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Research paper

Impact of low normality of cesium chloride ($n = 0.3\ N$) on the electrical features of nacrite-[$(CsCl)_n$] nanohybrid subjected to excitation of frequency under controlled temperature

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ABSTRACT

A series of nanohybrid materials with different $(CsCl)_n$ normalities ($n = 0.05\ N$, $0.1\ N$, $0.3\ N$, $0.5\ N$, $1\ N$, $2\ N$ and $3\ N$) was synthesized by indirect intercalation of nacrite. Systematic and kinetic X-ray diffraction surveys reveal that the optimal nanohybrid with the highest intercalation rate ($\tau = 0.943$) and degree of reaction ($\alpha = 0.860$) corresponds to ($n = 0.3\ N$) normality value of aqueous CsCl solution and was labeled nacrite-[$(CsCl)_{n\ =\ 0.3\ N}$]. Its half-unit cell structural formula as deduced by agreement between experimental and simulated patterns ($R_p = 7.30\%$) was $\mathbf{Si_2Al_2O_5(OH)_4{\cdot}CsCl{\cdot}H_2O}$ with a d_{002}-value equals to 1.05 nm. The atomic composition and the vibrational description of the nacrite-[$(CsCl)_{n\ =\ 0.3\ N}$] nanohybrid was made respectively by means of energy-dispersive X-ray spectroscopy coupled to transmission electron microscope and infrared spectroscopy techniques. The electrochemical impedance spectroscopy reveals that nacrite-[$(CsCl)_{n\ =\ 0.3\ N}$] nanohybrid material heated to higher temperatures exhibits an excellent ionic conductivity ($\sigma_{ac} \sim 10^{-2}\ S{\cdot}m^{-1}$) and can be classified as a superionic conductor.

1. Introduction

Over the past decades much attention has been paid to the direct or indirect intercalation of CsCl inorganic alkali halide into the interlamellar space of kaolin-type minerals (Weiss et al., 1966; Ben Haj Amara, 1997; Lapides et al., 1997; Yariv et al., 1999; Naamen et al., 2004, 2006, 2016). Weiss et al. (1966) intercalated CsCl into kaolinite using aqueous solutions of the salt and hydrazine or ammonium acetate as an entraining agent. Yariv et al. (1999) intercalated CsCl directly either (*i*) after long periods at 60 °C in concentrated aqueous solutions in sealed glass ampoules or as slurry, followed by long ageing in a damp atmosphere, or (*ii*) by mechanochemical treatment (grinding). Intercalation of CsCl into nacrite, a dioctahedral polytype of kaolin, has been also investigated by Naamen et al. (2016). The nacrite/CsCl complex was synthesized by immersing the hydrated nacrite in a saturated CsCl solution (Naamen et al., 2016). Hydrated nacrite was obtained by the method described by Ben Haj Amara (1997): 2 g of clay mineral were ground and kept in a saturated potassium acetate solution for several days until intercalation was complete. The resulting nacrite/potassium acetate complex was washed with water and air dried leading to the hydrate of nacrite.

Basal reflections determined by means of X-ray diffraction and corresponding to optimal intercalation observed in the work of Weiss et al. (1966) are similar to the data of Lapides et al. (1997). It may be concluded that similar intercalation complexes were obtained by both methods, although the complexes of Weiss et al. (1966) were obtained from aqueous solutions, whereas the complexes of Lapides et al. (1997) were obtained in solid state thermal reactions (Yariv et al., 1999). Furthermore, the main reflection, d_{002}[nacrite-CsCl] = 1.051 ± 0.002 nm (Naamen et al., 2004, 2006, 2016) strongly agreed with the earlier values gathered from the research of Lapides et al. (1997) and Weiss et al. (1966), respectively, d_{001}[kaolinite-CsCl] = 1.05 nm and d_{001}[kaolinite-CsCl] = 1.03 nm although they differ in the kaolin polytype.

