

Nano science, Nanotechnology, Graphene & 2D material: New method for intercalation and ion exchange utilizing solid state electrochemical reaction- Masaya Fujioka-RIES, Hokkaido University, Japan

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Abstract

Due to the development and improvement of synthesis apparatus and techniques, materials science and design have advanced drastically. Recently, we have developed a new synthesis method available for intercalation and ion exchange, utilizing a solid-state electrochemical reaction under ambient hydrogen pressure. This synthesis method is called proton-driven ion introduction (PDII). The protons (H⁺) generated by the electrolytic dissociation of hydrogen, drive other monovalent cations along a high electric field in the solid state. This phenomenon can be thought of as ion billiards. Such a liquid-free process of ion introduction allows the application of high voltage around several kilovolts to the sample. This high electric field strongly accelerates ion exchange. Actually, compared to conventional solid-state reaction, PDII introduced 15 times the amount of K ions into Na super ionic conductor (NASICON)-structured Na_{3-x}K_xV₂(PO₄)₃ as shown in figure 1. Powdered Na₃V₂(PO₄)₃ as host material was put in a shallow alumina cylinder and placed on a carbon cathode stage. Then, a potassium-containing phosphate glass was also placed on the alumina cylinder as a K ion source material. When a voltage was applied, protons replaced K ions in the glass and drove these ions into Na₃V₂(PO₄)₃. K ions continuously migrated and formed Na_{3-x}K_xV₂(PO₄)₃. The obtained compound exhibited a thermodynamically metastable phase, which has not been reported so far. At the current stage, H⁺, Li⁺, Na⁺, K⁺, Cu⁺ and Ag⁺ can be used as guest ions. Furthermore, various compounds with nanospaces can be candidates for host materials in this method. In this conference, details of PDII and obtained materials will be presented. Recent Publications 1. Fujioka M, et al. (2017) Proton-driven intercalation and ion substitution utilizing solid-state electrochemical reaction. *Journal of the American Chemical Society* 139:17987-17993. 2. Cagliaris F, et al. (2017) Quantum oscillations in the SmFeAsO parent compound and superconducting SmFeAs(O,F). *Physical Review B* 96:104508 3. Fujioka M, et al. (2016) Discovery of the Pt-based superconductor LaPt₅As. *Journal of the American Chemical Society* 138:9927-9934. 4. Fujioka M, et al. (2014) High-Tc

phase of PrO_{0.5}F_{0.5}BiS₂ single crystal induced by uniaxial pressure. *Applied Physics Letters* 105:052601. 5. Fujioka M, et al. (2014) The effect of exceptionally high fluorine doping on the anisotropy of single crystalline SmFeAsO_{1-x}F_x. *Applied Physics Letters* 105:102602

Layered double hydroxides (LDH) or hydrotalcite-like compounds (HTLC) can be represented by the general formula [M(1-x)₂M(x)₃(OH)₂]_x⁺(An⁻)_{x/n}•mH₂O, where M₂⁺ is a divalent metal ion, M₃⁺ is a trivalent metal ion, and An⁻ is the charge-balancing interlayer anion. These compounds find applications in varied fields, including sorption, catalysis, electrochemistry, and drug delivery. Naturally occurring mineral hydrotalcite, whose formula is Mg₆Al₂(OH)₁₆(CO₃)•4H₂O, belongs to this class and has carbonate in its interlayer as the charge-balancing interlayer anion. Carbonate anions are known to be held tenaciously in the interlayer, which restricts its use in the synthesis of LDH with other interlayer anions, and thus, chloride- or nitrate-containing LDH are generally preferred as the starting precursors for the synthesis of other derived LDH through anion exchange. However, this results in products with low crystallinity and the products are generally subjected to postsynthesis hydrothermal treatment to obtain better crystallinity. Also, synthesis of LDH with anion other than carbonate requires prevention of contamination due to carbonate from atmospheric carbon dioxide by a suitable method. Intercalation of a suitable anion into a layered solid depends upon its selectivity/affinity for the layered solid. There have been various studies on selective intercalation of organic or inorganic anions in layered solids, but it is well known that the selectivity of carbonate toward LDH is very high, due to which its removal or intercalation of ions other than carbonate in its presence becomes difficult.

Various methods for the deintercalation of carbonate ion to obtain another anion-intercalated LDH with higher crystallinity have been reported. It was observed that when takovite was treated with cold dilute HCl, interlayer carbonate could be deintercalated and chloride anions got intercalated. Decarbonative intercalation of chloride could also be achieved by passing a stream of water vapor and gaseous HCl through hydrotalcite sample maintained at 140–160 °C in a glass tube.

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It was found that the decarbonation was better in the presence of a salt with a common anion as that of the dilute acid used. It was proposed that deintercalation is enhanced due to the protonation of carbonate ions in the interlayer space and subsequent ion exchange of bicarbonate ions with a large excess of Cl⁻ ions present in solution. However, here the decarbonated product showed small peaks due to carbonate ion in the IR spectrum. It was found that decarbonation of CO₃-LDH is highly enhanced by adding NaCl to a dilute HCl solution to obtain chloride-intercalated LDH and that 0.005 N HCl with 13 wt % NaCl was required to obtain a pure chloride-intercalated LDH. It was easier to decarbonate Mg₆Al₂(OH)₁₆(CO₃)•mH₂O compared to carbonate-rich Mg₄Al₂(OH)₁₂(CO₃)•mH₂O. While the decarbonation of the former could be achieved with a NaCl concentration of ~2 mol L⁻¹, the latter required a NaCl concentration of >4 mol L⁻¹, and it proceeded slower than in the case of the former. When using a salt-acid mixed solution for decarbonation, almost complete substitution of carbonate ions was possible for the Cl⁻ and Br⁻ ions but not with I⁻, NO₃⁻, and ClO₄⁻ ions even at high salt concentrations.

Subsequently Iyi's group used acetate buffer/NaCl mixture to obtain good-quality Cl⁻ LDH. Later, they studied the decarbonation of carbonated LDH using acetate buffer/salt mixture in a closed vessel and under N₂ flow. It was found that N₂ flow gives better decarbonation and requires lower concentration of the salt for complete decarbonation. It has also been shown that acid-alcohol mixed solutions could be used for decarbonation of LDH to form the LDH intercalated with the corresponding conjugate base of the acid used.

Although there have been quite a few methods for the ion exchange of carbonate-LDH by other ions, many of them are limited to few anions, and in the methods involving acids, the yields would be low due to the dissolution of the LDH. Hence, it is important to find a universal method that could be employed to exchange the interlayer carbonate of LDH with a variety of anions.

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