



Electrochemical Performance of Iron Oxide Nanoflakes on Carbon Cloth under an **External Magnetic Field**

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Abstract: In this work, the iron oxide (Fe_2O_3) nanoflakes on carbon cloth ($Fe_2O_3@CC$) were triumphantly prepared and served as the electrode of supercapacitors. By applying an external magnetic field, we first find that the magnetic field could suppress the polarization phenomenon of electrochemical performance. Then, the influences of the mono-/bi-valent cations on the electrochemical properties of the Fe₂O₃@CC were investigated under a large external magnetic field (1 T) in this work. The chemical valences of the cations in the aqueous electrolytes (LiNO₃ and $Ca(NO_3)_2$) have almost no influences on the specific capacitance at different scan rates. As one of important parameters to describe the electrochemical properties, the working potential window of the Fe₂O₃@CC electrode was also investigated in this work. The broad potential window in room-temperature molten salt (LiTFSI + LiBETI (LiN(SO_2CF_3)₂ + LiN($SO_2C_2F_5$)₂)) has been obtained and reached 1.2 V, which is higher than that of the traditional aqueous electrolyte (~0.9 V).

Keywords: Fe₂O₃ nanoflakes; magnetic field; molten salt; wide working windows; electrochemical capacitors

1. Introduction

Electrochemical capacitors have been considered as a reliable supplement in power sources aspect, which is due to their fast charging/discharging processing, good cycling properties and high power density [1–3]. Nevertheless, their low energy density becomes a stumbling block to the rapid development of supercapacitors. In order to get higher energy density several strategies have been explored to design and fabricate electrode materials with various porous and hierarchical nanostructures, which are conducive to enhance specific capacitances and modify the rate performances [4–8]. Iron oxides (such as Fe_2O_3 and Fe_3O_4) have been brought into focus as electrode candidates for supercapacitors in a variety of materials [9–12]. Specifically, α -Fe₂O₃ materials have been synthesized and reported elsewhere because of their high theoretical capacitance, low cost, and abundant chemical valences. Currently, various α -Fe₂O₃ nanostructures, for instance nanoparticles, nanotubes, nanosheets, and nanospheres with high super-paramagnetic behaviors, porous structure, and high surface area have been researched and exhibited excellent electrochemical properties [13–17]. However, the weak electrical conductivity of α -Fe₂O₃ materials (10⁻⁴ $\Omega^{-1} \cdot m^{-1}$ for bulk and $2.5 \times 10^{-3} \Omega^{-1} \cdot m^{-1}$ for nanostructures) still makes it difficult to completely use the active material, giving rise to finite enhancement of the specific capacitance [18–20]. There is literature



reporting that very small external magnetic fields (mT) have induced capacitance enhancement of the Fe_2O_3 -graphene nanocomposites [21]. This could explain why the external magnetic field is deemed to facilitate the electrons/ions transmission between the electrolyte and the electrode during charging/discharging procedure. However, one wonders if the very large magnetic field has an effect on the capacitance. More recently, a finer morphology of nanoporous magnetic material has been prepared by applying an external magnetic field (~0.5 T) which modulates different dealloying stages of the nanoporous structure formation. We have reported the effect of an external magnetic field on the dealloying process of the Ni-Al alloy in alkaline solution [22].

Munichandraiah et al. found that the aqueous electrolytes with bivalent cations (Ca²⁺ or Mg²⁺) contributed to modify the MnO₂ electrochemical utilization and, thus, improved the specific capacitance [23,24]. However, the common aqueous electrolytes cannot overcome the thermodynamic limitation of water splitting, ~1.23 V [25,26], and the non-aqueous electrolytes (e.g., organic electrolytes) are generally combustible and expensive. Over the years, the inventive "water-in-salt" hybrids and room-temperature molten salts have been proven to broad the working voltage window (much larger than 1.23 V) [27–29]. Herein, this work investigates the influences of the mono-/bi-valent cations on the electrochemical properties of the Fe₂O₃@carbon cloth (Fe₂O₃@CC) under an external magnetic field (1 T). The electrochemical performances of the Fe₂O₃@CC electrode in a room-temperature molten salt electrolyte have been also studied for the broad working potential window.

