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Facile synthesis and electrochemical properties of alpha-phase ferric oxide hematite cocoons and rods as high-performance anodes for lithium-ion batteries

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Unique cocoon- and rod-shaped alpha-phase ferric oxide, hematite (α -Fe₂O₃) is prepared by a simple, scalable and surfactant-free chimie douce synthesis. The structure and morphology is confirmed by x-ray diffraction, field-emission scanning electron microscopy and high-resolution transmission electron microscopy. The electrochemical properties of α -Fe₂O₃ anodes are investigated using cyclic voltammetry, galvanostatic charge-discharge cycling and electrochemical impedance spectroscopy. The mesoporous α -Fe₂O₃ exhibited an initial discharge capacity >1741 mAh/g with excellent cycling performance and rate capabilities. The solvent used for the preparation of α -Fe₂O₃ plays a key role in determining the morphology of the materials, which greatly influenced its electrochemical properties.

I. INTRODUCTION

Rechargeable lithium-ion batteries (LIBs) have been commonly used as a power source for numerous portable electric devices due to their high energy density. Carbonaceous materials like graphite is widely used as anodes in commercial LIBs because of their stable voltage profile, good capacity and reasonable cost.¹ However, graphite suffers high irreversible capacity loss and poor cycling life due to which its overall performance is inadequate to satisfy the demands for the high power and/or energy densities applications such as electrical/hybrid vehicles and miscellaneous power devices. In recent years, metal oxides (MO_x, M = Co, Ni, Mn and Fe etc.) have been widely investigated as anode materials for LIBs, owing to their high theoretical capacity (greater than that of commercial graphite, 372 mAh/g). Among them, iron oxides are extensively studied because of many advantages such as low cost, nontoxicity, ecofriendliness, natural abundance and good

structural stability.^{2,3} Alpha-phase ferric oxide hematite (α -Fe₂O₃) is capable of lithium ion (Li⁺) insertion/extraction in excess of 6 Li⁺ per formula unit resulting in a significantly higher reversible capacity. The mechanism of Li-ion intercalation/deintercalation in α -Fe₂O₃ materials can be described by the following equation:

During cycling, Li⁺ insertion/extraction typically pulverize MO_x into smaller metal particles due to reaction with lithium (Li) to form dilithium monoxide (Li₂O), leading to a huge volume expansion and destruction of structure upon electrochemical cycling, especially at high rate. All these resulted in electrical isolation of electrodes causing poor electrical conductivity. Moreover, the extraction of Li⁺ from Li₂O is thermodynamically impossible which further caused severe loss of capacity with cycling.

The electrical conductivity of the material can be improved by preparing composites with conductive agents such as coating with carbon, graphene and carbon nanotubes (CNTs).^{4–6} Many attempts have been made to improve the reversible capacity and rate capabilities of

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iron oxides by controlling the particle size, morphology, surface area and robustness. Various micro-/nanostructures of iron oxides such as nanotubes,⁷ hollow microspheres,⁸ nanoflakes⁹ and nanowires¹⁰ have been reported as anode materials for LIBs. However, the reversible capacity and rate capabilities are not significantly improved. For instance, Liu et al.¹⁰ reported α -Fe₂O₃ nanowires synthesized by hydrothermal method, which showed initial discharge specific capacity of 1303 mAh/g at 0.1 C-rate and capacity fade to 456 mAh/g after 100 cycles. On the other hand, mesoporous α -Fe₂O₃ hollow spheres exhibited an initial discharge capacity of 1279 mAh/g at current density of 60 mA/g and sharply decreased to 830 mAh/g after 15 cycles (about 65% of its initial capacity).⁸ Nanoflakes of α -Fe₂O₃ prepared by thermal treatment method exhibited stable but low capacity of 680 ($\pm$ 20) mAh/g for 80 cycles at 0.1 C-rate.⁹ Zeng et al.¹¹ reported nanorods with large surface area and small particle size showed high discharge capacity at 0.2 mA/cm². However, no cycling performance results were reported. Nuli et al.¹² synthesized α -Fe₂O₃ by hydrothermal method demonstrating different morphologies such as cubic, spherical, sheet-like, rod-like and wire-like nanocrystals and tested at 20 mA/g for 30 cycles. Among these samples, nanospheres exhibited highest initial discharge capacity of 1248 mAh/g but showed poor cycling properties.

