Figure 5. SEM images of Co-doped Li_5FeO_4. **a**: $Li_5Fe_{0.8}Co_{0.2}O_4$; **b**: $Li_5Fe_{0.7}Co_{0.3}O_4$.

The effect of calcination time on the structure of $Li_5Fe_{0.8}Co_{0.2}O_4$ is probed as shown in Fig.4. It can be seen that the sintering time has a strong effect on the shape of the XRD patterns and the intensity of the peaks as well. Instead of enhancing the peak intensities, when the sintering time is 9h, as plotted by line **d,** weak peaks are observed, implying that a material with a poor crystal structure was prepared.

SEM images for Li_5FeO_4 doped with various content of Co are shown in Fig.5. Images **a** and **b** is for $Li_5Fe_{0.8}Co_{0.2}O_4$ and $Li_5Fe_{0.8}Co_{0.2}O_4$, respectively. It seems that Co content shows no obvious effect on the morphology of the as-prepared samples. Also, one can see that there are some small particles on the surface of the big particles, indicating that the sample is not a pure material, and more works should be done to reveal the relationship between the preparation conditions and the crystal structure. To our knowledge, the SEM images of Li_5FeO_4 doped with various content of Co is not reported so far though the report on Li_5FeO_4 has been published by other research groups.

3.2 Electrochemical performance of the Co-doped $Li_5Fe_{0.8}Co_{0.2}O_4$

The cyclic voltammograms (CVs) of the cathode material can clearly reflect the intercalation and deintercalation of lithium in the charge-discharge process. The CVs of $Li_5Fe_{0.8}Co_{0.2}O_4$ are shown in Fig. 6, it can be seen that several peaks are displayed. The oxidation peaks at 3.3 V (vs Li/Li^+) should correspond to the process as shown below:

$$Li_5\,Fe_{0.8}Co_{0.2}O_4 \rightarrow Li_4\,Fe_{0.8}Co_{0.2}O_4 + Li^+ + e \quad (1)$$

The peaks at above 3.75V (vs Li/Li^+) probably correspond to the reaction as shown below:

$$Li_4\,Fe_{0.8}Co_{0.2}O_4 \rightarrow Li_{4-x}\,Fe_{0.8}Co_{0.2}O_4 + xLi^+ + xe \quad (2)$$

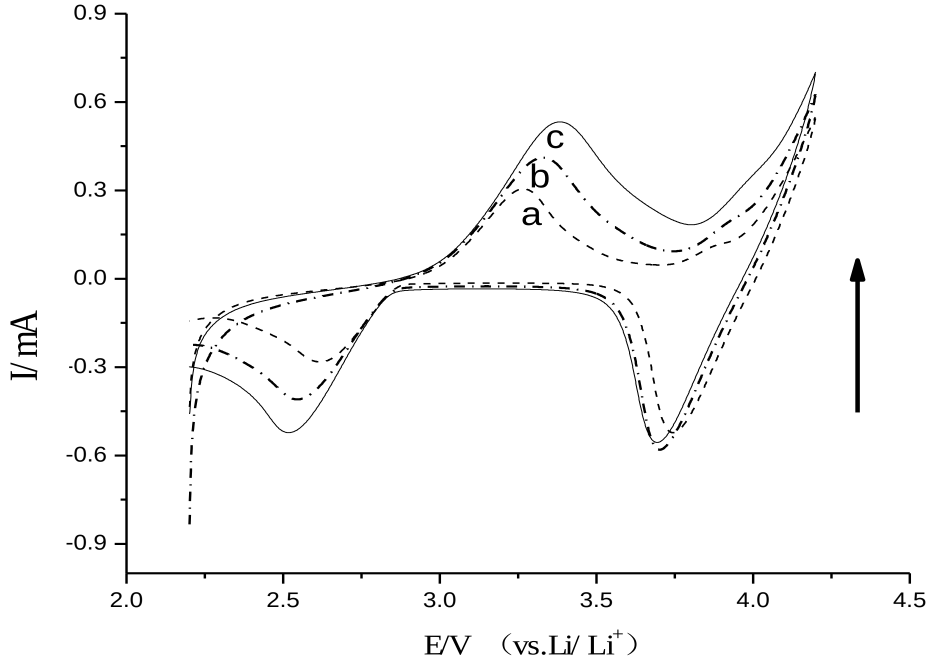

Figure 6. Cyclic voltammograms of Li|$Li_5Fe_{0.8}Co_{0.2}O_4$ half cell at various scan rates.

