

POLYACRYLATE-CaFe LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES – STRUCTURAL CHARACTERISATION BY DIELECTRIC RELAXATION SPECTROSCOPY

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Abstract

Polyacrylate–CaFe layered double hydroxide (LDH) has been prepared by the dehydration-rehydration method. The success of intercalation has been proven by X-ray diffractometry and transmission and scanning electron microscopies. The polymer–LDH composite was further characterised by thermal methods and dielectric relaxation spectroscopy. This latter method identified three relaxation processes in the pure LDH and the nanocomposite, and the predominance of electrode polarisation for the crystalline polymer salt. It was found that the polymer largely lost its mobility among the layers of the LDH.

1 Introduction

Layered materials with anion exchange property are (somewhat erroneously) often called anionic clays by the analogy of the cation-exchanging layered silicates. The accurate name is layered double hydroxide (LDH). Although LDHs exist in nature, for chemical use they are mostly synthesised. Their most often used representative is hydrotalcite, its layered structure resembles that of brucite [Mg(OH)₂], but a part of the Mg(II) ions are replaced by Al(III) ions [1-3]. The fundamental structure of the layer is not harmed, however, it becomes positively charged. This charge is compensated by anions in-between the layers. They are usually hydrated simple anions but they can be both organic and complex inorganic anions. The layered structure collapses on heat treatment, however, upon rehydration it is nearly fully reconstructed [4]. The calcined LDHs form mixed oxides with many dislocations and of basic character, therefore they may be used as efficient base catalysts in redox reactions.

The uncalcined double hydroxides are also basic, however, due to their close to regular structures they are not so efficient catalysts as their calcined counterparts. Their specific surface areas are also smaller. Due to the low interlayer spacings, the high inner surfaces are not accessible to the reactants. The specific surface area may be significantly increased by pillaring the layers with bulky anions. This can be done but not so simply as pillaring with polyhydroxy cations in montmorillonite [5, 6]. LDHs do not swell in aqueous solutions, therefore their direct pillaring with bulky inorganic anions is not an easy exercise. The general

practice is that firstly, the layers are propped open by intercalating long-chained dicarboxylic acids and then *via* anion exchange the bulky inorganic anions enter the interlayer space [7, 8]. As it is seen, pillaring with organic anions was used originally as an auxiliary tool on the way of preparing robust (inorganic) pillared structures. However, in the meantime it became clear that even though structures containing organic pillars are more sensitive to heat treatment, they form an important class of organic-inorganic hybrid materials [9]. They can be used as immobilised organocatalysts, containers of organic synthons, pharmaceuticals, pesticides/herbicides facilitating better targeting and/or controlled release, *etc.*

In this work we report on the preparation and characterisation a CaFe LDH containing intercalated polyacrylate anions. For intercalation the dehydration-rehydration method was applying ethanol/water solvent mixture. Beside the usual instrumental characterisation techniques (X-ray diffractometry [XRD], transmission and scanning electron microscopies [TEM, SEM], energy dispersive X-ray fluorescence microanalysis [EDX], thermal analysis methods, FT-IR spectroscopy) the product was studied by dielectric relaxation spectroscopy (DRS), a method relatively rarely used for materials like these.

2 Materials and testing methods

2.1 Methods of synthesis

CaFe LDH was prepared by the co-precipitation method, *via* dropwise addition of 3 M NaOH solution to vigorously stirred and N₂-blanketed CaCl₂/FeCl₃ solution with 3:1 molar ratio [11]. The precipitates formed were rapidly filtered until air dry in a practically CO₂-free atmosphere, with the aid of a caustic resistant vacuum filter unit (Nalgene) equipped with an appropriate membrane (Versapor 129, 0.45 μm). The host materials were calcined at 773 K for 5 hours in N₂ atmosphere before attempting intercalation.

The polyacrylate anions (sodium polyacrylate of M_r ~1200 g/mol from Aldrich Chemical Co.) were intercalated into CaFe LDH with the dehydration-rehydration method, utilising the memory effect of the layered double hydroxides. The polyacrylate was suspended in aqueous ethanol and was stirred for a week. Upon rehydration intercalation occurred. The solid catalyst was filtered and washed with distilled water. The crystals obtained were kept at room temperature in a desiccator over P₂O₅.

2.2 Characterisation

The fundamental method for verifying if intercalation was successful was powder X-ray diffraction. The diffractograms were taken in the 3–60° 2Θ region with 4°/min scanning rate on a Rigaku Miniflex II instrument using the Cu_{Kα} radiation (λ= 0.15418 nm). The first, *i.e.* the (003) reflection was used for calculating the basal spacing (interlayer distance plus the thickness of one layer).

