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# Electrolytically supported processes of capture and release of CO<sub>2</sub>

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### Abstract

According to present knowledge,  $CO_2$  capture and valorisation are possible solutions involving economic and industrial challenges, for reducing atmospheric  $CO_2$  emissions.

Chemisorption using amine-based solvents is the farthest advanced process in terms of industrial development [1-4] (performances: 0.4 ton CO<sub>2</sub>/ton MEA; energy cost: ~ 2.44 - 5.50 GJ/ton CO<sub>2</sub> [3, 5-9]; 0.72 GJ/ton CO<sub>2</sub> is hopefully to be achieved [10]). Various obstacles to its use must nevertheless be overcome. Notably health and environmental risks associated with the use and handling of amines must be duly specified and verified for industrial-scale facilities. Given this two-fold challenge, both economic and environmental, the development of alternative eco-compatible and efficient processes is crucial for cost-effective post-combustion CO<sub>2</sub> capture/release.

This research aims at developing a powerful technological breakthrough in the  $CO_2$  capture, using Layered Double Hydroxides (LDHs).

LDHs are anion exchange materials consisting of stacks of positively charged, mixed-metal hydroxide layers between which hydrated anionic species are interlayered. The general structural formula of LDH is  $[M^{II}_{1-x}M^{III}_x(OH)_2]_x(A^{n-x/n}).mH_2O$ , in which M are metal cations and A exchangeable hydrated anions. The anion exchange capacity can reach 2-3 meq/g [11, 12].

LDH benefits from a strong affinity for  $CO_3^{2-}$  [13-17]. Moreover, synthesized LDHs bearing electroactive metal cations within their sheets enable reversible electrochemical oxidation and reduction [18-22].

LDHs aim at covering a broad spectrum of specifications with respect to CO<sub>2</sub> capacity and selectivity [23, 24], low manufacturing cost [25], chemical stability for transportation and mechanical robustness under cycling [26-29].

These specific properties make it ultimately possible to control the ion exchange capacity [21, 22] and thus to envisage breakthrough electrolysis processes for the capture and release of anions [30].

The electrochemical control of the oxidation state of multiple valence cations, constituting the lamellar sheets, is the core process (Fig. 1A), which also includes CO<sub>2</sub> dissolution reaction to  $CO_3^{2-}$  from the gas effluent, as well as, after capture and release of  $CO_3^2$ , the CO<sub>2</sub> degassing from released  $CO_3^{2-}$  solution. The use of a unique redox system within the electrochemical process allows the cancellation of the term cell voltage (i.e.  $E_{a/i=0} - E_{c/i=0}$ ), which allows the significant decrease of the electrical power needed [30].

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Fig. 1: A. Electrolytically supported process of capture and release of CO<sub>3</sub><sup>2-</sup> using LDHs [30]

Co/Fe LDHs, in which  $Co^{III}/Co^{II}$  constitutes the electroactive redox couple, were selected as materials of interest for  $CO_3^{2-}$  capture and release in agreement with the ability of such LDHs to ensure 5000 electrochemical oxidation and reduction cycles [26].

The coupling of Cyclic Voltammetry and Quartz Crystal Microbalance, for the concomitant measurement of current densities and mass variations using thin LDHs films, as well as, the coupling of chronoamperometry and potentiometric titration for the concomitant measurement of current densities and alkalinities using LDHs slurries, allowed determining the mechanism and quantifying the kinetics of the physico-electro-chemical reactions occurring in NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> aqueous buffer solutions.

Synthesis and formulation of chemically co-precipitated Co/Fe LDH was optimized to perform electrochemical cycling according to:

$$Co_{6}^{H}Fe_{2}^{H}(OH)_{16}(CO_{3})_{1}, xH_{2}O + 1CO_{3}^{2-} \leftrightarrows Co_{4}^{H}Co_{2}^{H}Fe_{2}^{H}(OH)_{16}(CO_{3})_{2}, (x-3)H_{2}O + 2e^{-1}CO_{4}^{H}Fe_{2}^{H}(OH)_{16}(CO_{3})_{2}, (x-3)H_{2}O + 2e^{-1}CO_{4}^{H}Fe_{2}^{H}(OH)_{16}(OH$$

The charge modulation of the Co/Fe LDH via Co<sup>II</sup> oxidation and Co<sup>III</sup> reduction respectively allows reversible  $CO_3^{2-}$  intercalation and deintercalation into/from the interlayer space, in agreement with a counterflux of three water molecules and reversible sheet collapsing and expensing. The percentage of electroactive Co ranges from 5 to 12%. The oxidation-reduction heterogeneous kinetic constant of the Co<sup>III</sup>/Co<sup>II</sup> redox couple constituting the LDHs brucitic-like layers is 2.5 ×10<sup>-4</sup> m/s ( $\alpha = 0.6$ ,  $\beta = 0.4$ ).

