

## EFFECT OF MAGNETIC FIELD ON ANION-EXCHANGE IN COBALT-ALUMINIUM LAYERED DOUBLE HYDROXIDES

Vieira D.E.L.<sup>1</sup>, Cardoso J.P.V.<sup>1</sup>, Pashkevich Yu.G.<sup>2</sup>, Shilo A.V.<sup>2</sup>, Rubanik O.E.<sup>3</sup>,  
Shilin A.D.<sup>4</sup>, Rubanik V.V.jr.<sup>4</sup>, Vieira J.M.<sup>1</sup>, Salak A.N.<sup>1</sup>

<sup>1</sup>Department of Materials and Ceramics Engineering, CICECO – Aveiro Institute of Materials,  
University of Aveiro, Portugal, [danielevieira@ua.pt](mailto:danielevieira@ua.pt), [salak@ua.pt](mailto:salak@ua.pt)

<sup>2</sup>O. Galkin Donetsk Institute for Physics and Engineering of NASU, Kyiv, Ukraine,  
[yu.pashkevich@gmail.com](mailto:yu.pashkevich@gmail.com)

<sup>3</sup>Vitebsk State Technological University, Vitebsk, Belarus

<sup>4</sup>Institute of Technical Acoustics of NASB, Vitebsk, Belarus, [ita@vitebsk.by](mailto:ita@vitebsk.by)

Layered double hydroxides (LDH) are natural 2-D nanostructures composed of the parallel sheets of mixed metal hydroxides,  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}$  whose positive charge is compensated by anions ( $A^y$ ) intercalated into the interlayer gallery and screened from each other by water molecules [1] (hereinafter,  $M^{2+}_nM^{3+}_m-A^y$ , where  $n = (1-x)/x$  is the atomic ratio of cations  $M^{2+}$  and  $M^{3+}$  in the layer). One of the most prominent features of LDH is their anion-exchange ability. This feature is widely explored in respect of the application of layered hydroxides in water treatment, corrosion protection and *in vivo* delivery of drugs, genes and markers in biology and medicine [2]. The typical triggers used in a controllable anion exchange are temperature, pH, and the presence of particular anion species. We have recently shown that  $Co^{2+}$ -containing LDH are magnetically anisotropic and flake-like crystallites of these LDH can be arranged in external magnetic field [3]. One may suggest that a magnetic field can act as a trigger in an anion exchange in such LDH.

In this work, an effect of magnetic field on the  $NO_3^- \rightarrow CO_3^{2-}$  anion exchange in  $Co_2Al-NO_3$  LDH was studied using a spectrophotometric approach.  $Co_2Al-NO_3$  LDH was synthesized using the co-precipitation procedure described in our previous work [4]. The obtained suspension was centrifuged, and the resulting product was obtained in the form of a slurry containing about 80 wt.% of water. The phase content of the obtained product was controlled using X-ray diffraction at room temperature. The XRD study was performed on the powder obtained from the slurry dried at 60°C. Time-dependent variations in the anion content of the exchange solution were monitored using a Scan Sci UV-vis spectrophotometer equipped with a quartz cuvette with an optical path length of 1 cm. The absorption spectra of the solution were measured after certain periods of time after the beginning of the exchange reaction. The measurements were repeated three times to ensure the reproducibility of the results. Anion exchange from nitrate to carbonate was carried out in a 0.1 M solution of  $Na_2CO_3$  in deaerated water. The solution was put into a plastic tube placed between the magnet poles. Then 0.3 g of the  $Co_2Al-NO_3$  LDH slurry was added and continuously dispersed using a mechanical stirrer.

The anion exchange was carried out in a zero magnetic field and in a field of 0.5 T. The typical procedure was the following: after the certain periods of time upon the addition of the slurry, about 2 ml of the suspension was removed from the tube using a syringe and then squeezed out through a 0.45  $\mu m$  filter into the measuring cuvette (the procedure took about 2 s). The periods of the anion exchange time in the case of a zero magnetic field were 30, 60, 150, 180, 270, 300, 600 seconds and at 24, 48 and 120 hours. When the magnetic field was applied during the exchange reaction, the measurements were conducted after 30, 60, 150, 180, 270, 300, 900, 1800 and 3600 seconds after the beginning of the process. The absorption spectra of the exchange solution were collected *versus* the exchange reaction time at room temperature. The absorption curves of the exchange solution recorded in the range of 180-300 nm were compared with the peaks of  $CO_3^{2-}$  (225.65 nm) and  $NO_3^-$  (234.58 nm) measured in the reference  $NaCO_3$  and  $NaNO_3$  solutions, respectively.

The nitrate-to-carbonate exchange results in an increase of  $NO_3^-$  in a  $CO_3^{2-}$  containing solution. Therefore, one can expect a regular shift in the position of the absorbance peak with the progress of the anion exchange.

