Current efficiency of synthesis magnesium hydroxide nanoparticles via electrodeposition

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Abstract: The nanograde particles of magnesium hydroxide [$Mg(OH)_2$] with lamella morphology were synthesized by the method of electrodeposition. The effects of operation parameters, such as Mg^{2+} concentration and electric current density, interpolar distance and Na^+ concentration on current efficiency of synthesis magnesium hydroxide nanoparticles were investigated. The results show that the current efficiency can be reach to 76.53% under the conditions of Mg^{2+} concentration 0.5mol/L, Na^+ concentration 1%, electric current density 40mA/cm^2 and electrode interpolar distance 4cm. The samples were characterized by X-ray diffractions (XRD) and field emission scanning electron microscopy (FESEM).

Introduction

In recent years, the synthesis of nanoscale $Mg(OH)_2$ has been the focus of considerable interest because of its potential properties in electronic, mechanical, electrochemistry, optical and topological[1-5]. Several methods have been used to prepare $Mg(OH)_2$ with controlled shape and size, such as ultrasonic-assisted[6], precipitation[7], sol–gel technique[8], using bubbling setup[9], hydrothermal route[10] and electrolysis of an aqueous magnesium salt solution[11],etc. Ranjit and Klabunde[12] have synthesized mesostructured $Mg(OH)_2$ using different anionic surfactants as template, but their process limited due to low current efficiency and economically unacceptable. In present study, the $Mg(OH)_2$ deposition processes from magnesium chloride hexahydrate was researched, and the effects of the variation of Mg^{2+} concentration, electric current density, interpolar distance and Na^+ concentration on current efficiency were studied.

Experimental

Materials

Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), sodium chloride(NaCl), potassium chloride(KCl) were supplied from Shenyang Chemical Reagent Co. Ltd, China, all of these chemicals are analytical pure grade and without further purification. Deionized water was employed for all experiments.

Procedures of synthesis of $Mg(OH)_2$ nanoparticles

The electrolysis procedure were performed in a single conventional compartment cell(capacity is 2.5L). The anode is graphite plate and the cathode is stainless steel plates with smooth surface. The electrolysis experiments were took out at room temperature. In a typical run, 100g of $MgCl_2 \cdot 6H_2O$ is dissolve in 2L of deionized water to make a mother solution, the electrodes surface is both 100 cm^2 and the electrode interpolar distance is 4cm, the electric current density is 40 mA/cm^2 and the electrolysis time is 4h. When electrolysis reach a given time, nano-$Mg(OH)_2$ can be obtained after the precipitates are filtered, washed with deionized water three times and dried in a vacuum drying oven at 70℃ for 12 h.

Current efficiency

The current efficiency is calculated by the following formula:

$$\eta = m/m^* \quad (1)$$

where η is current efficiency, m is the actual mass of metal hydroxide deposited, m*is theoretical mass of metal hydroxide deposited. The actual mass of metal hydroxide deposited(m) is determined by the mass after dry. The theoretical mass of metal hydroxide(m*) is calculated by the Faraday's law:

$$m^*=ItM/(nF) \quad (2)$$

where I is the applied current, t is the time, n is the number of electrons transferred in the elementary act of the electrode reaction, M is the mole mass of the metal hydroxide and F is the faraday constant.

Physical characterization of $Mg(OH)_2$

The X-ray diffraction (XRD) scans were recorded at room temperature on a Philips X' Pert PRO SUPER apparatus (Nicolet Instrument Co., USA) using CuK_{α} radiation with β-Ni filter (λ= 0.15406 nm, 40kV, 80mA) at a scan rate of 5°/min (2θ). The morphology and size of the particles were characterized by a Zeiss field emission scanning electron microscopy (ULTRA PLUS at 25 kV for SEM imaging, the sample was sputtered with Au before the test).

Results and discussion

Compared to the current method of producing $Mg(OH)_2$, the method by a one-step cathodic electrodeposition process using magnesium chloride hexahydrate as raw material is simple and the pureness is high.

Effect of Mg^{2+} concentration on current efficiency

Mg^{2+} concentration in aqueous solution is one of the main factors affecting current efficiency of $Mg(OH)_2$ electrodeposition. When Mg^{2+} concentration is low, the OH^- which generated from cathode can not combine with Mg^{2+} quickly, affect the current efficiency. With the increase of Mg^{2+} concentration, the nanocrystals agglomeration became more serious[13], affect the current efficiency further growth. The current efficiency was measured at various Mg^{2+} concentration and the other parameters is the same to typical run.