Thus, cesium chloride was considered as one of the largest known alkali halide for the intercalation of kaolin subgroup such as kaolinite, halloysite, dickite (Yariv et al., 1999) and nacrite (Naamen et al., 2004, 2006, 2016). CsCl was also well-known as a very expansive alkali halide. Consequentially, the novelty of this work was the research of a low cost preparation route based on a systematic way for the intercalation of a small amount of CsCl into nacrite. Thereafter, considerable experimental and theoretical efforts have been undertaken to study the structural properties of the elaborated material by means of X-ray diffraction, energy-dispersive X-ray spectroscopy and infrared spectroscopy. The second part of this research was innovative and was devoted

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to study the electrical properties and to discuss the most probable conduction mechanism of this material containing Cs^+ ion recognized with a large ionic radius. The correlation between structural and electrical properties of the elaborated material opens new perspectives of application in future device generations based on heavy alkali elements.

2. Experimental section

2.1. Materials

2.1.1. Synthesis of the nacrite hydrate

In order to facilitate the intercalation, in a first step, 2 g of nacrite starting material (d_{002}–value equals to 0.72 nm) was contacted with a saturated potassium acetate solution (*normality = 26 N*) according to the method of *Ben Haj Amara* (Ben Haj Amara, 1997). After complete intercalation complex nacrite-CH_3 COOK was washed with deionized water until a homogeneous and stable hydrate of nacrite characterized by a d_{002}–value equals to 0.84 nm (Ben Haj Amara, 1997). This step was repeated several times under the same conditions until the elaboration of 7 test tubes containing the suitable quantity of hydrate of nacrite.

2.1.2. Preparation of aqueous solutions of CsCl with different normalities

Since CsCl is a hygroscopic salt very soluble in water and in order to facilitate the intercalation of CsCl into the clay mineral, we choose to dissolve CsCl in deionized water.

Experimental runs were prepared by weighing known masses of ultra pure cesium chloride (CsCl; 99.999%; Prolabo) on the highly precise Sartorius balance (model BP221S with a resolution of 0.1 mg). These amounts of CsCl were transferred in 7 test tubes, then dissolved in 30 mL of deionized water onto each tube. The mixtures were manually stirred at ambient temperature. Finally, we obtain seven aqueous solutions of $(CsCl)_n$ with different normalities (*n = 0.05 N*, *0.1 N*, *0.3 N*, *0.5 N*, *1 N*, *2 N* and *3 N*).

2.1.3. Synthesis of nacrite-[$(CsCl)_n$] (n = 0.05 N, 0.1 N, 0.3 N, 0.5 N, 1 N, 2 N and 3 N) nanohybrid

Then each prepared nacrite hydrate was added respectively to every alkaline solution of $(CsCl)_n$ where ($0.05\ N \leq n \leq 3\ N$). The mixtures were transferred into erlenmeyers and simultaneously placed on magnetic stirrer under the same vigorous stirring conditions (stirring speed = 400 rpm, stirring period = 4 h, at ambient temperature).

2.2. Methods

2.2.1. X-ray diffraction

X-ray diffraction (XRD) pattern of nacrite-[$(CsCl)_{0.05N-3\ N}$] nanohybrids were performed at ambient temperature using a reflection setting on a Bruker D8 installation monitored by the EVA-version Diffrac plus software (Bruker AXS GmbH, Karlsruhe, Germany) and CuKα_1 radiation. Usual scanning parameters were 0.02°2θ as step size and 6 s as counting time per step. Working voltage and current were 40 kV and 40 mA, respectively. The prepared clay suspensions were oriented by depositing on a glass slide then placed above the sample holder.

2.2.2. Energy-dispersive X-ray spectroscopy (EDXS)

The atomic composition of nacrite-[$(CsCl)_{0.3\ N}$] nanohybrid was characterized via local chemical microanalysis performed using energy-dispersive X-ray spectroscopy (EDXS) system attached to the transmission electron microscope (TEM) (FEI Tecnai G2) with an accelerating voltage of 200 kV.

2.2.3. Infrared spectroscopy

IR spectrum of the synthesized nacrite-[$(CsCl)_{0.3\ N}$] sample was recorded using Nicolet IR 200 FT-IR thermo-scientific spectro-photometer with a resolution of 4 cm^{-1} and operating between 4000 and 400 cm^{-1} (Mid- Infrared region).

