

Influence of Carbon Sources on the Preparation of $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ and its Electrochemical Performance

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For the first time, carbon-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ cathode materials were successfully prepared by a two-step solid-state method, in which four carbon sources, i.e., carbon black, graphite, glucose and octadecanoic acid, were employed. The obtained samples were thoroughly featured by X-ray diffraction (XRD), FTIR, scanning electron microscope (SEM), and their specific capacities were also measured by galvanostatic charge-discharge measurement. Interestingly, it was revealed that various carbon sources can not only affect the crystal structure of the as-prepared samples, but also influence the electrochemical performance of cells assembled by the prepared samples of carbon-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$. It indicated that under the same conditions, the glucose-doped sample showed the best electrochemical behavior among the as-prepared samples.

Keywords: lithium battery, $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$, carbon sources, electrochemical performance.

1. INTRODUCTION

Except for metal-element doping into the cathode materials [1, 2], carbon-coating or carbon-doping method is regarded as the main way for enhancing the conductivity of the cathode materials, leading to improved electrochemical performance. For example, Zhang et al.[3] reported that carbon-modified nano-crystalline LiFePO_4 can be prepared by a one-step microwave method, in which polyethylene glycol (PEG) was used as the carbon source. Sun [4] described the preparation of carbon-coated lithium vanadium phosphate ($\text{Li}_3\text{V}_2(\text{PO}_4)_3$), in which glucose was employed as the carbon sources. Oh [5] probed the effect of carbon additive on electrochemical performance of LiCoO_2 composite cathodes, in which two carbon blacks (Super P and acetylene black) and one graphite (Lonza KS6) are employed as the conducting agents. He pointed out that carbon additives play an

important role in influencing the electrode conductivity, utilization of active materials and cycleability. Gu et al.[6] reported the synthesis of LiFePO_4 -multiwalled carbon nanotubes (MWCNTs) composites prepared by a hydrothermal method, where carbon nanotubes were employed as the carbon sources. Peng et al.[7] published his work on the preparation of LiFePO_4 /carbon composites fabricated by a soluble starch sol assisted simple rheological phase method. Summarily, various kinds of carbon sources have been doped into cathode materials, largely showing an improved electrochemical performance. However, the exact roles of carbon in the cathode materials were not well revealed, though Suryanarayanan [8] has presented a review of the role of carbon host lattices in Li-ion intercalation/de-intercalation processes. That is to say, there are still more spaces for probing the roles of carbon in the cathode materials.

In our previous works of the preparation and characterization of the Li_5FeO_4 [9], it has been concluded that the cobalt-doped Li_5FeO_4 , especially the $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$, can deliver the better electrochemical performance when compared to the pure Li_5FeO_4 . Also it is inferred from our previous work [10] that the doped carbon (using carbon nanotubes as the carbon sources) can greatly affect the particle sizes of the as-prepared samples and the crystal structure of the resultant samples as well. It has also been proved that the carbon nanotubes-doped samples of $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ displayed better electrochemical performance, including the higher discharging capacity and rate capability, when compared to the carbon-free samples of $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$. Thus, it is very meaningful to probe the influence of carbon sources on the preparation and properties of the samples of $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$. To the best of our knowledge, there is no report on the role of carbon sources in the cathode materials of $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$.

In this work, carbon in various forms was doped into the $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ with an intention to probe the role of various carbon sources in the electrochemical performance of the cathode materials. Here, the starting materials are $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$. The carbons employed are carbon black, graphite, glucose, and octadecanoic acid. To compare the results obtained under identical conditions, the weight percent of each carbon source in the precursors was kept to be 7wt%.