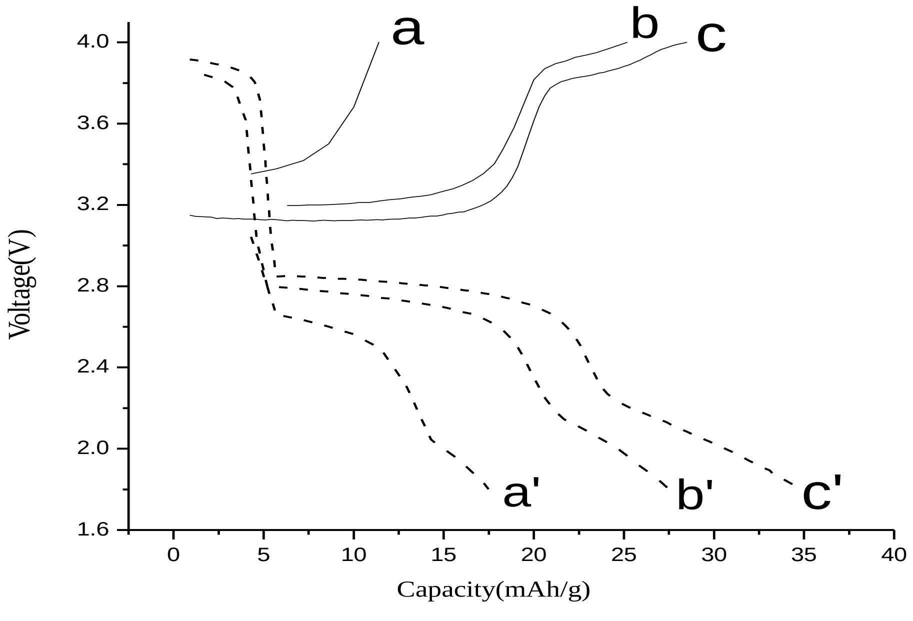

Figure 7. Charge-discharge curves Li|$Li_5Fe_{0.8}Co_{0.2}O_4$ half cell at 0.1C (line **c** and c'), 0.2C (line **b** and **b**') and 0.5C (line **a** and **a**') rate.

Thus, the reduction peaks correspond to the intercalation of Li^+. Therefore, it can be concluded that there should be two voltage plateaus in the charge-discharge curves. Also, one can see that as the scan rates increased the peak current enhanced correspondingly, suggesting that Li ion can intercalate and deintercalate freely.

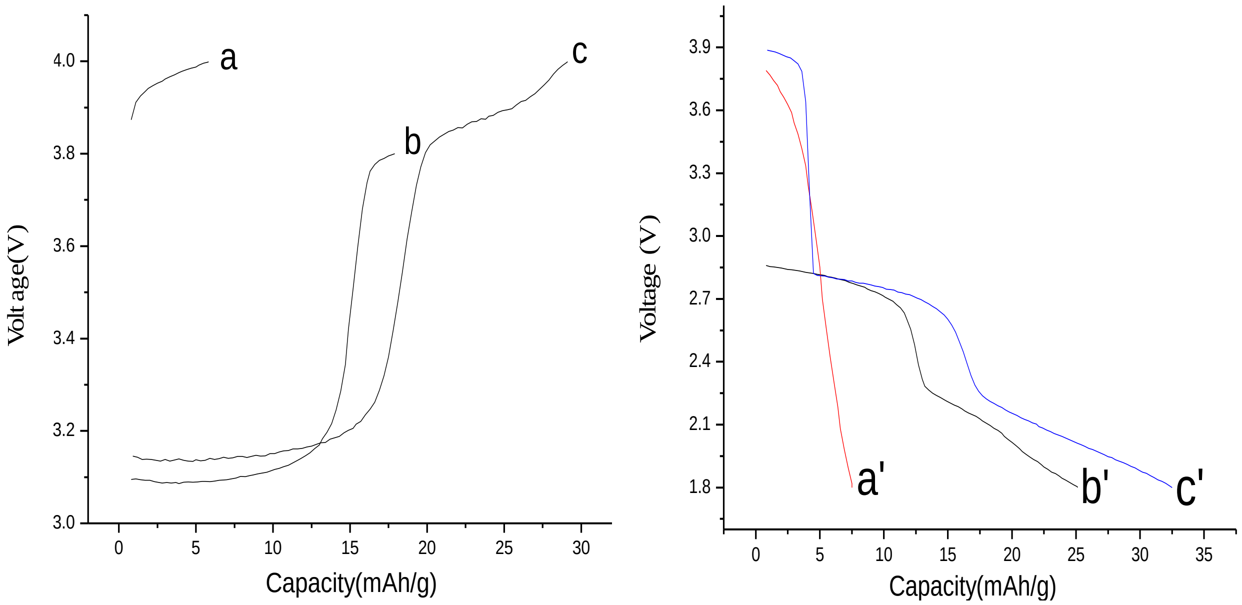

Figure 8. Charge (a)-discharge (b) curves for the cell assembled by the Co-doped Li_5FeO_4 at 0.1C. Curve **a, a'**: $Li_5Fe_{0.7}Co_{0.3}O_4$; curve **b, b'**: $Li_5Fe_{0.9}Co_{0.1}O_4$; curve **c, c'**: $Li_5Fe_{0.8}Co_{0.2}O_4$.