2. Materials and Methods

The carbon cloth (WOS 1002 PHYCHEMi Co., Ltd., Wuhan, China) in the work was conducted the hydrophilic treatment. The detailed process is following: the carbon cloth was washed with concentrated H_2SO_4 and H_2O_2 mixed solution, and deionized water under sonication for 2 h. The treated carbon cloth (CC) served as the substrate for the growth of Fe₂O₃nanoflakes. Electrochemical deposition was performed at 1.5 V for 5 min in a conventional three-electrode system: the treated CC, the Pt, and an Ag/AgCl as the working, counter and reference electrodes, respectively. The working electrolyte was 0.05 M FeCl₂ aqueous solution for iron deposition. Then the working electrode was washed with deionized water and ethanol, and dried for a night. Lastly, the dried precursors were calcinated at 650 °C for 2 h in an inert atmosphere.

The structural information, constitute and morphology features of the Fe₂O₃@CC composites were determined by X-ray diffraction (XRD, Rigaku D/Max-2500, Japan) with native Standard Measurement software, and field emission scanning electron microscopy (FESEM, FEI Verios 460 L, Eindhoven, The Netherlands). The electrochemical measurements were carried out in a three-electrode system: the Fe₂O₃@CC (5×5 mm), the Pt (50×50 mm) and Ag/AgCl were used as working electrode, counter electrode, and reference electrode, respectively. All electrochemical measurements were carried out under an external magnetic field (EMP-5, East Changing, Beijing, China). The magnetic field was controlled through adjusting the magnitude of the current and the magnetic flux density was then measured by a Digital Gauss Meter (PF-045B, Mianyang, China). The direction of magnetic field was perpendicular to the surface of working electrode. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of the Fe₂O₃@CC electrode were performed using electrochemical workstation (CHI 760E, Shanghai, China) in different aqueous electrolytes of 1 M LiNO₃, 1 M Li₂SO₄, 1 M KNO₃, 1 M Ca(NO₃)₂, and 1 M LiTFSI + LiBETI.

3. Results and Discussion

The phase and constitute of the composites were characterized by XRD analysis and the corresponding result is shown in Figure 1. The distinct diffraction peak located at around 25° can be ascribed to the carbon cloth substrate. Although the intensity of the remaining peaks is very weak, the peak positions can be matched well with the Fe₂O₃ (JCPDS No. 04-755), demonstrating the triumphant preparation of the Fe₂O₃@CC composite. The crystallite size of the Fe₂O₃ phase from XRD pattern was 3.7 nm estimated by using the Scherrer equation.



Figure 1. XRD pattern of the Fe₂O₃@CC composite.

Figure 2 shows the microstructure of the $Fe_2O_3@CC$ composite electrode. After electrochemical deposition, the whole braided structure of the carbon cloth is successfully maintained and the diameter of the carbon fiber is approximately unchanged. Comparing to the smooth surface of the carbon cloth, the $Fe_2O_3@CC$ composite exhibits a rough surface, which indicates the successful deposition of Fe_2O_3 . In Figure 2b, the flimsy Fe_2O_3 nanoflakes with around 20 nm thickness are interconnecting and uniformly decorate the carbon fiber.



Figure 2. Low-resolution SEM image (**a**) and high-resolution SEM image (**b**) of the Fe₂O₃@CC composite.

To verify the external magnetic field effect on the electrochemical performances of the $Fe_2O_3@CC$ electrode, the CVs were carried out in different electrolytes with or without applying an external magnetic field and the results are shown in Figure 3. In Figure 3a, it is seen that the contribution from the CC substrate can be negligible and the specific capacitance of the Fe₂O₃@CC electrode is mainly from the contribution of Fe₂O₃. In terms of CV shape, the specific capacitance of the Fe₂O₃@CC electrode is the combination of the double layer and pseudo-capacitive characteristic [30–32]. The specific capacitances of the Fe₂O₃@CC electrode are almost the same by integrating the enclosed area with or without the external magnetic field. But their shapes of the CV curves have some differences to a certain extent. Concretely, the polarization phenomenon of the CV plot is obtaining efficient control when adding the external magnetic field. That is to say, the splitting of water in the electrolyte is suppressed by the external magnetic field. Therefore, the following electrochemical tests in different aqueous electrolytes are conducted under the external magnetic field. Figure 3 depicts CV plots of the Fe₂O₃@CC electrode in various aqueous electrolytes of 1 M Li₂SO₄, 1 MLiNO₃, 1 MKNO₃, and 1 MCa(NO_3)₂, for exploring the better specific capacitance. The measurements were performed at the magnetic flux density (1 T). Among the CV in monovalent cationic electrolytes, the one in LiNO₃ solution presents the largestenclosed area. The CV plot shapes are nearly the same for the bivalent case,

