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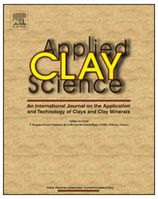

Research Paper

Doped nafion-layered double hydroxide nanoparticles as a modified ionic polymer metal composite sheet for a high-responsive humidity sensor

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ABSTRACT

In this paper, a novel Ionic Polymer Metal Composite (IPMC) has been fabricated by chemical electroless plating integrated with doping Layered Double Hydroxide (LDH) nanoparticles in the nafion polymeric matrix. Platinum, as a noble metal, was used for electrode deposition of the prepared doped nafion and successfully act as a high-quality electrode to transfer electrical signal. This IPMC, in fact, is a smart material suggesting to acts as a high responsive mechanical humidity sensor in biomedical devices since it produced a remarkably higher voltage with higher sensitivity and responsivity in comparison to the previous IPMC humidity sensors in literature. LDH nanoparticles own a layered ionic structure, which makes them highly hydrophilic. This property increases the water uptake of the IPMC. By increasing the penetration of water molecules in the nafion channels, the separation of positive and negative charges becomes easier and leads to higher and faster humidity sensing application. The humidity sensing applications of undoped and LDH-doped IPMC fabricated by facile chemical plating method were measured and compared at different bending angles. It was found that 1% doped nafion sheet had the highest water uptake of 30%, and consequently better humidity sensing compared to the undoped, 0.5%, 1.5%, 2% and 3% doped nafion. This means that doping concentration and modification has an optimized value.

1. Introduction

Ionic Polymer Metal Composite (IPMC) is a kind of electro-active polymer (EAP) with remarkable sensing and actuating properties which makes it a suitable soft material to be used in various devices such as biomedical ones due to its high biocompatibility (Zhu et al., 2016). Recently, sensing applications of IPMC have been emerged and reported on the displacement, pressure, humidity, force and structural health monitoring (Bonomo et al., 2008; Zangrilli and Weiland, 2011; Matsuura et al., 2014; Smith, 2007; Brufau-Penella et al., 2008; Aureli et al., 2010). This sensor generally consists of an electrically activated polymer layer (usually nafion) sandwiched by two metal electrodes. Inside the polymer, anions, which are covalently bound to the polymer chains, are balanced and made nanochannels by mobile cations. It can bend sharply through electrical conduction and has two major advantages of high curvature and high sensitivity. IPMCs have innate sensing properties in which a force or deformation on an IPMC beam produces a measurable electrical signal. Another amazing feature of this material is that different electrical responses are seen at various ranges of humidity, which is a key for developing a sensitive humidity sensor (Esmaeli et al., 2017). High responsive IPMCs are usually fabricated by facile chemical routes (Pt electrodes) which results in high quality electrodes with no cracks on the surface (Shahinpoor and Kim, 2001; Wang et al., 2016; Chung et al., 2006; Lee et al., 2012; Oguro, 1995; Shahinpoor and Kim, 2004; Kim and Shahinpoor, 2003; Ionic et al., 2016). To increase sensing responsivity, special particles with specific properties can be introduced into the nafion polymer (Narimani et al., 2016). One of the materials that has been introduced into the nafion so far is Layered Double Hydroxide (LDH). LDH are a class of natural and synthetic mixed metal hydroxides, historically described as anion-exchanging, clay-like materials. LDH are structurally similar to brucite, $Mg(OH)_2$, with one notable difference: LDH are mixed-metal hydroxides and brucite is magnesium hydroxide (Richardson, 2007). To understand the structure of these compounds, it is necessary to start from the structure of brucite where octahedra of Mg^{2+} (6-fold coordinated to OH^-) share edges to form infinite sheets. These sheets are stacked on top of each other and are held together by hydrogen bonding. When Mg^{2+} ions are substituted by a trivalent ion, having not too different radius (such as Fe^{3+} for pyroaurite and Al^{3+} for hydrotalcite, respectively), positive charges are generated in the hydroxyl sheet. This net

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positive charge is compensated by (CO_3^{2-}) anions, which lie in the interlayer region between the two brucite-like sheets. The water molecules find a place in the free space of this interlayer (Jaiswal et al., 2014). The most commonly studied LDH consists of divalent and trivalent metals, with the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^+[A]^{n-}\cdot yH_2O$, M(II) and M(III) are respectively divalent and trivalent metals, in which $0.2 < x < 0.33$, and A^{n-} is the exchangeable anion between the layers. The LDH exhibits high water uptake properties due to their ionic and layered structures. Water molecule are captured between their layers, absorbed by the anions and this makes the water molecules stable (Richardson, 2007; Jaiswal et al., 2014). LDH are easy and inexpensive to synthesize on laboratory and industrial scales. Several methods of LDH synthesis are known such as coprecipitation, sol-gel procedure, hydrothermal and mechanochemical method (Zhang and Li, 2013). Introducing LDH in the polymer matrix may have remarkable products with different applications such as nanocomposite hydrogels (Hu and Chen, 2014a), photoluminescence (Wu et al., 2017), thermal stabilizer (Liu et al., 2008), rheology (Hu and Chen, 2014b) and UV light shielding (Cao et al., 2013). One research, introduced LDH as nanofillers in the nafion applications (Angjeli et al., 2015). However, to the best of our knowledge, nafion-doped sheet has never been used as an electroactive polymer base for IPMC humidity sensor synthesis. Herein, we have developed a humidity sensor by chemical electroless plating of the doped nafion with LDH nanoparticles. In other words, an Ionic Polymer Metal Composite was fabricated which consequently applied in a sensor, sensitive to humidity changes with high sensitivity and responsivity hence the output voltage of the IPMC sensor was tremendously modified by this doping. This allows to have better exploitation of IPMC sensor in bio active and other mechanical sensing devices.