Various synthetic techniques such as hydrothermal process, gas–solid growth route, microwave heat method, thermal oxidation at high temperature and surfactant-assisted synthesis have been reported to obtain metal oxides with different morphologies. Among them, surfactant-assisted technique offers excellent control over particle morphology, size and distribution.^{13,14} However, to control the characteristics of the particles without any use of additional ligands, an easier method (chimie douce synthesis) using organic solvent acting as both reaction medium as well as monodentate ligand has been reported.^{15,16}

In the present work, α -Fe₂O₃ with different morphologies (cocoons and rods) is synthesized by simple, scalable and surfactant-free chimie douce technique and their morphological and structural properties are studied. The electrochemical properties of α -Fe₂O₃ are evaluated as anode in LIBs. Li/ α -Fe₂O₃ cell study showed markedly improved kinetics of Li intercalation/deintercalation, cycling stability and rate capabilities. It is observed that the size and morphology have remarkable effect on their electrochemical properties.

II. EXPERIMENTAL

A. Synthesis of α -Fe₂O₃

All the chemicals (analytical grade) were used as received without further purification. For the synthesis of α -Fe₂O₃ with different morphologies, *N*, *N*-diethylacetamide (DEAc) or *N*-methyl-2-pyrrolidione (NMP) was used as solvent while keeping other chemicals unchanged. One millimole

of oxalic acid (H₂C₂O₄) was dissolved in 10 mL of DEAc or NMP solvent. Thereafter, 1 mmol ferrous chloride tetrahydrate (FeCl₂·4H₂O) was dissolved in 5 mL of deionized water and mixed with the H₂C₂O₄ solution in one shot. The mixture was stirred for 20 min at room temperature to obtain a homogeneous solution. The resultant yellow-colored precipitate obtained was separated by centrifugation (8000 rpm, 10 min) and washed with excess ethanol followed by vacuum drying at 60 °C for 12 h. The obtained powder was sintered at 400 °C at heating rate of 3 °C/min in a muffle furnace for 2 h under air to obtain α -Fe₂O₃.

B. Material characterization

Surface morphology and microstructure of samples were observed by field emission scanning electron microscopy using a (FESEM; model No. JEOL 7600F, JEOL Ltd., Tokyo, Japan) field-emission scanning electron microscope with an accelerating voltage of 15 kV. FESEM samples were prepared by placing α -Fe₂O₃ on carbon tape and sputter-coated with platinum for 40 s. Elemental compositions of samples were measured by energy dispersive x-ray spectroscopy (EDS) using INCA mapping attached with FESEM. High-resolution transmission electron microscopy (was performed using HRTEM; model No. JEOL 2100F, JEOL Ltd., Tokyo, Japan) high-resolution transmission electron microscope at an accelerating voltage of 200 kV. The samples were prepared by dispersing the powder in ethanol by ultrasonication and dropping the dispersion on a carbon-coated copper grid and dried at ambient conditions. Crystallographic characterization was carried out by powder x-ray diffraction using (XRD; model No. Shimadzu XRD-6000, SHIMADZU Corporation, Japan) x-ray diffractometer operating at 40 kV and 40 mA using Cu K α 1 radiation (λ = 1.5406 Å) with the copper target and nickel filter. The samples were scanned between 10 to 80° (2 θ) at a scan rate of 2°/min. Specific surface area was determined by Brunauer-Emmett-Teller (BET) test using Micromeritics ASAP-2020 (Micromeritics Instrument Corporation, GA) nitrogen adsorption-desorption apparatus.

C. Electrode fabrication and electrochemical measurements

The composite anode was prepared by mixing α -Fe₂O₃, conductive additive (Super P Li Carbon, Timcal Graphite & Carbon, Switzerland) and polyvinylidene fluoride (PVDF) binder (Kynar 2801, Arkema Inc., PA) in the weight ratio of 30:50:20 respectively in NMP under magnetic stirring. The resulting slurry was casted onto etched copper foil by doctor-blade technique followed by vacuum drying at 80 °C for 24 h. Test cells, Li/ α -Fe₂O₃ were fabricated in coin cell (CR2016) using 1 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC): diethyl carbonate (DEC) (1:1 wt%, Danvec, Charlston Technologies Pte Ltd., Singapore) as the electrolyte and Celgard 2400 membrane (Celgard LLC, Charlotte, NC) as the separator. Cyclic voltammetry (CV)