As shown in Fig. 1, it was found that when Mg^{2+} concentration is low, the current efficiency is about 50%, with the Mg^{2+} concentration increase the current efficiency increases rapidly from 50% to 73%. The current efficiency is stabilization when Mg^{2+} concentration is above 0.5mol/L. The fact reveals that 0.5mol/L Mg^{2+} concentration is optimal.

Effect of electric current density on current efficiency

Electric current density is another of the main factors affecting current efficiency of $Mg(OH)_2$ electrodeposition. When electric current density is low, the formation rate of $Mg(OH)_2$ is low too, it will affect $Mg(OH)_2$ fall off from cathode, bring low current efficiency. While exaggerated elevate electric current density, will lead to electrodes calorific value increase, then the temperature of the electrolytic solution rises that will increase the solvent evaporation and change the electrolyte composition. It also increase energy consumption by elevate electric current density, affect its economy. The current efficiency of the $Mg(OH)_2$ electrodeposition reactions were measured at various electric current density and the other parameters is the same to typical run.

As shown in Fig. 2, with the increase of current density, the current efficiency is increased then basically remain unchanged. When the electric current density is $10mA/cm^2$, the current efficiency is 46%, and it quickly increases to 64% as the electric current density increases to 40mA/cm^2. Above 40mA/cm^2, the current efficiency is stabilization. The fact reveals that 40mA/cm^2 electric current density is optimal.

Effect of interpolar distance on current efficiency

In the process of electrolysis, some of chlorine, produced by the cathode, conduct hydrolysis reaction and then formation Cl^-. It will dissolve the precipitated magnesium hydroxide again when the interpolar distance is too small, affect the current efficiency. When plus the distance, the electrical resistance between electrodes is increases, so in order to maintain the electric current density need improve electric tension, which will increases more energy consumption. The current efficiency of the $Mg(OH)_2$ electrodeposition reactions were measured at various interpolar distance and the other parameters is the same to typical run.

As shown in Fig. 3 the current efficiency increases with the increases of interpolar distance. When the interpolar distance is 2cm, the current efficiency is 44%, and it increase to 65% when the interpolar distance became to 4cm. but it is stabilization when the interpolar distance is over 4cm. The result reveals that 4cm interpolar distance is optimal.

Effect of Na^+ concentration on current efficiency

In the process of electrolysis, sodium chloride is added to the electrolytic solution can greatly reduce the solution resistance, namely, under the condition of not changing the interpolar distance can reduce the voltage between the electrodes, save power. The current efficiency of the $Mg(OH)_2$ electrodeposition reactions were measured at various Na+ concentrations(mass concentration) and the other parameters is the same to typical run.

As shown in Fig. 4, the current efficiency is increases firstly and then decreases with the increase of Na^+ concentration. Adding appropriate amount of NaCl is beneficial to improve the $Mg(OH)_2$ electrodeposition reactions and increase current efficiency. But excessive Na^+ concentration will hinder Mg^{2+} combine with OH^-, and decrease current efficiency. The fact reveals that Na^+ concentration 1% is optimal. It was found that raising K^+ concentration had the same influence on current efficiency as increasing Na^+ concentration as discussed above.

In order to verification the result，a replication experiment was proceed. The experiment condition is Mg^{2+} concentration 0.5mol/L, Na^+ concentration 1%, electrodes surface 100cm^2, electrode interpolar distance 4cm and the electric current density 40 mA/cm^2. Under this condition, the current efficiency can be reach to 76.53%.

Structure and morphology of $Mg(OH)_2$ nanoparticle

Fig.5 shows the XRD pattern of the nano-$Mg(OH)_2$ product. All diffraction peaks can be indexed very well as hexagonal phase $Mg(OH)_2$ with calculated lattice constants of a= 0.315nm and c=0.477nm, which is agrees with the standard data (JCPDS 7-239). The size of $Mg(OH)_2$ particles is calculated by the Debye-Scherrer formula[14], based on the full width at half-maximum. The calculated crystal sizes is 23.7 nm, 15.6 nm and 21.7 nm correspond to (001), (101) and (102) diffraction peaks, respectively, which shows that as-synthesized $Mg(OH)_2$ nanoparticles have nanometer level crystal size. In addition, the product prepared with this process has a high purity(the content of magnesium oxide is more than 99.6%, which is measure by X-Ray fluorimetry)

The morphology of the nano-$Mg(OH)_2$ sample was examined with FESEM. As shown in Fig. 6, the as-synthesized nano-$Mg(OH)_2$ possess a lamella structure and the particle size distribution ranges from 40 nm to 200 nm. Some nanoparticles are perpendicular to the picture, which clearly shows the thickness of these $Mg(OH)_2$ nanolamellas below 20 nm.