The layered structure of the intercalated material was studied by transmission electron microscopy (TEM – FEI TECNAI G²20 X-TWIN, 200kV accelerating voltage). From the dark-field image the layer thickness and the interlayer distance could be estimated.

The morphologies of the pristine LDH and the intercalated nanocomposite were studied with a Hitachi S-4700 scanning electron microscope (18 kV acceleration voltages) at various magnifications. The elemental maps of the substances were determined with a Röntec QX2 energy dispersive X-ray fluorescence spectrometer (equipped with Be window) coupled to the microscope. It was mainly concentrated on verifying the presence of the host anions in the sample *via* detecting the carbon of the polyacrylate and displaying its distribution.

In order to learn about the thermal behaviour of the materials, the thermogravimetric curves and their derivatives were registered with a Setaram Labsys derivatograph. TG-DTG curves were recorded in N₂ atmosphere applying 4 °C/min heating rate.

The Fe³⁺-content of the pristine LDH was determined with a Thermo's IRIS Intrepid II ICP-OES spectrometer, and was found to be 6.859×10^{-4} mol/g.

Dielectric relaxation spectra were registered on a Novocontrol Alpha-A FRA instrument, in the 5×10^{-3} – 10^7 Hz range at 293 K. A somewhat modified BDS1200 sample holder was connected to a ZG2 interface containing the I–U converter and the reference. This interface was connected to the Alpha-A head unit where the sinus generator and correlators for the lock-in measurements are found. The units are connected with BNC cables. Data were collected with the WinDETA software, while for data processing the OriginPro 8.1 [11] was applied.

3 Results and discussion

Powder XRD measurements were performed on the pristine LDH, the sodium salt of the polyacrylate as well as the intercalated sample. The obtained diffractograms are seen in Fig. 1.

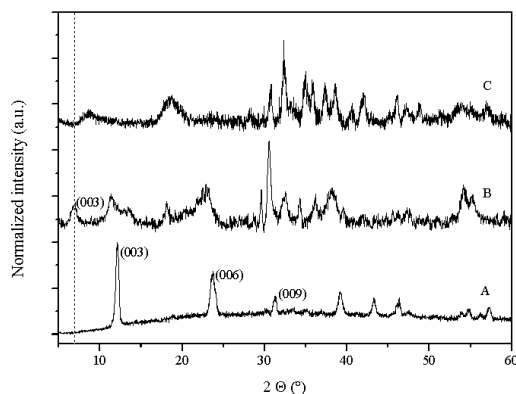


Figure 1. The powder X-ray diffractograms of the host Ca₃Fe LDH (trace A), the polyacrylate–Ca₃Fe LDH (trace B) and the sodium polyacrylate (trace C).

Basal spacing of the polyacrylate–Ca₃Fe LDH was calculated from the (003) reflection and it was found to be 1.28 nm (it was 0.78 nm for the pristine LDH). The TEM image of the sample (Fig. 2) verified that layered structure has been retained in the intercalated sample and allowed the estimation of the layer thickness of the LDH (0.60 nm – which is in good agreement with the recently published 0.59 nm based on refined XRD pattern [12]) as well as the interlayer spacing (0.69 nm). The sum of these two values, 1.29 nm gives the basal spacing this data is in very good agreement with that obtained from the (003) reflection.

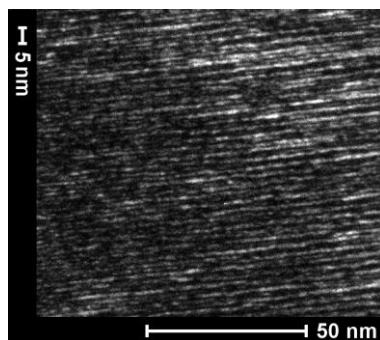


Figure 2. The TEM image of the polyacrylate–CaFe LDH nanocomposite.

In order to give further proof that the organic material is not simply on the outer surface of the LDH but it resides among the layers, the pristine LDH the polyacrylate salt as well as the intercalated samples were further studied by scanning electron microscopy (Fig. 3).