The mass transport coefficient of LDHs towards the electrode is  $4.72 \times 10^{-5}$  m/s; the electrochemical oxidation and reduction constants of cobalt are respectively  $1.48 \times 10^{-3}$  s<sup>-1</sup> and  $1.27 \times 10^{-3}$  s<sup>-1</sup>.

Under optimal cycling conditions, the process efficiency, for one cycle of capture and release, is higher than 170 kg of CO<sub>2</sub> per ton of LDH.

This result suggests particularly interesting perspectives for the optimization of an electrolytically supported process of capture and release of CO<sub>2</sub> using Co/Fe LDHs.

Keywords: CO2 capture ; Electrolytic processes ; Layered Double Hydroxides ; Redox-Controlled Host-Guest Interactions

#### References

- G.P. Towler, Gas Purification, 5th edition, Arthur Kohl, Richard Nielsen. Gulf Publishing Company (1997), 1369 pp, £157.00, ISBN: 0 88415 220 0, 1998.
- [2] M.T. Sander, C.L. Mariz, The Fluor Daniel®Econamine<sup>™</sup> FG Process: Past Experience and Present Day Focus, Energy Conversion and Management, 33 (1992) 341-348.
- [3] R. Barchas, R. Davis, The Kerr-McGee/ABB Lummus Crest Technology for the Recovery of CO<sub>2</sub> from Stack Gases, Energy Conversion and Management, 33 (1992) 333-340.
- [4] T. Mimura, S. Shimojo, T. Suda, M. Iijima, S. Mitsuoka, Research and Development on Energy Saving Technology for Flue Gas Carbon Dioxide Recovery and Steam System in Power Plant, Energy Conversion and Management, 36 (1995) 397-400.
- [5] T. Ogawa, Y. Ohashi, S.u. Yamanaka, K. Miyaike, Development of Carbon dioxide removal system from the flue gas of coal fired power plant, Energy Procedia, 1 (2009) 721-724.
- [6] M.R.M. Abu-Zahra, L.H.J. Schneiders, J.P.M. Niederer, P.H.M. Feron, G.F. Versteeg, CO<sub>2</sub> capture from power plants. Part I. A parametric study of the technical performance based on monoethanolamine, International Journal of Greenhouse Gas Control, 1 (2007) 37-46.
- [7] D. Chapel, J. Ernst, C. Mariz, Recovery of CO<sub>2</sub> from flue gases: commercial trends, The 1999 Canadian Society of Chemical Engineers annual meeting, Saskatoon, Canada, 1999.

