An Effective Route for Porous Ferrihydrite Preparation from Layered Double Hydroxide Precursors

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A porous ferrihydrite has been synthesized from layered double hydroxide precursors via selective extraction. The characterization results show that the porous ferrihydrite possesses not only large total pore volume but also uniform micropore size distribution, which make it exhibit a good charge/discharge capacity and cycling performance as the lithium battery cathode.

During the past few years, the search for new cathode materials for rechargeable lithium batteries has mainly focused on lithium transition-metal oxides.[1,2] Among them, $LiCoO_2$ and $LiMn_2O_4$ have already been extensively investigated and used. However, their obvious shortages like high cost and environmental toxicity stimulate continuous research on developing of other transition-metal oxide hosts. Undoubtedly, iron oxides are the most promising candidates, and a number of iron-based materials have been investigated as positive active materials for lithium secondary cells; such as $LiFeO_2$,[3] $LiFePO_4$,[4] γ-FeOOH derivatives,[5] $Fe_4[Fe(CH)_6]$,[6] and β-FeOOH.[7] Among them, the iron-based materials for Fe^{2+}/Fe^{3+} redox couple reaction have attracted much more attention because of their better reversibility. β-FeOOH cathode exhibited a high discharge capacity of over 200 mA h g^{-1}; however, which had a drawback of poor cycle performance. Porous ferrihydrite is another possible candidate and has not been reported yet. Ferrihydrite is generally prepared as the initial precipitate from rapid hydrolysis of Fe^{3+} solutions,[8] but this simple process always gives ferrihydrite with random pore size distribution and small pore volume, which obstructs its extensive application. Thus, traditional porous ferrihydrite has the limited use as adsorbent to toxic ions.[9] In the present work, a new approach to porous ferrihydrite from layered double hydroxide precursors is revealed. The synthesized ferrihydrite exhibits not only uniform pore size but also large pore volume. Furthermore, when employed as lithium battery cathode material, these porous ferrihydrites showed good initial discharge capacity and cycling performance.

Layered double hydroxides (LDHs), a class of synthetic anionic clays, can be represented by the general formula $[M^{II}{}_{1-x}M^{III}{}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$. The identities of the di- and trivalent cations (M^{II} and M^{III}, respectively) and the interlayer anion (A^{n-}) together with the value of the stoichiometric coefficient (x) may be varied over a wide range. On the basis of the unique layered structure and diversity of the di- and trivalent cations of LDHs, it is very possible to obtain porous materials via a selective extraction method from them. For LDHs with suitable compositions, one of their metal atoms could be selectively extracted with dilute acid under controllable pH value, and the other metal atoms might be left in a porous architecture of the final product. In the present work, three appropriate LDH systems, $Mg_2Fe(OH)_6(CO_3)_{0.5}\cdot 1.7H_2O$ ($MgFe–CO_3$ LDH), $Ca_2Fe(OH)_6(NO_3)\cdot 1.3H_2O$ ($CaFe–NO_3$ LDH), and $Zn_2Fe(OH)_6(SO_4)_{0.5}\cdot H_2O$ ($ZnFe–SO_4$ LDH) were selected, by using the simple selective extracting method, porous iron compounds were obtained, and their corresponding electric properties as lithium cathode materials were also characterized.

Three LDHs were synthesized by a modified procedure of the literature.[10,11] The as-synthesized LDHs were characterized by XRD, TEM, and elemental analysis. Dilute nitric acid was employed for the selective extraction of LDHs to obtain porous ferrihydrites, which were further characterized by XRD, TEM, ICP, TG-DTA, and BET gas sorptometry measurement for specific surface area and pore volume.

The XRD patterns of the LDHs shown in Figure 1 exhibit the characteristic reflections[12] of LDH materials and no other crystalline phases are present. The basal spacing of $MgFe–CO_3$ LDH, $CaFe–NO_3$ LDH, and $ZnFe–SO_4$ LDH are 0.77, 0.86, and 0.90 nm, respectively. Elemental analysis results for the LDHs indicated that their M^{2+}/Fe^{3+} ratios are consistent with those in the corresponding starting mixture.

The XRD patterns of the materials produced from $MgFe–CO_3$ LDH, $CaFe–NO_3$ LDH, and $ZnFe–SO_4$ LDH treated with dilute nitric acid indicate the disappearance of the characteristic reflections of LDHs, and two new broad reflections at about $2\theta = 35°$ (0.25 nm) and 63° (0.15 nm) appeared, which agree well with those of the X-ray pattern of "2-line ferrihydrite."[8,9] Apparently, treating LDHs with dilute nitric acid will lead to the selective extraction of the nonferrous atoms and the forma-

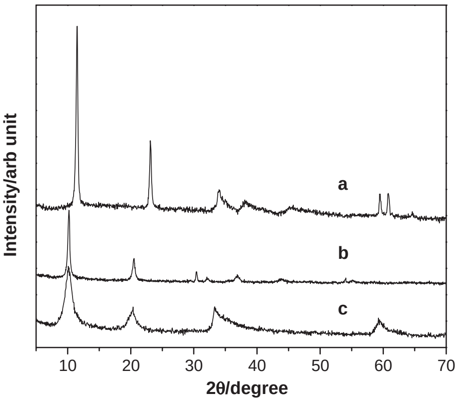

Figure 1. Powder X-ray diffraction patterns for (a) $MgFe–CO_3$, (b) $CaFe–NO_3$, and (c) $ZnFe–SO_4$ LDH.