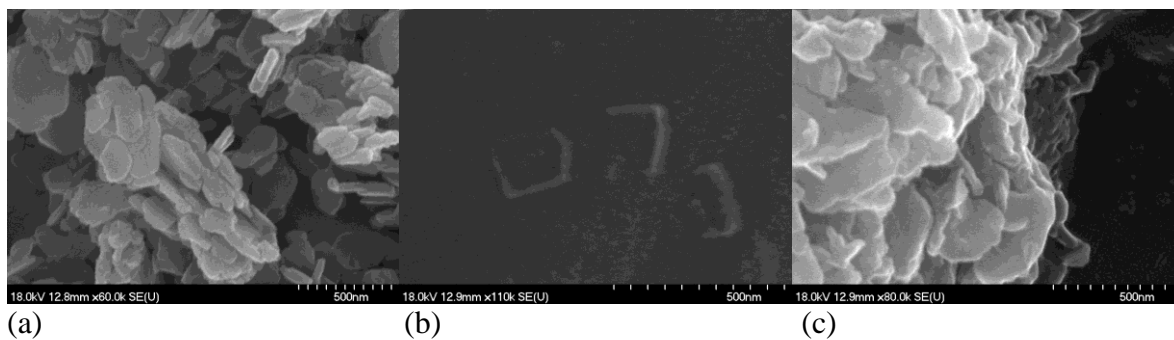


Figure 3. SEM images of the pristine Ca_3Fe LDH (a), the sodium salt of polyacrylate (b) and the polyacrylate- Ca_3Fe LDH.

The lamellar morphologies of the LDHs are reflected in the images both for the pristine LDH (Fig. 3/a) and the nanocomposite (Fig. 3/c) and they are very different from that of the salt (Fig. 3/b). The elemental maps made on the basis of SEM-EDX measurements have also been made (Fig. 4). The close to even distribution of the ions on the Ca-Fe elemental map indicated that double hydroxides are formed, indeed (Fig. 4/b). The C elemental maps revealed that the organic material were present and again in close to even distribution (Fig. 4/c).

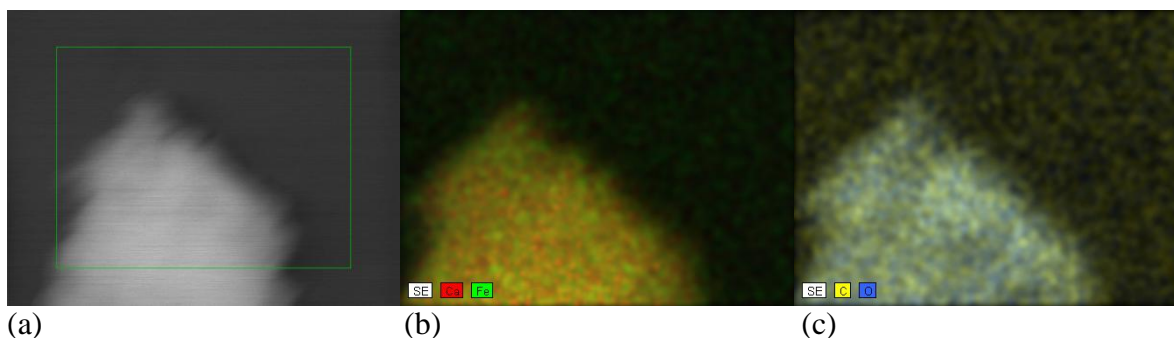


Figure 4. The SEM-EDX elemental maps of the polyacrylate- Ca_3Fe LDH: the sample (a), Ca-Fe map (b) and the C-O map.

The thermal behaviour of the samples is seen in Fig. 5.

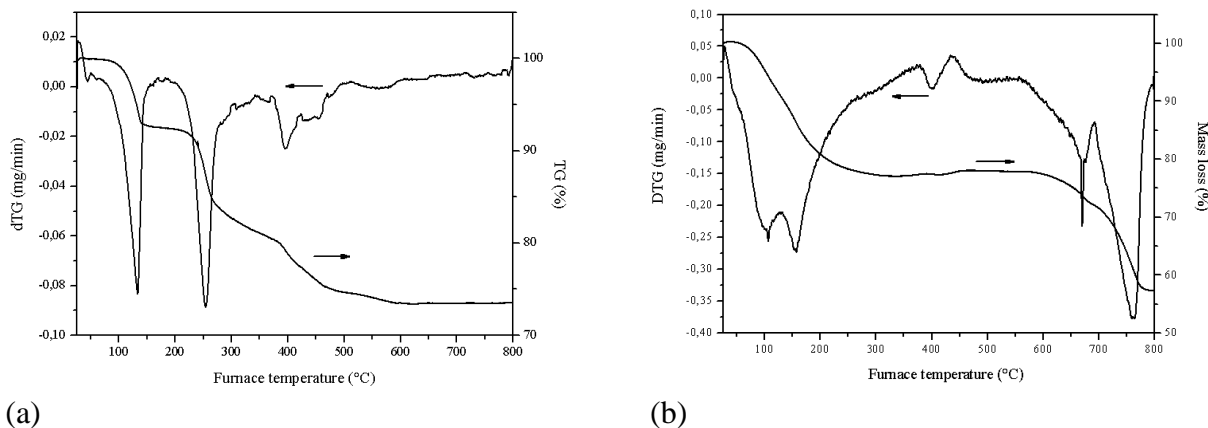


Figure 5. Thermogravimetric analysis (TG, DTG) of (a) the pristine Ca_3Fe LDH, (b) the polyacrylate- Ca_3Fe LDH acetone/ H_2O .