and electrochemical impedance spectroscopy measurements were carried out on a (EIS; Solartron electrochemical impedance spectroscopy, model No. 1470E and SI 1255B impedance/gain-phase analyzer coupled with a potentiostat) electrochemical workstation. CV was studied at 0.1 mV/s in the voltage range of 0.01–3 V and EIS was studied by applying an alternating current (AC) perturbation of 10 mV over frequency range of 100 kHz to 5 mHz at open circuit potential. The Nyquist plots were analyzed using Zplot and Zview programs (Version 2.2, Scribner Associates Inc., WA). Galvanostatic charge-discharge properties and cycling performance were studied using a battery test system (XWJ Neware Tech. Co. Ltd., China) between 0.01–3 V at C-rates of 1–6 C (1 C-rate $\sim$ 1005 mA/g). All the test cells were fabricated in argon (Ar)-filled glove box (H_2O , $\text{O}_2 < 1$ ppm, Mbraun, Unilab Glovebox, MBraun, Germany) using Li metal foil ($\sim$ 0.59 mm thick, Hohsen Corporation, Japan) as counter- and reference electrodes.

III. RESULTS AND DISCUSSION

A. Structural and morphological characterization

The crystallographic structure of α -Fe₂O₃ cocoons and rods were analyzed by XRD and presented in Fig. 1(a). It can be seen that all the reflection peaks are matching

FIG. 1. (a) XRD patterns for α -Fe₂O₃ samples and (b) EDS spectra for α -Fe₂O₃ cocoons.

with the pure rhombohedral phase of α -Fe₂O₃ (Hematite, space group: $R\bar{3}c$) with lattice constants $a = 5.03$ Å and $c = 13.74$ Å which are consistent with values given on the standard card [International Centre for Diffraction Data (ICDD) PDF No. 01-087–1166]. This indicates that the as-synthesized materials are phase pure and well crystallized. The characteristic peaks centered at $2\theta = 24.17$, 33.19 , 35.66 , 40.90 , 49.51 , 54.12 , 62.50 , 64.06 , 72.02 and 75.53° correspond to $(hkl) = (012)$, (104) , (110) , (113) , (024) , (116) , (214) , (300) , (1010) and (220) Miller indices

FIG. 2. FESEM micrograph: α -Fe₂O₃ (a) cocoons (b) rods.

FIG. 3. TEM, SAED pattern, HRTEM micrographs: α -Fe₂O₃ (a), (c) and (e) cocoons; (b), (d) and (f) rods.

respectively. It is observed that the reflection peaks of α -Fe₂O₃ cocoons and rods are relatively broad, suggesting small crystallite sizes. Figure 1(b) shows the EDS spectra of α -Fe₂O₃ cocoons as a representative sample and the results are consistent with the XRD data. The detected platinum (Pt) was sputter-coated onto the samples prior to EDS and no impurities are being detected.

From the FESEM micrographs in Fig. 2, α -Fe₂O₃ cocoons are seen to be boat-shaped and have onion-like layered structure. It is clear that cocoons have rough surfaces and dimensions of 0.3–2 μ m in width and 3–5 μ m in length. For the case of α -Fe₂O₃ rods, it is observed that average diameter is $\sim$ 0.3 μ m and length in the range of submicrometer to micrometer having length/diameter ratio as high as 13. It can also be observed that the rods have relatively smooth surfaces and are much densely packed, as compared with the cocoons. It is observed that there are no significant changes in the morphology of the precipitate (i.e., iron oxalates) after sintering, whereas only crystallization from iron oxalates to α -Fe₂O₃ products occurs. The type and feeding order of solvent clearly play a key role in the morphologies of the precipitate prepared in DEAc (cocoon) and NMP (rods). Previous reports show that variation in solubility, nucleation and growth of the products, reaction kinetics, solution properties and stability of particles in different solvent systems, are important factors for forming different shapes.¹⁷ Similarly, there exist other forms of driving force for particle structural organization that can be based on ionic, covalent, hydrogen, noncovalent, metal-ligand and colloidal interactions.¹⁸ Due to the low dielectric constant of DEAc (32.1) and NMP (32.5), oxalic acid does not dissociate readily (as opposed to in water) and hence iron ion and oxalic acid do not react immediately in an organic solvent medium.¹⁹ As a result, the large differences in surface energy between crystallographic planes lead to anisotropic growth of crystal structure forming distinct morphologies.²⁰ The differences in the molecular structure

and weight of the solvents are also the probable reasons for variation in the kinetics factor and ion exchange reactions between iron (Fe²⁺) cations and intermediate oxalate (C₂O₄²⁻) anions in DEAc and NMP, thus resulted in α -Fe₂O₃ with distinct morphologies.