- [8] T. Mimura, H. Simayoshi, T. Suda, M. Iijima, S. Mitsuoka, Development of Energy Saving Technology for Flue Gas Carbon Dioxide Recovery in Power Plant by Chemical Absorption Method and Steam System, Energy Conversion and Management, 38 (1997) S57-S62.
- [9] T. Mimura, S. Satsumi, M. Iijima, S. Mitsuoka, Development on Energy Saving Technology for Flue Gas Carbon Dioxide Recovery by the Chemical Absorption Method and Steam System in: P. Riemer, B. Eliasson, A. Wokaun (Eds.) Power Plant, Greenhouse Gas Control Technologies, Elsevier Science, Ltd., Kidlington, United Kingdom, 1999, pp. 71-76.
- [10] G.T. Rochelle, Amine Scrubbing for CO<sub>2</sub> Capture, Science, 325 (2009) 1652-1654.
- [11] D.L. Bish, Anion exchange in takovite: Applications to other hydroxide minerals, Bull. Mineral, 103 (1980) 170-175.
- [12] S.V. Prasanna, P.V. Kamath, Anion-Exchange Reactions of Layered Double Hydroxides: Interplay between Coulombic and H-Bonding Interactions, Industrial & Engineering Chemistry Research, 48 (2009) 6315-6320.
- [13] S. Miyata, Anion-exchange properties of hydrotalcite-like compounds, Clays Clay Miner., 31 (1983) 305-311.
- [14] A. Di Bitetto, G. Kervern, E. Andre, P. Durand, C. Carteret, Carbonate-Hydrogenocarbonate Coexistence and Dynamics in Layered Double Hydroxides, The Journal of Physical Chemistry C, 121 (2017) 6104-6112.
- [15] L.O. Torres-Dorante, J. Lammel, H. Kuhlmann, T. Witzke, H.-W. Olfs, Capacity, selectivity, and reversibility for nitrate exchange of a layered double-hydroxide (LDH) mineral in simulated soil solutions and in soil, Journal of Plant Nutrition and Soil Science, 171 (2008) 777-784.
- [16] S. Ishihara, P. Sahoo, K. Deguchi, S. Ohki, M. Tansho, T. Shimizu, J. Labuta, J.P. Hill, K. Ariga, K. Watanabe, Y. Yamauchi, S. Suehara, N. Iyi, Dynamic Breathing of CO<sub>2</sub> by Hydrotalcite, Journal of the American Chemical Society, 135 (2013) 18040-18043.
- [17] P. Sahoo, S. Ishihara, K. Yamada, K. Deguchi, S. Ohki, M. Tansho, T. Shimizu, N. Eisaku, R. Sasai, J. Labuta, D. Ishikawa, J.P. Hill, K. Ariga, B.P. Bastakoti, Y. Yamauchi, N. Iyi, Rapid Exchange between Atmospheric CO<sub>2</sub> and Carbonate Anion Intercalated within Magnesium Rich Layered Double Hydroxide, ACS Applied Materials & Interfaces, 6 (2014) 18352-18359.
- [18] C. Taviot-Guého, P. Vialat, F. Leroux, F. Razzaghi, H. Perrot, O. Sel, N.D. Jensen, U.G. Nielsen, S. Peulon, E. Elkaim, C. Mousty, Dynamic Characterization of Inter- and Intralamellar Domains of Cobalt-Based Layered Double Hydroxides upon Electrochemical Oxidation, Chemistry of Materials, 28 (2016) 7793-7806.
- [19] R. Roto, A. Yamagishi, G. Villemure, Electrochemical quartz crystal microbalance study of mass transport in thin film of a redox active Ni-Al-Cl layered double hydroxide, Journal of Electroanalytical Chemistry, 572 (2004) 101-108.
- [20] E. Scavetta, B. Ballarin, C. Corticelli, I. Gualandi, D. Tonelli, V. Prevot, C. Forano, C. Mousty, An insight into the electrochemical behavior of Co/Al layered double hydroxide thin films prepared by electrodeposition, Journal of Power Sources, 201 (2012) 360-367.
- [21] E. Duquesne, S. Betelu, C. Bazin, A. Seron, I. Ignatiadis, H. Perrot, O. Sel, C. Debiemme-Chouvy, Insights into Redox Reactions and Ionic Transfers in Nickel/Iron Layered Double Hydroxide in Potassium Hydroxide, The Journal of Physical Chemistry C, 124 (2020) 3037-3049.
- [22] E. Duquesne, S. Betelu, A. Seron, I. Ignatiadis, H. Perrot, C. Debiemme-Chouvy, Tuning redox state and ionic transfers of Mg/Fe-layered double hydroxide nanosheets by electrochemical and electrogravimetric methods, Nanomaterials, 10 (2020) 1-7.
- [23] A. Seron, F. Delorme, C. Fouillac, Carbon dioxide gas separating method for e.g. purifying carbon dioxide gas, involves dispersing nitrogen and carbon dioxide gas mixture in liquid phase at specific temperature and at pressure equal to/higher than atmospheric pressure (2007) FR2911517A1; US2010061917A1; WO2008110676A2..
- [24] A. Seron, F. Delorme, P Galle-Cavalloni. E. Proust, C. Vagner, R. Denoyel, P. Llewellyn, F. Delorme, Procédé de capture, séparation et purification de dioxyde de carbone par des oxydes mixtes amorphes issus du traitement thermique d'Hydroxydes Doubles Lamellaires, en humidité contrôlée (2010) FR2946893A1; WO2010149871A1.
- [25] A. Seron, F. Delorme, P Galle-Cavalloni, Synthesis of lamellar double hydroxide compounds, comprises solubilizing precursory elements e.g. natural minerals or industrial byproducts, to obtain di/trivalent cation solution and coprecipitating the cation solution with a base (2005) FR2882549A1; WO2006090069A1.
- [26] Y. Xiao, D. Su, X. Wang, S. Wu, L. Zhou, Z. Sun, Z. Wang, S. Fang, F. Li, Ultrahigh energy density and stable supercapacitor with 2D NiCoAl Layered double hydroxide, Electrochimica Acta, 253 (2017) 324-332.
- [27] P. Guoxiang, X. Xinhui, L. Jingshan, C. Feng, Y. Zhihong, F. Hongjin, Preparation of CoAl layered double hydroxide nanoflake arrays and their high supercapacitance performance, Applied Clay Science, 102 (2014) 28-32.
- [28] P.Y. Loh, K.K. Lee, Y. Ng, C.H. Sow, W.S. Chin, Co/Al layered double hydroxides nanostructures: A binderless electrode for electrochemical capacitor, Electrochemistry Communications, 43 (2014) 9-12.
- [29] K.Y. Ma, J.P. Cheng, F. Liu, X.B. Zhang, Co-Fe layered double hydroxides nanosheets vertically grown on carbon fiber cloth for electrochemical capacitors, Journal of Alloys and Compounds, 679 (2016) 277-284.
- [30] S. Betelu, I. Ignatiadis, A. Seron, Procédé et dispositif de capture et/ou de libération d'espèces anioniques assisté par électrolyse (2018) FR1850597.