The pristine CaFe LDH sample displayed three mass losses attributed to the removal of the physisorbed (383–423 K), the interlayer (423–613 K) and the structural (643–723 K) water; at this temperature the layered structure collapsed. The intercalated structure behaved qualitatively similarly (the second loss slipped towards lower temperatures and thus, the first two DTG bands became less resolved) except that the loss of the organic material is seen in a very narrow temperature range centred at 943 K.

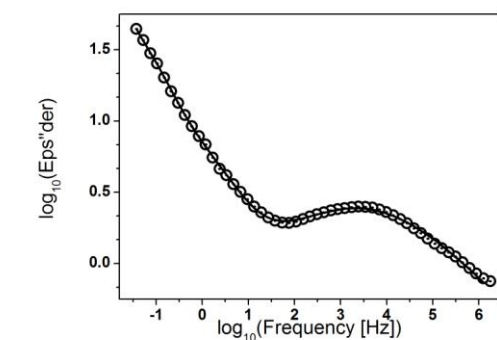
In order to display changes to the DRS spectrum of polymer due to confinement the spectra of the sodium polyacrylate, the pristine CaFe LDH and the polyacrylate–CaFe LDH have been registered (Fig. 6). For evaluation the Havriliak-Negami parameterised [13] Debye equation including the conductivity and the electrode polarization terms was fitted to the observed DRS data points. The equation is as follows:

$$\varepsilon^*(\omega) = \varepsilon''(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \sum_{i=1}^3 \frac{\Delta\varepsilon}{\{1 + (i\omega\tau)^\alpha\}^\beta} - ia \left(\frac{\sigma_0}{\varepsilon_0 \omega^S} \right) + \frac{A}{\omega^S}$$

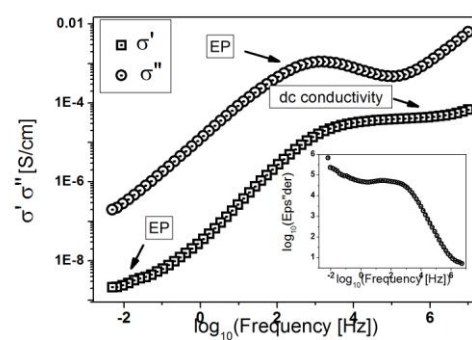
where $\omega = 2\pi f$, ε^* is the complex dielectric function, $\Delta\varepsilon = \varepsilon_S - \varepsilon_\infty$ is the dielectric strength, ε_S and ε_∞ is the dielectric constant at very low and at very high frequencies, respectively, $\varepsilon_0 = 8.8542 \cdot 10^{-12}$ F/m is the permittivity of vacuum, τ is the relaxation time α and β are fitting parameters characterising the peak broadening, σ_0 is the specific conductivity. $S \leq 1$ determines the slope of the conductivity tail in double logarithm formalism, the factor A has the dimension of $(\text{rad} \cdot \text{Hz})^S / \text{Hz}$, and $0 \leq A$ is the magnitude of electrode polarization (EP in the followings). During the fitting procedure the β parameter was found to be close to 1, therefore the relaxation equation employed could be reduced to a Cole-Cole function [14].

Differences are better seen if the derivatives of the dielectric losses (ε'') vs. $\log_{10}(\text{frequency})$ functions are depicted (Fig. 6/a and c and the inset in Fig. 6/b). In the main part of Fig. 6/b the conductivity values (both the real and the imaginary parts) are displayed, because they give convincing evidence on the predominance of electrode polarization in crystalline sodium polyacrylate system.