It has been revealed that the anion-exchange processes with or without application of the magnetic field start immediately, and after 60 s, the presence of nitrate in the solution is already detectable. In a zero field, after a fast increase in the nitrate content in the initial 60 s, the peak value and the peak position remained near the same for about 5 min. The further changes of these spectra characteristics with time were small, demonstrating a slow anion-exchange process, which was still incomplete after 120 h. It was rather expectable since the complete nitrate-to-carbonate exchange in  $M^{2+}M^{3+}$  LDHs at room temperature takes about one week [4].

When the magnetic field was applied, an increase of the nitrate concentration in the exchange solution was gradual for 1 h. After this period, the exchange was still incomplete; however, the exchange rate was undoubtedly higher than that after the 120-h exchange in a zero field. Figure 1 shows the absorbance peak position and the maximum value of the relative absorbance as a function of time for the anion-exchange experiments carried out with and without application of an external magnetic field of 0.5 T.

The simple characteristics of the obtained absorption spectra, namely the peak position and

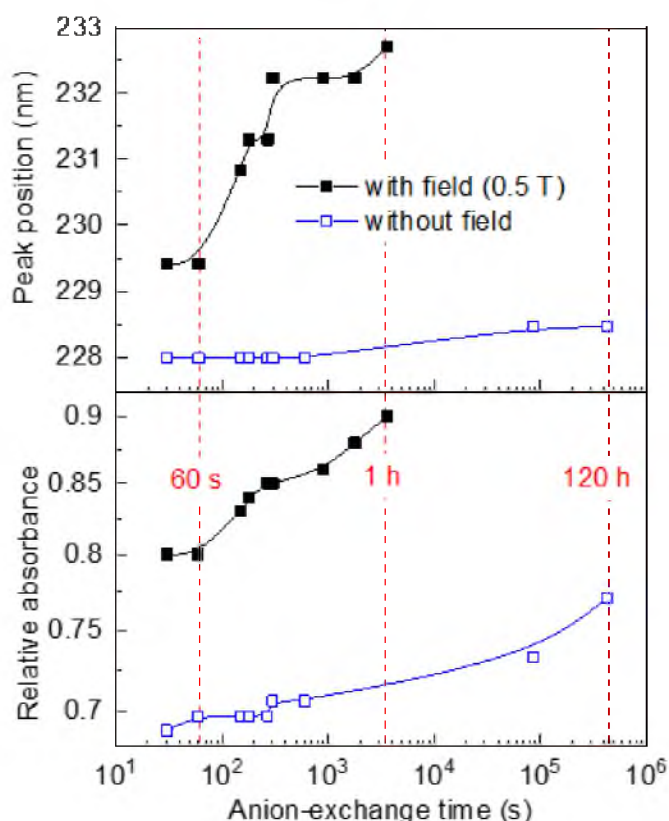


Figure 1 - The time variations of the absorbance peak position (top panel) and the maximum value of the relative absorbance (bottom panel) measured in the solution, in which the nitrate-to-carbonate anion exchange reaction was carried either in a zero magnetic field or in a field of 0.5 T

acceleration of the process. This effect certainly deserves a detailed study. Extended experiments, in which the anion exchange will be carried out at various values and directions of magnetic field as well as with different combinations of the intercalated and substituting anions are in progress and will be reported elsewhere.

*This work was supported by the Belarus-Ukraine grant T20YKA-020/N0120U000216 (2020-2021). The authors also acknowledge the Slovakia-Portugal bilateral project FAST-LDH (2019-2020)/APVV-SK-PT-18-0019. The research done in University of Aveiro was supported by the project CICECO-Aveiro Institute of*

**Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Portuguese Foundation for Science and Technology (FCT)/MCTES. D.E.L. Vieira acknowledges the financial support of FCT-Portugal through the individual PhD grant PD/BD/143033/2018. A.N. Salak acknowledges the financial support of national funds (OE) through FCT - Portugal in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19.**

#### REFERENCES

1. X. Duan, D.G. Evans, Layered double hydroxides, *Structure & Bonding*, Springer-Verlag Berlin Heidelberg, 2006, 119, 121-159.
2. G. Mishra, B. Dash, S. Pandey, Layered double hydroxides: A brief review from fundamentals to application as evolving biomaterials. *Appl. Clay Sci.* 2018, 153, 172-186.
3. D.E.L. Vieira, J.P.V. Cardoso, A.V. Fedorchenko, E.L. Fertman, E. Čižmár, A. Feher, R.Yu. Babkin, Yu.G. Pashkevich, C.M.A. Brett, J.M. Vieira, A.N. Salak, Magnetic-field-assisted deposition of self-assembling crystallite layers of Co<sup>2+</sup>-containing layered double hydroxides, *Chem. Comm.* 2021, 57, 6899-6902.
4. A.N. Salak, D.E.L. Vieira, I.M. Lukienko, Yu.O. Shapovalov, A.V. Fedorchenko, E.L. Fertman, Yu.G. Pashkevich, R.Yu. Babkin, A.D. Shilin, V.V. Rubanik, M.G.S. Ferreira, J.M. Vieira, High-power ultrasonic synthesis and magnetic-field-assisted arrangement of nanosized crystallites of cobalt-containing layered double hydroxides, *ChemEngineering* 2019, 3, 62.