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A symmetric aqueous rechargeable battery based on $NiFe_2O_4$ derived from industrial effluents

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ABSTRACT

Two different industrial effluents, spent pickle liquor and Ni-containing wastewater, were simultaneously treated via chemical precipitation and hydrothermal reaction to generate valuable $NiFe_2O_4$. Subsequently, the $NiFe_2O_4$ was used to construct a $NiFe_2O_4$//$NiFe_2O_4$ symmetric battery. The assembling process of $NiFe_2O_4$//$NiFe_2O_4$ symmetric battery is very simple since both the cathode and anode are the same material and the manufacturing cost for practical application is low. The $NiFe_2O_4$//$NiFe_2O_4$ symmetric battery was able to deliver specific capacity 23.1 mAh/g based on the total mass of the active materials at discharging current densities 0.5 A/g. After 500 charge-discharges cycles, the crystalline structure of $NiFe_2O_4$ still exhibit good stability and can pass the TCLP limits to be regarded as a general industrial waste. This research not only removes the heavy metal from two wastewaters to avoid the environmental risks but also provides an effective method to turn "waste" into useful materials.

1. Introduction

Wastewater with toxic heavy metal ions brings many detrimental effects on environment and human health. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living bodies and cause serious diseases even at very low concentration [1,2]. Therefore, these toxic heavy metals should be removed from the wastewater to protect the people as well as the environment. Heavy metals contaminated wastewaters derived from a lot of sources, including metal plating facilities, steel plant, battery manufacture, mining operations, paint manufacture, tanneries, etc. Various techniques for treating wastewater containing heavy metals have been developed such as chemical precipitation, adsorption, membrane separation, and coagulation [3–6]. Chemical precipitation, mainly including hydroxide precipitation and sulfide precipitation, is very efficient and by far the most widely used process in industry because it is simple and inexpensive to operate [7,8]. However, the sludge generated by chemical precipitation has a loose structure and dissolves easily in acid. Due to the instability of sludge from chemical precipitation process, the secondary pollution from the release of heavy metals into the environment become one of the major concerns in the chemical precipitation technique [9,10]. Thus, the sludge based on metal hydroxide is often solidified before being disposed in a landfill, which leads to increased treatment costs and environmental loading [11].

Sludge based on ferrite is chemically and mechanically stable and no heavy metals are leached under normal environmental conditions, thus allowing their disposal with a minimum environmental impact [12]. The common formula of ferrite can be expressed as $MeFe_2O_4$ (AB_2O_4), where Me^{2+} (A sites) can be any divalent ion (Ni^{2+}, Fe^{2+}, Co^{2+}, Mn^{2+}, Mg^{2+}, or Zn^{2+}), and Fe^{3+} is the main component in B sites but can be substituted by any of trivalent ions (Al^{3+}, Cr^{3+}, Co^{3+}) [13,14]. Among them, $NiFe_2O_4$ have received much research attention due to its peculiar inverse spinel structure, electrical, and magnetic properties [15,16]. The synthesis of $NiFe_2O_4$ needs Ni source and iron source. Due to the relatively high price of Ni sources ($Ni(NO_3)_2{\cdot}6H_2O$ or $NiCl_2{\cdot}6H_2O$) and Fe sources ($FeCl_3{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$), both nickel source and iron source derived from wastewater is an attractive option as it not only avoids the environmental risks but also provides a means to recycling the metal values. The conventional method of treating

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Table 1
Element contents of heavy metals and nonmetal in spent pickle liquor and Ni-containing wastewater.

samples	Concentration (mg/L)									
	Total Fe	Ni	Na	Cr	Al	Ca	B	P	S	pH
spent pickle liquor	4527.27	9.91	19.87	15.33	17.56	59.13	UD[a]	34.66	17.27	1.2
Ni-containing wastewater	0.53	171.53	222.68	10.67	2.21	14.73	102.06	9.62	91.56	1.4

[a] Undetected.

Table 2
Heavy metal concentrations in supernatant after the chemical precipitation.

elements	Total Fe	Ni	Cr	Al	Ca
Supernatant (mg/L)	0.05	0.09	0.01	UD[a]	1.89
GB 21900-2008 (Chinese standard) (mg/L)	3.0	0.5	1.0	3.0	

[a] Undetected.