2. Experimental details

2.1. Synthesis of LDH nanoparticles

Co—Al Layered double hydroxide was synthesized via mechanochemical method in a mortar (Ay et al., 2009). First, hydrated cobalt and aluminum nitrates were grounded with molar ratio of 2:1. Then, NaOH was added to the mixture with molar ratio of 3:1 (Co(II):NaOH) and grinding was continued until a pink powder obtained. Finally, the resulting powder was washed with deionized water and dried in a vacuum oven at 60 °C for 2 h. X-ray diffraction (XRD) method, Fourier Transform Infrared (FTIR) spectroscopy and Field Emission Scanning Electron Microscopy (FESEM) were used to characterize LDH nanoparticles.

2.2. Preparation of layered double hydroxide/nafion nanocomposites

Initially, a 5 wt% nafion solution was evaporated to remove its solvent. Then, the dry nafion was used to produce a solution with a final concentration of 25 wt% in dimethylformamide (DMF). To the polymer solution was added a 3 wt% LDH solution which was previously dispersed by sonication for 40 min. The resultant solution was again sonicated for 3 h. Finally, it was evaporated and baked at 60 °C for 5 h. To study the influence of LDH content on the sensing properties of nanocomposites, different solutions (0.5, 1, 1.5, 2 wt%) of LDH were prepared. XRD was used to characterize LDH doped nafion composite.

2.3. IPMC synthesis

The LDH-doped nafion sheets and the commercial nafion (115) went under chemical electrode deposition process to compare their humidity sensing applications. To do so, both sides of the sheets were roughened by oxygen plasma (100 sccm O_2 flow with 200-watt plasma power for 5 min) to activate the polymer surface for metal deposition. The roughened sheets were then boiled in deionized water for 30 min to remove contamination from the surfaces.

Adsorption of the Pt ions for electrode formation on the polymer surface was conducted as noted in previous studies (Lee et al., 2012), albeit with an optimization. As mentioned in the literature, the nafion sheet should be immersed in the aqueous solution of platinum complex ($Pt(NH_3)_4Cl_2$) containing 3 mg of Pt per cm^2 overnight. The Pt ions should traditionally be reduced to a Pt layer by adding a solution of sodium borohydride every 30 min that the whole process is highly time consuming. However, our sheets were immersed and sonicated in the solution of tetraamine platinum (II) chloride ($Pt(NH_3)_4Cl_2$, 10 mM) for 3 h. Sonication helps the adsorbing process to get completed in a shorter time. To reduce the Pt ions, the nafion sheet was immersed in the aqueous solution of $NaBH_4$ (6 mM) with the rising temperature of 40 °C to 60 °C for 2 h. It is believed that sudden reduction of Pt ions is performed completely in this warm reductant, which eliminating the hydroxylamine hydrochloride usage for further Pt ion reduction. The time efficient chemical deposition method produced high quality Pt layer on the sheets with the surface resistivity of about 2 Ω on each side. The final IPMC membranes were trimmed from every edge to avoid any shorting between two surfaces.

The last step is to put IPMCs in a solution of LiCl (1 M) so that the H^+ cations get replaced with smaller ions of Li^+. This replacement helps in better separation of positive and negative charges through the channels due to faster migration of smaller cations. The reason that IPMC bends in an electrical field or acts as a sensor is the displacement of the positive cations. H^+ ions are so small that IPMC doesn't show remarkable deflection by applying voltage when it is used as n actuator. Li^+ ions are both small to move fast through channels and have enough size to exhibit deflection when repelling each other. However, when using IPMC as a sensor, and it is under deflection, the cation displacement remarkably changes the response. Even in 0° bending angle, IPMC has a slight deflection due to compression of the clamp holding it.

3. Results and discussion

3.1. LDH characterization

3.1.1. X-ray diffraction analysis

XRD is the main analytical technique for characterization of layered and crystalline LDH structures. It is also used to determine the interlayer spacing and thickness of layers in a crystalline composition (Jaiswal et al., 2014). XRD patterns show some general features that are typical of all hydrotalcite-like compounds (ASTM card number: JCPDS #51-0045); the presence of sharp and intense lines at low 2θ angles, and less intense and generally asymmetric lines at higher angular values (Cavani et al., 1991). The XRD pattern of Co–Al–LDH is shown in Fig. 1. XRD pattern of the as-prepared sample, indexing the diffraction peaks to a typical layered double hydroxide with JCPDS reference code 51-0045. The diffraction peaks of (003) at $2\theta = 9.85°$ and (006) at $2\theta = 20.109°$ are intense, while other peaks have relatively weak intensities, showing that the high-quality crystal grew along a certain axis (Su et al., 2009). The interlayer distance of Co–Al–LDH was determined as 0.885 nm based on the (003) diffraction peak by Expert analytical software, which is lower than the one reported in the literature due to presence of nitrate ions in the interlayer (Jaiswal et al., 2014).

3.1.2. FTIR characterization of LDH

The FTIR spectrum of the Co-Al-LDH is shown in Fig. 2. A broad absorption band at 3446 cm^{-1} is assigned to the stretching vibration of the OH groups from both the hydroxide layers and the nterlayer water molecules. The shoulder around 2900 cm^{-1} can be attributed to interaction of interlayer carbonate ions and water molecules present in LDH (Palmer et al., 2009). The corresponding band close to 1625 cm^{-1} is attributed to H—O—H bending vibration of the interlayer water molecules (Palmer et al., 2009). A very strong absorption band near 1380 cm^{-1} is an asymmetric stretching vibration corresponds to the