suggesting the same electrochemical procedure. Moreover, the enclosed areas in CV for the bivalent casepossess larger enclosed area than that in LiNO₃ solution.



Figure 3. CV curves of the Fe_2O_3 @CC and CC electrodes with or without magnetic field in various aqueous electrolyte: (**a**) LiNO₃, (**b**) Li₂SO₄, (**c**) KNO₃, and (**d**) Ca(NO₃)₂.

The variation of the corresponding specific capacitance with the scan rates of the Fe₂O₃@CC electrode in different electrolytes has exhibited in Figure 4. The calculated specific capacitance of the Fe₂O₃@CC electrode measured in 1 M Li₂SO₄ electrolyte are 52, 40, 29, 26, 23, and 19 mF cm⁻² at 1, 2, 5, 8, 10, and 20 mV s⁻¹, respectively. As reported in the literature, the specific capacitances reduce with increase in the scan rate in any electrolytes [33–36]. The situation could be seen in other electrolytes. The values of specific capacitance obtained in 1 M LiNO₃ solution are 53, 44, 28, 24, 24, and 18 mF·cm⁻², respectively. However, these values obtained in 1 M KNO₃ solution decrease to 30, 24, 20, 17, 15, and 9 mF·cm⁻², respectively. The slightly higherspecific capacitance of Fe₂O₃@CC electrodeobtained in lithium ions electrolyte could be ascribed to more effortless migration for lithium ions. It possesses the applicable crystal size (0.69 Å for Li⁺, 1.38 Å for K⁺, and 0.99 Å for Ca²⁺) [37]. Simultaneously, the lower saturated concentration of the KNO₃ solution (only 3.1 M, about 10 M for LiNO₃) results in its lowest specific capacitances at all scan rates. Interestingly, the specific capacitance, variation trend and retention are practically consistent in both LiNO₃ and Ca(NO₃)₂ solutions. Thus, the different valence of the cations in the electrolytes has no effects on the electrochemical performances of the Fe₂O₃@CC electrode.



Figure 4. The corresponding variation of the specific capacitances with the scan rate of the Fe₂O₃@CC electrode in different electrolytes.

EIS measurements were carried out to get more information about the impact of the cations valency on the electrochemical properties of the Fe₂O₃@CC electrode. Using Zview software (V2.0.1.6, Southern Pines, NC, USA), the equivalent circuit and the best fitting of Nyquist plots in LiNO₃ and Ca(NO₃)₂ solutions are exhibited in Figure 5. The best fitting gives the R_s values for the Fe₂O₃@CC electrode in LiNO₃ and Ca(NO₃)₂ solutionas2.32 and 2.34 Ω , respectively, which are almost the same. The R_{ct} values for the Fe₂O₃@CC electrode in LiNO₃ and Ca(NO₃)₂ solution are 287.12 and 289.35 Ω , respectively. There is not strictly parallel to each other in the low-frequencies, indicating similar Warburg impedance. According to the literatures, the R_{ct} value could be usually linked to the diffusive resistance and the distributed resistance of the electrode material, which hints the negligible influences by the nature of electrolyte [25]. Therefore, there is no distinct differences on the EIS between LiNO₃ and Ca(NO₃)₂ solution.



Figure 5. Nyquist plots of the Fe₂O₃@CC electrode in aqueous LiNO₃ and Ca(NO₃)₂ electrolytes. The circuit for fitting is inserted in the figure.