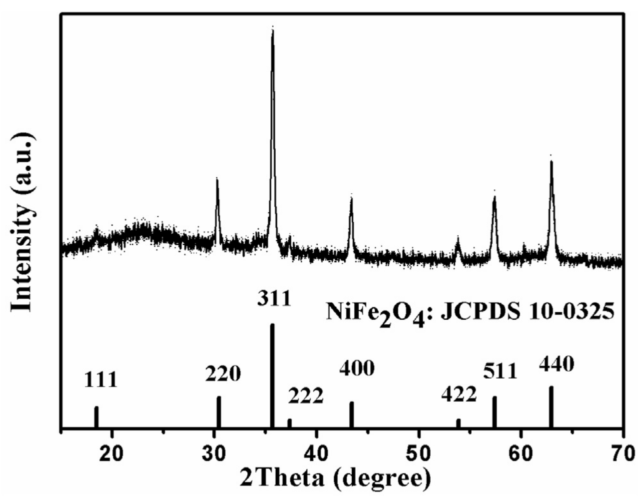

Fig. 1. XRD pattern of $NiFe_2O_4$.

Ni-containing wastewater or Fe-containing wastewater is precipitation with lime or other alkaline precipitator, which generates a great amount of residue waste if not reused appropriately [17].

Due to the use of cheap aqueous electrolyte, aqueous rechargeable batteries possess the advantages of environmental benign, low-cost, easy cell assembly process. Especially, the aqueous rechargeable batteries are safer than the non-aqueous rechargeable batteries [18,19]. The motivation of the present research originated from the idea that $NiFe_2O_4$ electrode materials, which can assemble into a symmetric aqueous rechargeable battery, can be synthesized by two industrial wastewaters, i.e. the spent pickle liquor generated in the steel industry and Ni-containing wastewater from Ni plating plant. Via the synthesis process of $NiFe_2O_4$, heavy metals in Ni-containing wastewater and spent pickle liquor were simultaneous removed. $NiFe_2O_4$ was used as electrode material to assemble the $NiFe_2O_4$//$NiFe_2O_4$ symmetric battery, which both cathode and anode of the battery used the same material. After 500 charge-discharges cycles, $NiFe_2O_4$ still exhibit good stability demonstrated by XRD analysis and TCLP test, which means that the $NiFe_2O_4$ can be disposed as a general industrial waste.

2. Experimental

2.1. Wastewater quality

Before the study, two wastewaters, spent pickle liquor and Ni-containing wastewater was filtrated in order to remove suspended solid (SS).

The spent pickle liquor was obtained from the acid pickling procedure in a steel mill (Jiangsu, China). The characteristics of the spent pickle liquor sampled from the workshop are provided in Table 1. The spent pickle liquor shows very low pH values, high concentration of Fe ions (45272 mg/L) and trace amounts of other metals. Ni-containing wastewater was obtained from a Ni plating plant (Jiangsu, China) and the characteristics of wastewater are shown in Table 1. The Ni-containing wastewater also shows very low pH values. The wastewater contains a high concentration of B, which should come from the boronic acid. Boronic acid often acts as brightener in the Ni plating process. The high Na concentration in wastewater may be come from the electrolyte (NaCl and Na_2SO_4) and the sodium dodecylbenzene sulfonate. In addition, the high S concentration should derive from the sodium dodecylbenzene sulfonate, which is often used in the Ni plating process.

2.2. Preparation of $NiFe_2O_4$

By using Ni-containing wastewater and spent pickle liquor as Ni source and Fe source, respectively, $NiFe_2O_4$ was prepared by

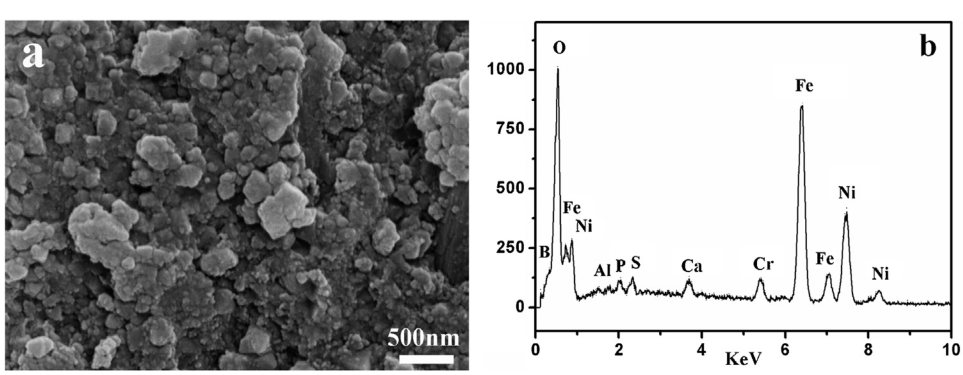

Fig. 2. SEM image (a) and EDS pattern (b) of $NiFe_2O_4$.