Figure 3 shows the TEM/HRTEM micrographs and corresponding selected area electron diffraction (SAED) pattern of α -Fe₂O₃ cocoons and rods. As shown in the TEM, cocoon's onion-like layered structure is clearly portrayed in details. TEM shows that α -Fe₂O₃ cocoons and rods are composed of multiple small crystallites/grains, which indicate the polycrystalline nature of the samples. There are well-defined lattice fringes observed from HRTEM micrograph [Figs. 3(e) and 3(f)], which further demonstrates its polycrystalline characteristic. It is also observed that both samples are mesoporous in nature. SAED patterns of cocoons and rods [Figs. 3(c) and 3(d)] display the diffraction rings confirming polycrystalline α -Fe₂O₃ phase. The calculated ring spot distances of 0.36, 0.27, 0.25 and 0.22 nm can be referred to crystal planes of (012), (104), (110) and (113) respectively. These results are in good agreement with the crystallographic direction of (*hkl*) planes observed in XRD data.

FIG. 4. N₂ adsorption-desorption isotherm curves. Inset: BJH pore size distribution.

FIG. 5. CV profile at 0.01–3 V at a scan rate of 0.1 mV/s: α -Fe₂O₃ (a) cocoons and (b) rods.

B. Porosity and surface area

BET gas-sorption measurements were carried out on α -Fe₂O₃ samples to study the porosity and specific surface area. The nitrogen adsorption-desorption isotherms (at 77 K) of these samples are shown in Fig. 4. The isotherms are clearly of Type IV showing a hysteresis loop at high values of P/P_0 (0.65–1.0).²¹ The sudden increase after relative pressure $P/P_0 > 0.65$ indicates the presence of secondary pores due to aggregation of the micrometer-sized particles. In the intermediate relative pressure, the adsorption of N₂ for α -Fe₂O₃ cocoons gradually increases with P/P_0 and show higher adsorptive capacity as compared with rods. The initial gas adsorbed by α -Fe₂O₃ cocoons is 8.94 cm³/g which is ~148% higher than rods. The BET surface area of α -Fe₂O₃ cocoon and rods is 48.4 and 27.9 m²/g respectively. The high surface area of α -Fe₂O₃ cocoon is considered as one of the important factors for achieving enhanced reversible Li storage capacity. The inset (Fig. 5) shows the pore size distribution data corresponding to N₂ desorption isotherm obtained by Barrett-Joyner-Halenda (BJH) method. The pore size distribution for α -Fe₂O₃ displays a dominant

peak at 90 and 141 Å for cocoon and rods respectively, indicating that the mesopores are widely distributed over the range of 39 and 155 Å. The mesoporous structure for α -Fe₂O₃ cocoons and rods confirmed by BET measurements is in good agreement with HRTEM analysis.

C. Cyclic voltammetry

Figure 5 shows the cyclic voltammogram of α -Fe₂O₃ anodes for the first 4 cycles at a scan rate of 0.1 mV/s cycled between 0.01 and 3 V. It is clear that there is substantial difference between first and the subsequent cycles. Three cathodic current peaks positioned at about 1.61, 0.99 and 0.73 V is observed in the first cycle. In subsequent cycles, the high intensity peak initially located at 0.73 V is shifted slightly to higher potential (0.8 V) with decreased peak intensity and other peaks have disappeared. This may be associated with the decomposition of electrolyte to form an organic layer deposited on the surface of the electrodes i.e., solid-electrolyte interface (SEI) layer,⁷ lithium-ion intercalation into the crystal structure of α -Fe₂O₃, reversible conversion reaction of α -Fe₂O₃ to form Li₂O and

FIG. 6. Charge-discharge profile versus specific capacity (1 C-rate): α -Fe₂O₃ (a) cocoons (b) rods, (c) galvanostatic cycling performance (1 C-rate) and (d) rate capabilities performance.

metallic iron (Fe⁰) particles.²² In the anodic process, only one broad peak (1.66–1.91 V) which corresponds to the reversible oxidation step of Fe⁰ to Fe³⁺ is seen in the first and subsequent cycles. There are no differences observed for the anodic peak during cycling. From the first to third cycle, both the peak current and the integrated area of the CV curve are decreased, which indicate irreversible capacity loss during discharge. However, integrated area of the CV curve remains constant and well matched after 3rd cycle indicating good reversibility of α -Fe₂O₃ cocoons and rods. The fact that the peak current and integrated peak area are much higher for α -Fe₂O₃ cocoons than for the rods, reveals that α -Fe₂O₃ cocoons electrode has higher capacity and reactivity.