Lately, Yamada et al. explored a room-temperature hydrate melt of Li salts (LiTFSI + LiBETI) served as aqueous electrolyte, which expanded the stable working voltage window [28]. In this work, 1 M LiTFSI + LiBETI aqueous solution was configured, and used as the electrolyte to investigate the electrochemical performances compared with 1 M LiNO₃ aqueous solution. Firstly, Figure 6a depicts CV curves of the Fe₂O₃@CC electrode with different working voltage window in 1 M LiTFSI +

LiBETI electrolyte. Through expanding the negative voltage from -0.9 to -1.4 V, we investigate the stable working voltage window of the LiTFSI + LiBETI electrolyte. The CV shape always maintains rectangular-like when expanding the negative voltage from -0.9 to -1.2 V. With further expanding the negative voltage, the response current increases rapidly, hinting the splitting of water in electrolyte. Thus, the stable working voltage window is -1.2 to 0 V, while it is -0.9 to 0 V in the above aqueous electrolyte. Then the stability of the Fe₂O₃@CC electrode in 1 M LiTFSI + LiBETI is in comparison with that in 1 M LiNO₃ solution (Figure 6b). The primary rectangular-like shapes are similar, while a severe polarizationoccurred in 1 M LiNO₃ solution due to the easier ions migration than 1 M LiTFSI + LiBETI with relatively high viscosity. This finding is in accordance with the expanded working voltage window obtained for the room-temperature hydrate melt of Li salts electrolyte.



Figure 6. CV curves of the Fe₂O₃@CC electrode: by increasing the negative potential limit from -0.9 to -1.4 V in 1 M LiTFSI + LiBETI (**a**), from -1.2 and 0 V in LiNO₃ and LiTFSI + LiBETI (**b**), variation of the specific capacitance with the scan rates (**c**), the Nyquist plots of the Fe₂O₃@CC electrode in LiNO₃ and LiTFSI + LiBETI(**d**).

The variations of the specific capacitances in these two different electrolytes with the scan rates are exhibited in Figure 6c to illustrate the electrolytes effects. Not surprisingly, the variation trends of the specific capacitances are similar, and the specific capacitances decrease with increasing the scan rates. Moreover, the specific capacitances in 1 M LiNO₃ at all scan rates are higher than that in 1 M LiTFSI + LiBETI, which is due to the lower ionic conductivity, slower ions transportation and diffusion limitation between the electrode and electrolyte. However, the capacitance retention in 1 M LiTFSI + LiBETI is higher than that in 1 M LiNO₃, that is to say, the capacitance attenuation in traditional Li-salt aqueous electrolytes is more significant.

Likewise, the EIS (after fitting) of the $Fe_2O_3@CC$ electrode in 1 M LiTFSI + LiBETI electrolyte has been measured to contrast with that in 1 M LiNO₃. The whole shapes are similar, which are constituted by a semi-circle and a straight line. By best fitting with the some equivalent circuit in

and 3.72 Ω , respectively, which are approximately equal. The R_{ct} values in LiNO₃ and LiTFSI + LiBETI solution are 287.12 and 379.28 Ω , respectively. The higher charge transfer resistance may be attributed to the high viscosity and the low ionic conductivity. Thus the straight line in 1 M LiTFSI + LiBETI is more inclined, suggesting larger Warburg impedance. [38] And above all, the EIS plot in 1 M LiTFSI + LiBETI indicates a higher resistance and more difficult ions diffusion than that in 1 M LiNO₃.

4. Conclusions

In summary, the electrochemical properties of the prepared $Fe_2O_3@CC$ electrode have been investigated in various aqueous electrolytes with or without external magnetic field. There is no distinct influence of the larger external magnetic field (1 T) on the specific capacitance, while the external magnetic field suppresses the water splitting. In addition, the specific capacitances at all scan rates of the $Fe_2O_3@CC$ electrode in usual aqueous electrolytes have been virtually unaffected by the chemical valences of the cations. Finally, the $Fe_2O_3@CC$ electrode in 1 M LiTFSI + LiBETI electrolyte exhibits a broad working voltage window (1.2 V), but shows slightly low specific capacitances at all scan rates. This may be due to the high viscosity and low conductivity of the room-temperature molten salts.

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