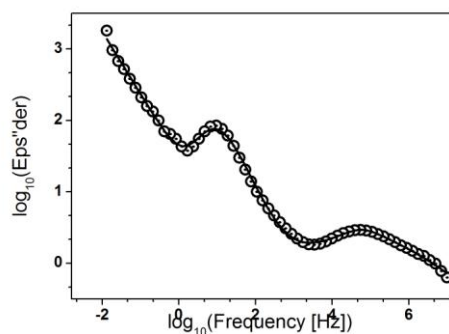
The DRS spectrum of the pristine LDH reflects two major and one minor relaxation processes (Fig. 6/a). The hardly visible minor one (~ 0.4 Hz) can be attributed to interfacial polarization, the most intense one is most probably due to the polarisation of the anions along the charged LDH layer (~ 3.2 kHz), while the one at the highest frequency (~ 320 kHz) belongs to orientational polarisation of the interlayer water. These processes are also present in the polyacrylate–CaFe LDH nanocomposite (Fig. 6/c), however, they are shifted towards higher frequencies with about an order of magnitude, respectively. The intensity of the relaxation at the lowest frequency, which is attributed to interfacial polarization, increased due to the increased inhomogeneity of the system. The relaxation processes seen on the spectrum sodium polyacrylate cannot be recognized on that of the polyacrylate–LDH system (Fig. 6/b), because they are suppressed by the predominant EP.



(a)



(b)



(c)

Figure 6. The derivatives of ϵ'' vs. $\log(\text{frequency})$ functions for (a) the pristine CaFe LDH, (b) the sodium polyacrylate and (c) the polyacrylate–Ca Fe LDH composite.

4 Conclusions

Polyacrylate anions could be introduced among the layers of Ca_3Fe LDH with the dehydration-rehydration method. The success of intercalation was verified with XRD, TEM and SEM measurements. The TEM directly verified that the layered system remained after intercalation and allowed to estimate both the thickness of the LDH layer and that of the interlayer spacing. On the TG-DTG curves the temperature of losing the organic material could be identified. A comparison of the DRS spectra of the pristine LDH, the sodium salt of polyacrylate and the polyacrylate–LDH composite revealed that the polymer is tightly bound among the layers of the LDH.

Acknowledgements

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References

- [1] Cavani F., Trifirò F., Vaccari, A. Hydrotalcite-type anionic clays: Preparation, properties and applications. *Catal. Today*, **11**, 173-301 (1991).
- [2] Vaccari A. Preparation and catalytic properties of cationic and anionic clays. *Catal. Today*, **41**, 53-71 (1998).
- [3] Evans D.G., Slade R.C.T. Structural aspects of layered double hydroxides. *Structure & Bonding*, **119**, 1-87 (2006).
- [4] Miyata S. Physico-chemical properties of synthetic hydrotalcites in relation to composition. *Clays Clay Miner.*, **28**, 50-56 (1980).
- [5] Corma A., Fairness V., Martín-Aranda V., Frey F. Determination of base properties of hydrotalcites: Condensation of benzaldehyde with ethyl acetoacetate. *J. Catal.*, **134**, 58-65 (1992).
- [6] Roelofs J.C.A., Lensveld D.J., van Dillen A.J., de Jong K.P. On the structure of activated hydrotalcites as solid base catalysts for liquid-phase aldol condensation. *J. Catal.*, **203**, 184-191 (2001).

- [7] Reichle W.T. Catalytic reactions by thermally activated, synthetic, anionic clay minerals. *J. Catal.*, **94**, 547-557 (1985).
- [8] Reichle W.T. Anionic clay minerals. *CHEMTECH*, 58-63 (1986).
- [9] Pálinkó I. Organic-inorganic nanohybrids of biologically important molecules and layered double hydroxides. *Nanopages*, **1**, 295-314 (2006).
- [10] Srankó D., Pallagi A., Kuzmann E., Canton S.E., Walczak M., Sápi A., Kukovecz Á., Kónya Z., Sipos P., Pálinkó, I. Synthesis and properties of novel Ba(II)-Fe(III)-layered double hydroxides. *Appl. Clay Sci.*, **48**, 214-217 (2010).
- [11] Origin 8.1, Originlab Corporation, Northampton, MA, USA, 2010.
- [12] Zhou J., Xu Z.P., Qiao S., Liu Q., Xu Y., Qian G. Enhanced removal of triphosphate by MgCaFe-Cl LDH: Synergism of precipitation with intercalation and surface uptake. *J. Hazardous Mater.*, **189**, 586-594 (2011).
- [13] Havriliak S., Negami S. Complex plane analysis of α -dispersions in some polymer systems. *J. Polym. Sci. C*, **16**, 99-103 (1966); Havriliak S., Negami S. A complex plane representation of dielectric and mechanical relaxation processes in some polymers. *Polymer*, **8**, 161-205 (1967).
- [14] Cole K.S., Cole R.H. 1. Dispersion and absorption in dielectrics. I. Alternating-current characteristics. *J. Chem. Phys.*, **9**, 341-351 (1941).