Conclusions

Magnesium hydroxide with lamella morphology and high-purity could be synthesized by the method of electrodeposition. The current efficiency of $Mg(OH)_2$ deposition can be over 76% under the condition of Mg^{2+} concentration 0.5mol/L , Na^+ concentration 1%, electric current density 40mA/cm^2 and electrode interpolar distance is 4 cm.

Acknowledgements

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Figure Captions

Fig. 1. Relationship between Mg^{2+} concentration and current efficiency for $Mg(OH)_2$ deposits

Fig. 2. Relationship between electric current density and current efficiency for $Mg(OH)_2$ deposits

Fig. 3. Relationship between interpolar distance and current efficiency for $Mg(OH)_2$ deposits

Fig. 4. Relationship between Na^+ concentration and current efficiency for $Mg(OH)_2$ deposits

Fig. 5. X-ray diffraction (XRD) pattern of $Mg(OH)_2$ nanolamella.

Fig. 6. Scanning electron microscopy (SEM) image of $Mg(OH)_2$ nanolamella.

Fig. 1.

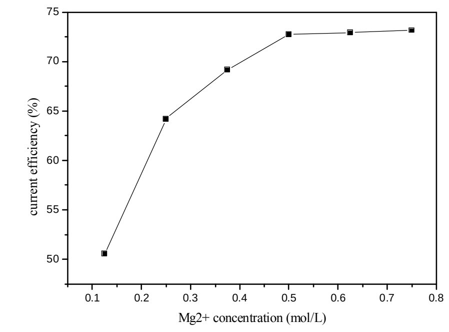

Fig. 2.

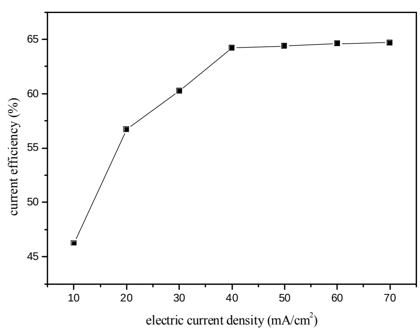

Fig. 3.

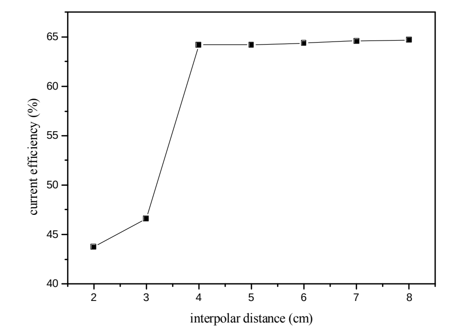

Fig. 4.

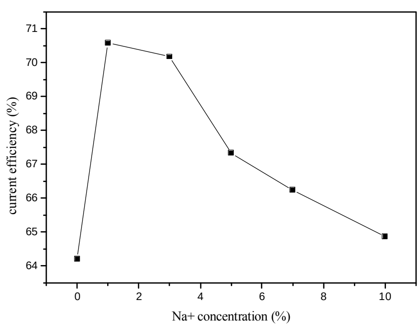

Fig. 5.

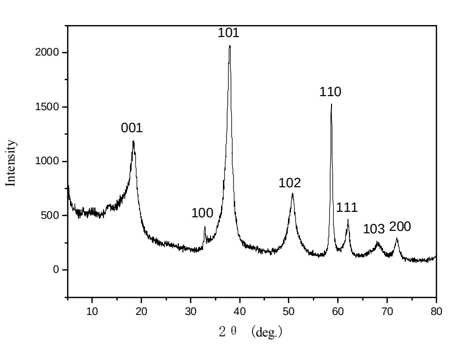

Fig. 6.