D. Evaluation in half-cells

Figures 6(a) and 6(b) shows the selected charge-discharge voltage profiles of α -Fe₂O₃ electrodes cycled between 0.01–3 V and constant current rate of 1 C (~1005 mA/g). It is observed that the charge-discharge curves are almost similar for cocoons and rods, indicating identical electrochemical behavior of α -Fe₂O₃ with Li and are in good agreement to earlier reports.^{8,10,23} In the first discharge curve, it is observed that potential decreases sharply to ~1.5 V for α -Fe₂O₃ cocoons and ~1 V for the rods, followed by a weak slope corresponding to Li insertion into the crystal structure of α -Fe₂O₃. When the potential decreases to ~0.8 V, an obvious voltage plateau is seen, indicating the reduction of iron from Fe³⁺ to Fe⁰ and thereafter followed by a smooth decrease in the voltage during discharge. The electrochemical behavior is in good agreement with the results observed in CV measurements.

It is observed that initial discharge capacity of 1830 and 1741 mAh/g for cocoons and rods respectively is much higher than the theoretical capacity of α -Fe₂O₃ (1005 mAh/g). This is probably due to the well-known phenomenon of decomposition of the electrolyte, SEI layer formation and the reversible formation of a gel-like layer.^{23–25} From the second discharge profile, only one voltage plateau between 1 and 0.8 V corresponding to the final reduction of α -Fe₂O₃ to metallic Fe⁰ is observed. The cell delivers with a discharge capacity of ~1481 and 1490 mAh/g for α -Fe₂O₃ cocoons and ~1263 and 1050 mAh/g for rods after 50 and 100 cycles respectively.

Figure 6(c) shows the cycle performance of α -Fe₂O₃ cell cycled at 1 C-rate for 100 cycles. It is observed that there is no significant capacity loss for α -Fe₂O₃ cocoons after 100 cycles while a sharp capacity fade is observed for rods after 80 cycles amounting to ~16.8% capacity fade (based on 50th cycle). The stable cycling performance of α -Fe₂O₃ cocoons is better than the same for the composite reported elsewhere.²³ These results revealed that morphological discrepancies such as particle size, surface area and porosity affect the Li⁺ intercalation/deintercalation in the

FIG. 7. Nyquist plots of α -Fe₂O₃ samples: (a) fresh cells, (b) after 100 cycles and (c) equivalent circuit.

crystal structure of α -Fe₂O₃. It is worth noting that α -Fe₂O₃ cocoons exhibit better cycling performance than rods, which may be due to size effect and morphology-dependent electrochemical properties. The high surface area of α -Fe₂O₃ cocoons favor Li⁺ insertion/extraction in the process of charge/discharge and maintain the integrity of the electrode materials leading to better cycling performance.

The electrochemical performance of α -Fe₂O₃ electrodes at different current densities (at 1, 2, 4, 6 C-rate and back to 1 C-rate for 10 cycles each continuously) are evaluated and shown in Fig. 6(d). The cell is capable of delivering a discharge capacity of 1253 and 896 mAh/g for α -Fe₂O₃ cocoons and rods respectively even at high current density of 6 C-rate. It is observed that α -Fe₂O₃ cocoons exhibit better and stable capacity retention at 6 C-rate as compared with rods. The cells exhibit a discharge capacity of 1535 and 1263 mAh/g for α -Fe₂O₃ cocoons and rods respectively after the current density is changed back to 1 C-rate after

TABLE I. Fitting parameters of the cell with α -Fe₂O₃ electrodes for the fresh cell equilibrated overnight and after 100 charge-discharge cycles at an open circuit potential.

Active material	Cell configuration (tested)	R_s (Ω)	$R_{(sf+ct)}$ (Ω)	$CPE_{(sf+dl)}$ (μ F)	α	Z_w (Ω)	C_{int} (mF)
α -Fe ₂ O ₃ -cocoons	Fresh cell	2.68	60.25	39.81	0.82	668.8	29.50
	After 100 cycles	9.16	12.02	941	0.59	126.3	1115
α -Fe ₂ O ₃ -rods	Fresh cell	2.94	72.16	40.55	0.79	749.70	6.64
	After 100 cycles	4.64	15.35	245	0.74	158.3	832

40 cycles, which clearly demonstrates a high capacity retention of ~ 84 and 73% (based on its initial discharge capacity) for α -Fe₂O₃ cocoons and rods respectively.

