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Layered double hydroxide materials coated carbon electrode: New challenge to future electrochemical power devices

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ABSTRACT

Layered double hydroxides (LDHs) have been widely used in the past years due to their unique physico-chemical properties and promising applications in electroanalytical chemistry. The present paper is going to focus exclusively on magnesium-aluminum and zinc-aluminum layered double hydroxides (MgAl & ZnAl LDHs) in order to investigate the property and structure of active cation sites located within the layer structure. The MgAl and ZnAl LDH nanosheets were prepared by the constant pH co-precipitation method and uniformly supported on carbon-based electrode materials to fabricate an LDH electrode. Characterization by powder x-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and transmission electron microscopy revealed the LDH form and well-crystallized materials. Wetting surface properties (hydrophilicity and hydrophobicity) of both prepared LDHs were recorded by contact angle measurement show hydrophilic character and basic property. The electrochemical performance of these hybrid materials was investigated by mainly cyclic voltammetry, electrochemical impedance spectroscopy and chronoamperometry techniques to identify the oxidation/reduction processes at the electrode/electrolyte interface and the effect of the divalent metal cations in total reactivity. The hierarchy of the modified electrode proves that the electronic conductivity of the bulk material is considerably dependent on the divalent cation and affects the limiting parameter of the overall redox process. However, MgAl LDH shows better performance than ZnAl LDH, due to the presence of magnesium cations in the layers. Following the structural, morphological and electrochemical behavior studies of both synthesized LDHs, the prepared LDH modified electrodes were tested through microbial fuel cell configuration, revealing a remarkable, potential new pathway for high-performance and cost-effective electrode use in electrochemical power devices.

1. Introduction

Microbial fuel cells (MFCs) are novel bioelectrochemical systems that exploit electrogenic bacterial to generate electrical power while degrading organic pollutants in wastewater [1,2]. However, improving anode performance in MFCs remains one of the deciding factors for their applications, because the biological reactions mainly occur over its surface. During anodic bioelectrocatalysis, microorganisms oxidize organic matter and released electrons are transferred to the solid electrode material. Hence, the development of new and simple strategies to fabricate efficient anode materials to increase the bacterial loading capacity and improve substrate transport is of great interest and importance.

Nowadays, a major challenge for microbial fuel cells (MFCs) is to develop new anode materials for practical applications in bioelectroremediation devices. Commercial graphite-based materials such as carbon felt, carbon cloth, glassy carbon, carbon paper and graphite rods have been widely used as convenient materials for anode MFCs [3–6]. Thus, improving anode performance is important for increasing power production. Previous research has shown that electrode performance can be improved through chemical modification of the anodes.

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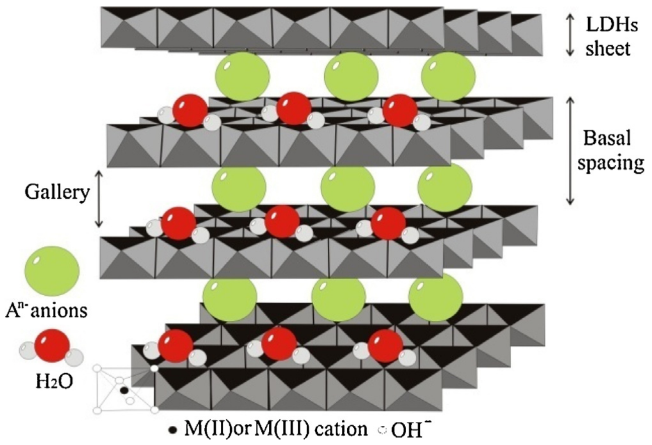

Scheme 1. Schematic representation of the crystal structure of the layered double hydroxide.

Clay's minerals have emerged as one of the most promising modified electrode materials for developing high-performance due to their unique properties such as high metal dispersion, high surface area, controllable particle size and high thermal stability [7], all of which benefit the formation of highly stable and dispersed electrochemical active metal [8,9]. Particularly interesting is the anionic clays, especially hydrotalcite-like compounds (HTs), which are relatively easy to synthesize and have an environmentally friendly nature. HTs exhibit a broad versatility which allows their synthesis with different ions for specific applications [10,11], including degradation and adsorption of a wide variety of pollutants such as phenols, oxyanions and dyes [12–14]. Recently, Tonelli et al. [15] and Mousty et al. [16,17] have reviewed the HT materials as electrode modifiers to be used for both electrochemical detection (chemical sensors and biosensors) and energy-storage devices.