2. EXPERIMENTAL

2.1. Preparation of carbon-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$

Due to its simplicity, the solid-state method was still used for fabricating the cathode materials of carbon-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$. Herein, a two step sintering method [9] was utilized for preparing carbon-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$. That is to say, the mixture having $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, carbon sources and $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was pressed into pieces, and heated at a temperature of 470 °C for around 10h. And then the obtained samples were ground thoroughly before it was calcinated again at a temperature of 750 °C for 3h. It should be noticed that in this process, the inert gas protection method was not employed. Instead, a carbon-coating method was used as has been well addressed in our previous report [10].

2.2 Characterization

X-ray diffraction (XRD) analysis of the catalyst is carried out on a Bruker D8ADVANCE X-ray diffractometer equipped with a Cu K α source ($\lambda = 0.154$ nm) at 40kV and 30mA. The 2θ angular region between 10 and 90° is recorded at a scan rate of 1°/step. The particle morphology was observed by scanning electron microscope (SEM, HITACHI S- 570, Japan). Electron dispersive X-ray analysis (EDS, PV-9900, USA) is performed by the WD-8X software established by Wuhan University. Fourier transform infrared spectrometry (FT-IR) measurements are carried out on a Hitachi FT-IR-8900 spectrometer (Japan).

In this work, the electrochemical experiments were carried out using the coin-type cells. The working electrode was prepared by mixing active material with poly (tetrafluoroethylene) (PTFE) and acetylene black at a weight ratio of 85:10: 5 in N-methyl-2-pyrrolidone (NMP) to form slurry. Then, the resultant slurry was uniformly pasted on an aluminum foil with a blade, dried at 120 °C in a vacuum oven and pressed under a pressure of 20Mpa. The dried foil was transferred to a vacuum oven and kept under 80°C overnight for further drying. The active material loading density of the electrode is ca. 1.0mg·cm⁻². The Celgard 2400 microporous membrane was used as a separator. Coin type cell was assembled with the cathode as a working electrode and lithium foil as a counter electrode in an N₂-filled glove box. The cells were first charged and then discharged between 1.7V and 4.0V vs. metallic Li with a current density of 0.1C at room temperature. The electrolyte is 1 M LiClO₄ in a organic solution (ethylene carbonate, diethyl carbonate and dimethyl carbonate, i.e., EC +DEC+DMC) in a volume ratio of 2:5:11.

3. RESULTS AND DISCUSSION

3.1 Characterization of the carbon-doped Li₅Fe_{0.8}Co_{0.2}O₄

Fig.1 is the XRD patterns for the carbon-doped Li₅Fe_{0.8}Co_{0.2}O₄. One can see sharp diffraction peaks are displayed in the XRD patterns, suggesting that particles with higher crystalline were obtained. For the carbon black-doped Li₅Fe_{0.8}Co_{0.2}O₄, no diffraction peak at around 26° corresponding to the crystal plane of (111) was displayed. While for other three samples, the crystal plane of (111) was clearly observed. It indicated that the crystal structure of the carbon black doped one is rather different from the other three samples. Interestingly, as glucose was doped, as shown by pattern c, the diffraction peaks at 18° was observed. Also, the intensity of XRD pattern for the glucose-doped one is stronger than that of the octadecanoic acid-doped Li₅Fe_{0.8}Co_{0.2}O₄, though their diffraction peak shapes are similar to each other. Meanwhile, the XRD patterns of the glucose doped sample are similar to the reported XRD patterns of pure Li₅FeO₄[11]. Thus, the well-defined XRD pattern of glucose doped sample may promise its better electrochemical performance when compared to other samples. Various XRD patterns may imply different crystal structure, giving rise to different electrochemical performance. But how do the doped carbon sources interact with the Li₅Fe_{0.8}Co_{0.2}O₄? How do the

doped various carbon sources affect the electrochemical performance of the resultant cathode materials of $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$. More works should be done to reveal above questions.