2.2.4. Complex impedance techniques

Ionic conductivity measurements were made on nacrite-[$(CsCl)_{0.3\ N}$] sample using Hewlett-Packard 4192 impedance analyzer in the range from 10 Hz to 13 MHz under controlled temperature. Pellet was prepared from finely grinding powder of the air–dried specimen by pressing it into disc using a hydraulic press. The pellet was maintained between platinum plates to ensure good electrode–electrolyte contact. The cell was eventually placed into a programmable oven coupled with a temperature controller. Before collecting data at each given temperature point, the temperature was kept for a few minutes to ensure temperature uniformity. The collected data were fitted using the equivalent circuit of the Zview software.

3. Results and discussion

3.1. Effects of the normality (n = 0.05 N, 0.1 N, 0.3 N, 0.5 N, 1 N, 2 N and 3 N) of $(CsCl)_n$ solution in the intercalation efficiency of nacrite

The experimental XRD patterns of the nanohybrids elaborated at various salt normalities (*n = 0.05 N*, *0.1 N*, *0.3 N*, *0.5 N*, *1 N*, *2 N* and *3 N*) and at a fixed period of stirring (4 h) were recorded within a timeframe of 2 h over the angular range 5–35°2θ (Fig. 1a).

All samples exhibited a pronounced reflection located at around $2\theta_{002(nanohybrid)} = 8.46°$ with the following d_{002}-values: d_{002}{nacrite-[$(CsCl)_{0.1N}$]} = 1.014 nm, d_{002}{nacrite-[$(CsCl)_{0.3N}$]} = 1.044 nm, d_{002}{nacrite-[$(CsCl)_{0.5N}$]} = 1.026 nm, d_{002}{nacrite-[$(CsCl)_{1N}$]} q= 1.030 nm, d_{002}{nacrite-[$(CsCl)_{2N}$]} = 1.024 nm, d_{002} {nacrite-[$(CsCl)_{3N}$]} = 1.029 nm (Table 1). The d_{002}-values reflected the expansion of the interlamellar space and the sensitivity of the basal reflection to the variation of the normality of the intercalated salt. It was evident that the position, shape and intensity of the 002 reflection varied according to the state of intercalation. We deduced a narrow dependence between the normality of $(CsCl)_n$ solution and the intercalation efficiency of nacrite. In the case of {nacrite-[$(CsCl)_{0.05\ N}$]}, a weak 002 reflection appeared indicating the beginning of the intercalation.

All these samples exhibited reflections located at around $2\theta_{002(hydrate)} = 10.52°$ and around $2\theta_{002(nacrite)} = 12.35°$ attributed to the persistence of hydrate ($d_{002(hydrate)} = 0.84$ nm) and nacrite ($d_{002(nacrite)} \cong 0.72$ nm) phases, respectively. The weakness of these reflections was an indication of the success of intercalation.

By exploiting the 2θ range diffraction from lower toward higher angles, supplementary reflections located at 21.69°2θ and 30.80°2θ appeared. These reflections were very strong for the nanohybrids elaborated by inclusion of high content of CsCl such as *n = 1 N*, *2 N* and *3 N* in comparison with the nanohybrids elaborated by inclusion of low content of CsCl such as *n = 0.05 N*, *0.1 N*, *0.3 N* and *0.5 N*. These reflections signified the presence of excess of salt in the solution; therefore the intensity of salt reflection was proportional to the normality as shown in the XRD patterns in (Fig. 1a).

The overall evaluation of the XRD patterns of these nanohybrids (Fig. 1a) revealed that nacrite-[$(CsCl)_{0.3\ N}$] nanohybrid behaved differently: it presented no reflection of hydrate, a weak reflection of nacrite indicating that the intercalation was strongly complete and the nanohybrid was homogeneous. However, by decreasing the salt normality to *0.05 N* and by increasing the normality up to *3 N*, the nanohybrids became relatively less uniform and inhomogeneous.

Accordingly, this preliminary study revealed that the nanohybrid prepared at cesium chloride normality of *0.3 N* was the more homogeneous.

3.1.1. Systematic study

Plotting $\tau = f(Normality)$ and $\alpha = f(Normality)$ curves (Fig. 1b and