The naturally occurring mineral hydrotalcite, $Mg_6Al_2(OH)_6CO_3{\cdot}4H_2O$, belongs to this class of materials, and consequently layered double hydroxides (LDHs) are also known as hydrotalcite-like materials. LDHs are a family of synthetic lamellar solids with positively charged brucite-like layers of mixed metal hydroxides separated by interlayer hydrated anions (Scheme 1) [18,19], described by the general formula: $[M(II)_{1\text{-}x}M(III)_x.(OH)_2]^{x+}[(A^{n-})_{x/n},yH_2O]$ (abbreviated as M(II)M(III)–A, where M(II) is a divalent metal cation, such as Mg, Mn, Ni, Zn, Co, Fe and Cu; M(III) is a trivalent metal cation, such as Al, Fe, Co, Ni, Mn and Cr; A^{n-} is an interlayer anion, such as Cl^-, F^-, $CO_3{}^{2-}$, $NO_3{}^-$ and $SO_4{}^{2-}$; the value of x is between 0.2 and 0.33 generally represent the molar ratio M(II)/[M(II) + M(III)]).

As an inorganic clay that have been widely reported, layered double hydroxides (LDHs) have been subjected to intense research by the electrochemist community. However, the exploration of LDH-based materials as electrode modifiers is one of the important issues to be of concern [20–23]. Previously, we reported that LDHs in which M(II) is a transition metal, undergoing a redox reaction in the range of applied potential, have been proposed as materials with improved charge transport [24–28]. Indeed, electron transfer within these Inorganic lamellar materials can further be promoted by two strategies: (i) the intercalation of redox active anions between the LDH layers and (ii) the presence of transition metal cations within the LDH intralayer domain, itself [17]. Accordingly, the modulation of the intrinsic properties of LDHs (electronic conductivity, redox or acid-base properties) is dependant on the nature of the cations in the layers [29], can render the LDH hybrid structure electroactive and endow redox properties to the LDH layers. However, to our knowledge, very few studies describe the electrochemical behavior of LDH in function of the cations. They have been dedicated to LDHs with Ni and Co divalent cations [28,30–35]. Because of their desirable properties including low cost, good biocompatibility, high catalytic activity, and high chemical stability, LDH materials could find application also as anode materials in the so-called biofuel cell, as very recently reported in literature [36,37]. LDH modified electrodes are thus mainly prepared as a thin film coated on a working electrode surface through solvent casting, layer by layer assembly, or electrode position [38–40].

Table 1
Chemical composition of MgAl and ZnAl LDHs.

LDH compounds	Molar ratio		
	Mg^{2+}/Al^{3+}	Cl^-/Al^{3+}	$CO_3{}^{2-}/Al^{3+}$
MgAl	1.95	0.91	0.19
ZnAl	1.97	0.95	0.17

A comprehensive study of the electrochemistry of layered double hydroxides is evident to open new potentialities in regard to application in area of electrochemical devices. The current paper is devoted to investigate and hence improve electron transfer reaction using divalent cation metals containing LDH (Mg & Zn) supported on carbon electrodes. A special attention is paid on MgAl-LDH and ZnAl-LDH as illustrative examples of electrocatalyst materials in energy conversion. Furthermore, microbial fuel cell configuration has been tested.

2. Experimental section

2.1. Reagents

Aluminum chloride hexahydrate ($AlCl_3{\cdot}6H_2O$), magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$), nitric acid (HNO_3), phosphate buffered saline tablet, potassium ferrocyanide trihydrate ($K_4Fe(CN)_6{\cdot}3H_2O$), sodium acetate (CH_3COONa), sodium hydroxide (NaOH) and zinc chloride ($ZnCl_2$) were purchased form Sigma–Aldrich. All chemical reagents were of analytical grade and used without further purification. Deionized water was employed for all the experiments.

2.2. LDH synthesis

MgAl and ZnAl LDH materials potentially intercalated chloride anions were prepared by the co-precipitation method as previously described [41–43]. Initially, 50 mL of a 1 M metallic salt solution containing 0.66 M of magnesium salts $MgCl_2$ or zinc salts $ZnCl_2$ and 0.33 M of aluminum salts $AlCl_3$ (corresponding to a M^{2+}/Al^{3+} ratio of 2) was slowly added to a second solution containing 2.0 M NaOH (50 mL) into a reactor with a constant flow of 0.12 mL/min by syringe-pump system for about 7 h under vigorous mechanical stirring at 400 rpm. Throughout this addition, the pH of the solution was maintained constant; 9 and 7.5 respectively for MgAl and ZnAl phases. The reaction was carried out under N_2 atmosphere to avoid carbonate contamination. The formed suspensions were immediately centrifuged at 5000 rpm without any ageing in order to quench the crystal growth and therefore obtain small platelets. The solids recovered by centrifugation were washed several times with deionized water to remove sodium chloride residue and kept at room temperature for 24 h.

Chemical analysis of the sample is given in Table 1. We noted a general contamination of all phases by carbonates from air. The experimental $Mg^{2+}/Al^{3+}$and Zn^{2+}/Al^{3+} molar ratio was close to the theoretical value.