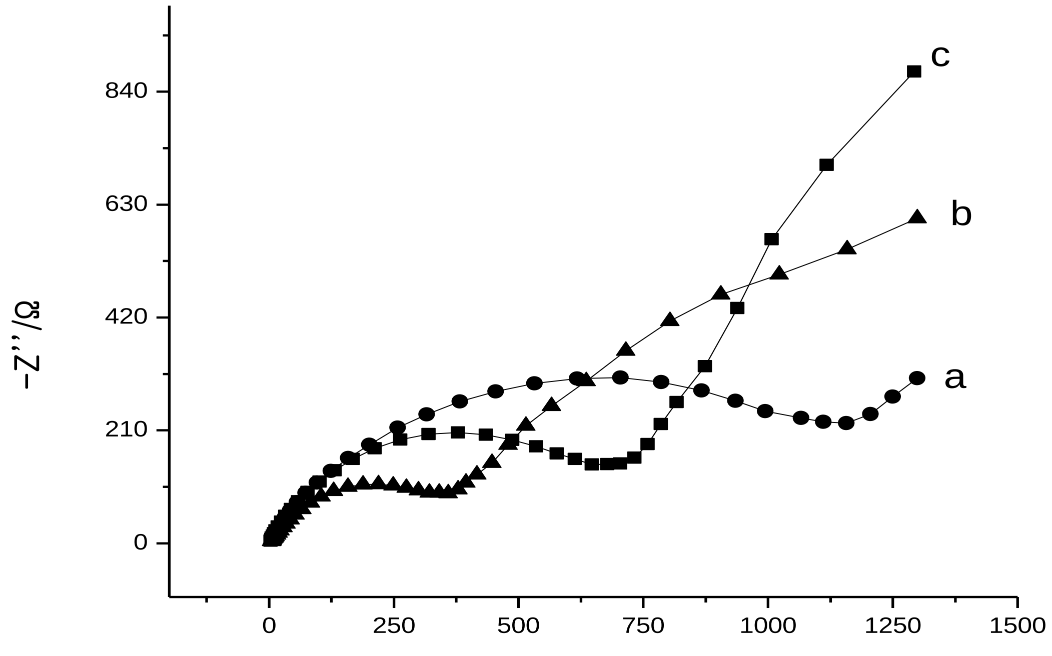

Figure 9. -Nyquist plots for the cell assembled by Li and Co-doped Li_5FeO_4.Line **a**: $Li_{5.0}Fe_{0.7}Co_{0.3}O_4$, line **b**:$Li_{5.0}Fe_{0.8}Co_{0.2}O_4$,line **c**: $Li_{5.0}Fe_{0.9}Co_{0.1}O_4$.

Fig.7 shows charge-discharge curves of the cell assembled by the Li_5 $Fe_{0.8}Co_{0.2}O_4$. One can see that as the charge-discharge rate changed the capacity of the cell altered dramatically, suggesting that the properties of $Li_5Fe_{0.8}Co_{0.2}O_4$ should be improved in the further investigation. At 0.1C, the discharge capacity of the Li- Li_5 $Fe_{0.8}Co_{0.2}O_4$ cell is about 37mAh/g, while as the discharge rate is 0.5C, the capacity was decreased greatly to be around 17mAh/g. This indicated that the polarization of the cathode of $Li_5Fe_{0.8}Co_{0.2}O_4$ increased when the current enhanced. The influence of Co content on the charge-discharge curve at 0.1C of the cell assembled by Co-doped Li_5FeO_4 was also probed, as shown in Fig.8a and Fig.8b. It indicated that when the molar ratio of Fe to Co is 4, the largest capacity of the cell was displayed. As shown in the previous work [12], EIS is one of the most powerful tools to analyze electrochemical reactions, such as those processes occurring at electrode/electrolyte interfaces and the lithium ion intercalation/deintercalation. In this experiment, the Nyquist curves of Li- Li_5FeO_4 (doped with Co) were plotted at open circuit potential as shown in Fig.9. Generally, the semicircle appearing at the high frequency region corresponds to a circuit containing a resistance element parallel to a capacitance element, and the larger semicircle is displayed, the bigger resistance element is obtained. Thus, it can be concluded that the smallest charge transfer resistance was presented by the cell of Li-$Li_5Fe_{0.8}Co_{0.2}O_4$, which is consistent with the results obtained from Fig.8a and Fig.8b very well. We do admit the capacity value of the as-prepared $Li_5Fe_{0.8}Co_{0.2}O_4$ is lower than the reported date by N. Imanishi [10]. But in this work the Fe source is $Fe(NO_3)_3$ and no inert gas was introduced, which is the novelty of this preliminary work.

4. CONCLUSIONS

Li_5FeO_4 is synthesized by a solid-state method using $Fe(NO_3)_3$ as the iron sources. More importantly, in this process, instead of inert gas protection, carbon-coating protection was introduced, which is very helpful for the preparation of Li_5FeO_4 in a large scale. XRD patterns and SEM images strongly demonstrated that the Co content in Li_5FeO_4 is a key factor, affecting not only the crystal structure but also the electrochemical performance of Li_5FeO_4. Especially, $Li_5Fe_{0.8}Co_{0.2}O_4$ presents the best electrochemical performance among as-prepared Co doped Li_5FeO_4. Presenting a novel way for preparing Co-doped Li_5FeO_4 is the main contribution of this preliminary work. We do admit that more works should be done to improve the electrochemical performance of Li_5FeO_4.

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