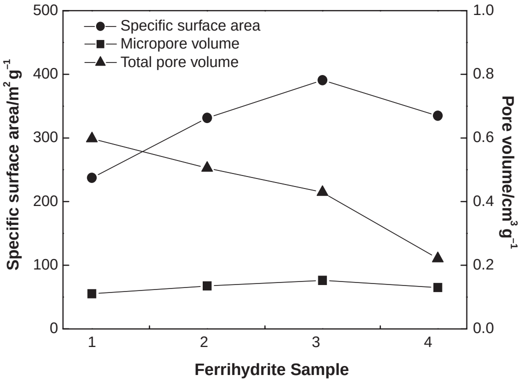

Figure 2. Specific surface area, micropore volume, and total pore volume of ferrihydrites from (1) ZnFe–SO_4 LDH, (2) CaFe–NO_3 LDH, (3) MgFe–CO_3 LDH), and (4) rapid hydrolysis of Fe^{3+} solution.

tion of ferrihydrite. Elemental analysis of the ferrihydrites verifies that the removal of Mg^{2+} and Ca^{2+} oxides from LDHs are essentially complete, and Fe^{3+} content of the final ferrihydrites is consistent with that of ferrihydrite $Fe_5HO_8 \cdot 4H_2O$. In the case of ZnFe–SO_4 LDH, although complete removal of the Zn^{2+} oxide has not been realized yet, a porous product could be obtained.

To quantify the porous nature of the as-synthesized ferrihydrites, BET gas sorptometry measurements were conducted. The values of BET surface area and pore volume of three ferrihydrites are shown in Figure 2, and the corresponding values of ferrihydrite prepared via the rapid Fe^{3+} solutions hydrolysis is given as a comparison. Interestingly, the samples from LDHs show much larger total pore volume than that of sample from Fe^{3+} solutions. Because all the samples possess similar specific surface area (value for the sample from ZnFe–SO_4 LDH is confusing because of remaining Zn^{2+}) and micropore volume, it is conceivable that the large total pore volume is attributed to use of the layered LDHs precursors. The lamellar spaces of the layered LDHs can not only make the selective extraction possible and form the ordered micropore on the original layers, but also make themselves the pores in the final products. Moreover, from pore width distribution curve, the nanoscaled pores could also be detected. When these larger pores are dominant in the product, it will show large total pore volume and small surface area. Moreover, samples from LDHs possess narrower micropore distribution than those of the sample from Fe^{3+} solutions.

To study the electrochemical property, the ferrihydrite from MgFe–NO_3 LDH were used as cathode with metal Li as anode. Figure 3 shows the cycle performances of the ferrihydrite cathode. It is seen that an activated process is necessary and after this process, the capacity of charge and discharge could achieve the maximum of about 180 mA h g^{-1} at 4.2–1.5 V, which is close to the capacity of β-FeOOH (200 mA h g^{-1}),[7] with a good cyclic performance. The corresponding result of ferrihydrite prepared via the rapid Fe^{3+} solutions hydrolysis had a drawback of poor cyclic performance and electrochemical properties (See Supporting Information).[13] Obviously, porous ferrihydrites synthesized from LDHs precursors have the advantages as the Li battery cathode in obtaining enhanced capacity, which might be due to their large pore volume and uniform pore size. With this type of porous structure, Li^+ insertion/deinsertion can be carried out easily. The data indicated that the ferrihydrite produced by selective extraction of the LDH precursors has a potential as Li battery materials.

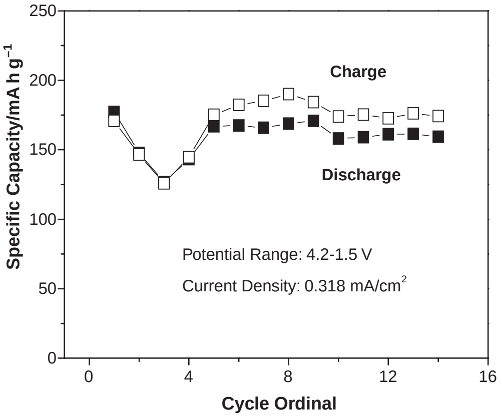

Figure 3. Cyclic performances of the ferrihydrite cathode from MgFe–NO_3 LDH.

A simple approach to ferrihydrites with large and uniform pores from LDHs was developed in this work, and as a promising Li battery cathode, the electrochemical property of the ferrihydrites was studied. Owing to a wide variety of LDHs with different framework M^{II}/M^{III} ratios and different interlayer anions, many useful porous materials could be designed and synthesized by similar selective extraction method. Further work on the synthesis of new LDH precursors and porous materials is currently underway in our laboratory.

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