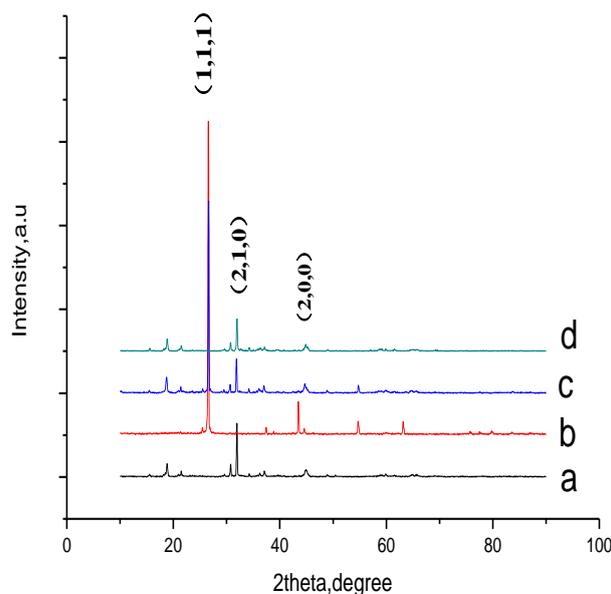


Figure 1. XRD patterns for the carbon-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ prepared from various carbon sources. Pattern **a**: carbon black; pattern **b**: graphite; pattern **c**: glucose; pattern **d**: octadecanoic acid.

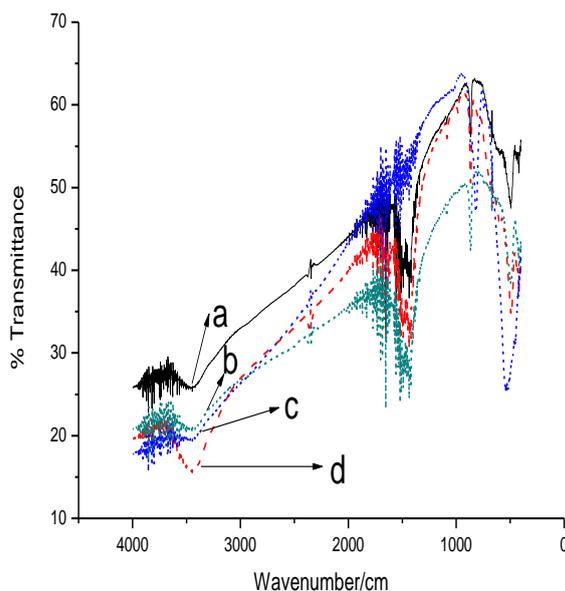


Figure 2. FTIR spectra for the carbon-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ prepared from various carbon sources. Line **a**: carbon black; Line **b**: graphite; Line **c**: octadecanoic acid; Line **d**: glucose.

Fig.2 is the FTIR spectra for the samples prepared from various carbon sources. Generally, the band centered on 3423cm^{-1} is attributed to stretching and bending vibrations of water. The water may

be introduced during the process of preparing the sample[12]. The band at about 1432cm^{-1} may be the absorption of CO_3^{2-} that may be introduced into the carbon-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ lattice during preparation or the absorbed CO_2 from air.

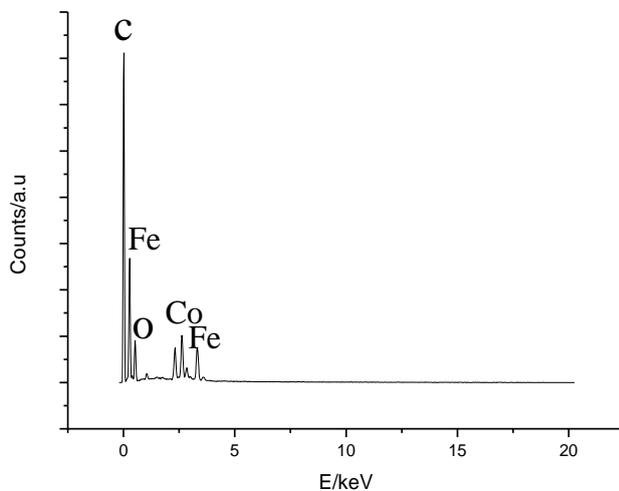


Figure 3. EDS spectra for the glucose-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$.