For understanding the reaction kinetics during intercalation/deintercalation process, EIS has been carried out. The Nyquist plots of Li/ α -Fe₂O₃ symmetric cells at an open circuit potential using the fresh cells equilibrated overnight and after 100 galvanostatic charge-discharge cycles are shown in Fig. 7. Nyquist plots in Figs. 7(a) and 7(b) showed almost similar electrochemical impedance response irrespective of distinct morphological characteristics and can be generally divided into two regions: (i) one depressed semicircle in the high-to-middle frequency (100 kHz–20 Hz) region, and (ii) a sloped line in the low-frequency region. The semicircle with characteristic frequency of 251 and 200 Hz can be observed [inset of Figs. 7(a) and 7(b)] for α -Fe₂O₃ cocoons and rods, respectively while the magnitude of the semicircle decreases for α -Fe₂O₃ cocoons and rods after galvanostatic charge-discharge cycles. An equivalent circuit as shown in Fig. 7(c) is proposed to fit the impedance spectra. An intercept at the Z_{real} axis (Z') in high frequency corresponded to the ohmic resistance (R_s), which accounts for the total resistance of the electrolyte, separator, and electrical contacts. The depressed semicircle in the high-to-medium frequency range is related to the combination of Li-ion migration resistance (R_{sf}) through the SEI film formed on the electrode and the charge transfer resistance (R_{ct}). The inclined line in the lower frequency represents a finite length Warburg diffusion element (W_s) that includes the impedances encountered when the electrolyte ions diffuse from the bulk (α -Fe₂O₃ cocoons and rods particles) to the electrode-electrolyte interfaces. A double-layer capacitor [$CPE_{(sf+dl)}$] is indicated for the double layers formed on the surfaces of the electrode in contact with the electrolyte. The introduction of constant phase element (CPE) in the equivalent circuit can obtain a good approach to the surface roughness, physical nonuniformity or nonuniform distribution of surface reaction site.²⁶

Table I displays the analysis results obtained by modeling the experimental Nyquist plots recorded for the fresh cell and the cell after 100 cycles. In particular, the R_{ct} of the fresh α -Fe₂O₃ cocoons as well as rods electrode decreased after 100 cycles; whereas R_s of α -Fe₂O₃ cocoons is increased drastically after 100 cycles. $R_{(sf+ct)}$ of α -Fe₂O₃ fresh cell is observed to be 60.25 and 72.16 Ω for cocoons and rods respectively. The result of small charge transfer

resistance after cycling might be attributable to the larger contact area between α -Fe₂O₃ electrode and electrolyte. The $R_{(sf+ct)}$ values are observed to be slightly lower for α -Fe₂O₃ cocoons, suggesting that the resistance of Li⁺ migration was decreased when cycling. The corresponding $CPE_{(sf+dl)}$ is observed to be almost same for the fresh cells, while the value is 941 and 245 μ F, respectively for cocoons and rods after 100 cycles. After cycling, the diameter of the semicircle reduces drastically followed by the well-defined Warburg region at low frequencies. This shows that R_{sf} is reduced significantly and R_{ct} comes in to prominence because of the initiation of the intercalation/deintercalation reaction of Li into α -Fe₂O₃ cocoons and rods. The EIS results are consistent with cyclic voltammetry and galvanostatic charge-discharge tests. The improved electrochemical properties of α -Fe₂O₃ cocoons, therefore, appeared to be due to following factors: (i) enhanced BET surface area facilitates electrode-electrolyte interface, (ii) intrapores within α -Fe₂O₃ cocoons, which effectively enhanced the Li⁺ diffusion and restrained the increase of interfacial resistance among particles during the cycles and (iii) the improved electrical conductivity of α -Fe₂O₃ cocoons due to small micrometer-sized particles.

IV. CONCLUSIONS

Unique α -Fe₂O₃ cocoons and rods were successfully prepared by surfactant-free chimie douce synthesis and tested as anode materials for LIBs. The morphology of α -Fe₂O₃ is dependent on the solvent used during synthesis. The initial discharge capacity is 1830 and 1741 mAh/g for cocoons and rods respectively and showed stable cycling performance. The studies showed that α -Fe₂O₃ cocoons exhibit better electrochemical performance as compared with rods, which reveals size effect and morphology-dependent electrochemical properties of α -Fe₂O₃. This synthesis technique is a viable option to be applied to synthesize other functional materials with controlled morphologies. The investigation indicates that there are good prospects for using α -Fe₂O₃ as anode materials in LIBs.

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