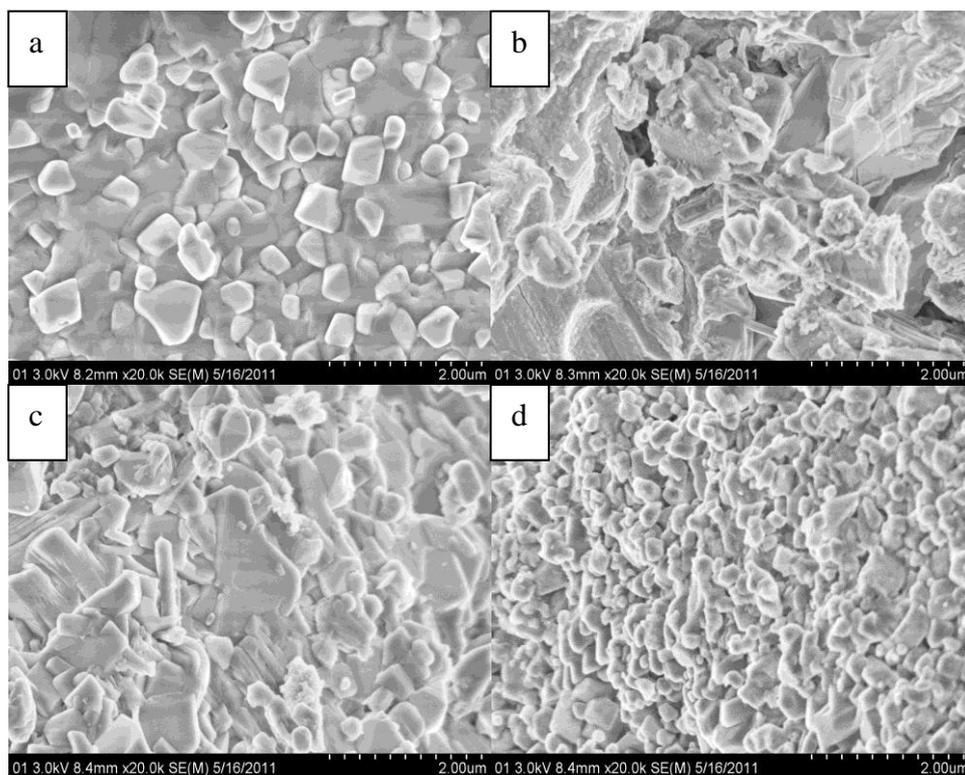


Figure 4. SEM images of the CNT-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ prepared from various carbon sources. Image a: carbon black; Image b: graphite; Image c: octadecanoic acid; Image d: glucose.

The band centered at the range from 550 cm^{-1} to 1000 cm^{-1} may correspond to the characteristic bands of $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$. One can see that when the carbon sources are octadecanoic acid (line **c**) and glucose(line **d**), the intensity of the bands located between 500 cm^{-1} and 1000 cm^{-1} is greatly enhanced compared with other samples, suggesting that various carbon sources have affected the functional groups in the resultant samples. EDS spectra of the glucose -doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ is clearly displayed in Fig.3, in which the elements of Fe, Co, O and C were all exhibited, suggesting that no other impurities were involved in the obtained samples. In other words, the method we developed here is a feasible method for preparing carbon-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$.

To discuss the role of different carbon sources on the morphologies of as-prepared samples. SEM images of carbon-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ were shown in Fig.4. It can be seen that the morphology of the samples was impressively affected by the doped carbon sources when the weight percent of carbon is kept to be 7 wt%. As the carbon sources are graphite and octadecanoic acid, as shown by image **b** and **c**, larger and irregular particles were displayed. Interestingly, when the carbon sources are black carbon and glucose, as shown by image **a** and image **d**, smaller and regular particles were observed. Evidently, the smallest particles were observed by the glucose-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$. It was reported in the previous paper [13,14] that the shape and particle size are the main factors affecting the electrochemical performance of the cathode materials, and smaller particles are favorable to the diffusion process of Li^+ due to the shortened diffusion path. Thus, 7wt% glucose-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ should show the best electrochemical performance among the four samples, since it has the smallest particle sizes.

3.2. Electrochemical performance of the carbon-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$

Nyquist plots, one type of curves in Electrochemical Impedance Spectroscopy (EIS), is a main method for evaluating the electrochemical performance of cells assembled by the as-prepared samples when using the as-prepared samples as cathode materials [15]. Nyquist plots for the cells assembled by our samples were conducted as illustrated in Fig.5. Generally, based on the previous report [16,17], the semicircle appearing at the high frequency region corresponds to a circuit having a resistance element parallel to a capacitance element, and a semicircle with a larger diameter corresponds to a larger charge transfer resistance. Thus, approximately, the diameter of the semicircle stands for the value of charge transfer resistance. Interestingly, the diameter of the semicircle greatly varied when the kinds of carbon sources are different. It indicated that under the same conditions, various carbon sources played different roles in forming the resultant samples. For the sample containing glucose, i.e., curve **a**, the smallest semicircle was observed, indicating a better electrochemical performance. While for other samples, i.e., curve **b**, **c** and **d**, an evident semicircle in the higher frequency region, along with a 45° line in the lower frequency region, was clearly observed. Thus, it can be concluded that the doped carbon has strongly influenced the electrochemical performance of $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$, which is consistent with the results from XRD patterns shown in Fig.1 very well. It seemed that the sample of glucose-doped one should manifest the best electrochemical performance among these samples due to its smallest diameter of the semicircle in the high frequency region.

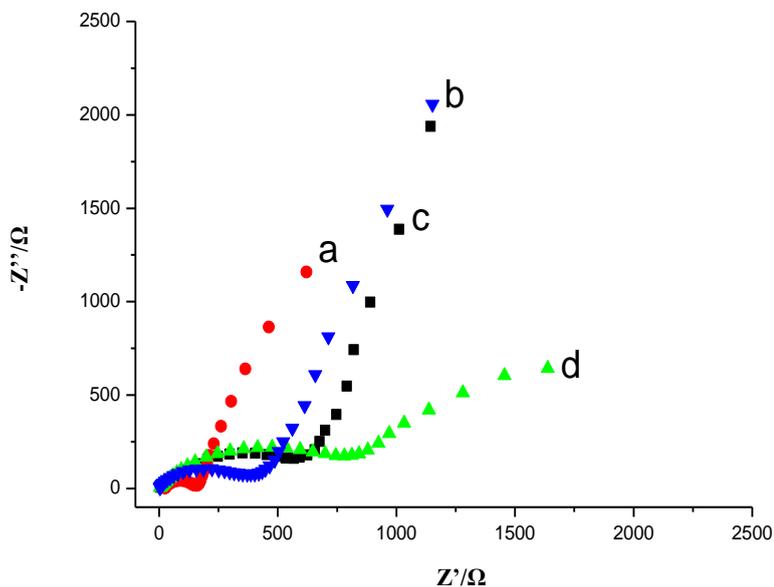


Figure 5. Nyquist plots for the carbon-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ prepared from various carbon sources. Line **a**: glucose; line **b**: graphite; line **c**: carbon black; line **d**: octadecanoic acid.

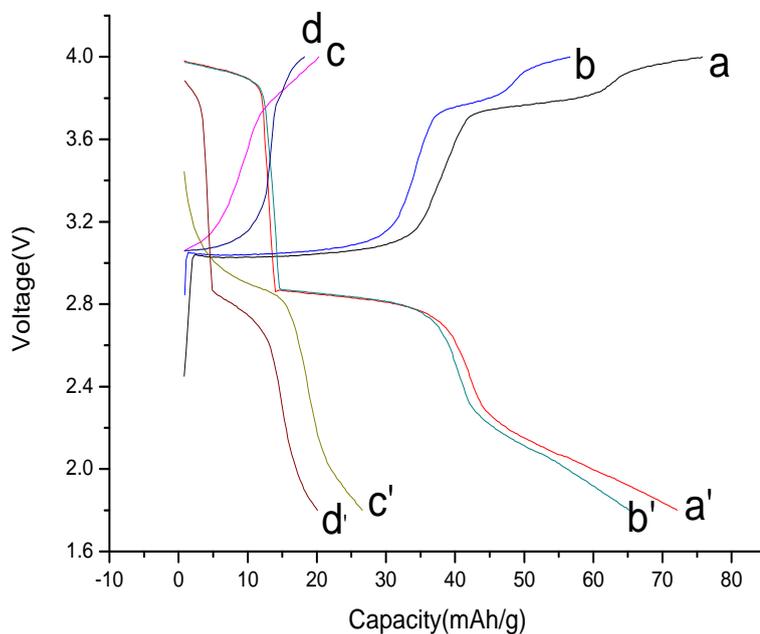


Figure 6. The first charge/discharge curves at 0.1C for the carbon-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ prepared from various carbon sources. Line **a** and **a'**: glucose; line **b** and **b'**: octadecanoic acid; line **c** and **c'**: graphite; line **d** and **d'**: carbon black.

The discharge capacity value of the cell is the main parameter reflecting the electrochemical property of the as-prepared cathode materials. Therefore, the galvanostatic charge-discharge curves for the cell assembled by our prepared samples were also plotted as shown in Fig. 6. From Fig. 6, one can see that the first discharge capacity at 0.1C for carbon black, graphite, octadecanoic acid and glucose-

doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ are 25.8, 34.1, 61.0 and 73.6mAh/g, respectively. It indicated that the glucose-doped one showed the best electrochemical performance. This result is consistent with the result shown in the Nyquist plots of Fig. 5 very well. Interestingly, for the charging curve **a** and **b**, two clear steps, one at around 3.0V and one 3.7V versus Li, respectively, were exhibited, suggesting lithium removal took place at these voltage. Unfortunately, for the carbon black and graphite doped samples, as shown by curve **c** and **d**, the charging voltage plateau, and the discharging voltage plateau as well, were not displayed. Very recently, Johnson [18] represented a voltage profile of a Li/Li₅FeO₄ cell, in which the cell was charged at a very slow rate of C/40. In his report, lithium removal takes place in two steps, the first between ~3.5 and 4.0V and the second on a voltage plateau at 4V. In Takeda's report [11], no voltage plateau was displayed in the charging-discharging curves, though the discharging capacity is above 100mAh/g at 0.3mA/cm². Here, the charge-discharge curves for the glucose-doped sample is similar to the charging curves for the Li₅FeO₄ reported by Imanishi[19]. We do admit that the discharge capacity value of the as-prepared sample is lower than the previously published data [19]. Thus, more works should be done to enhance the electrochemical performance of as-prepared samples.

4. CONCLUSIONS

For the first time, the effect of various carbon sources on the preparation and electrochemical performance of $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ was preliminary investigated. It was revealed that (1) The doping of various carbon sources in $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ has an evident influence on the crystal structure of $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$. (2) Nyquist plots of EIS also proved that glucose-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ having a weight percent of 7wt% displayed the smallest charge transfer resistance among the four prepared samples, which can partially account for its satisfactory electrochemical behavior, when compared to other carbon sources doped samples. SEM images also revealed that 7wt% glucose-doped $\text{Li}_5\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_4$ showed the smallest particles among the as-prepared samples, which strongly supported the results obtained from the charge-discharge curves.

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