

Cite this: *Dalton Trans.*, 2024, **53**, 14520

DOI: 10.1039/d4dt90129k

rsc.li/dalton

Intercalation compounds: properties, mechanisms and advanced applications

Chiara Bisio,^a Sébastien Cahen^{b,c} and Fabrice Leroux^d

It is with great pleasure that we welcome you to this *Dalton Transactions* themed collection devoted to “*Intercalation compounds: properties, mechanisms and advanced applications*”.

Due to their peculiar properties, intercalation materials are interesting for the large community of researchers working on organic, inorganic and hybrid compounds, either from natural or synthetic origins. The chemistry of the intercalation processes is of course related to the study of the synthesis, structure, chemical and physical properties of the so-obtained intercalation materials. Novel synthesis methods are under development for the preparation of original intercalated phases, and, in this respect, huge progress has been realized concerning the characterization of these materials. On this basis, the intercalation compounds are being exploited for various applications spanning catalysis, energy, environment, health, biomaterials, coatings, composites as polymer filler, and water remediation.

This themed collection is intended to gather the most recent and noteworthy

contributions on intercalation compounds with particular emphasis on intercalation mechanisms, synthesis methods, host–guest interactions, and structure/property relationships determined by experimental and theoretical techniques. The articles comprising the themed collection can be thus considered as a representative selection of the current research on intercalation compounds.

Two perspective review papers are dedicated to intercalation layered compounds (ILCs), especially focusing on their design and applications in the field of energy (part 1) and for catalysis, environment and health (part 2). These manuscripts are authored by researchers from the Advisory Board of the *International Symposium on Intercalation Compounds* (ISIC) and contain a rational (even if not comprehensive) literature survey of the last few years on layered materials (with particular emphasis on LDHs, clays, Zr phosphate, graphene and graphite-based intercalation compounds, MXenes, *etc.*) giving particular emphasis to the strategies to synthesize the host structures and then the successive guest–host hybrid assembly. Moreover, the possible application in the field of energy through electrochemical storage (mostly as electrode materials, but also as electrolyte additives) and supercapacitors, as well as their relevance in other fields regarding (opto)electronics, is discussed, to point out why ILCs are expected to meet the challenge of tomorrow as electrode materials (C. Bisio *et al.*, <https://doi.org/10.1039/D4DT00755G>).

The role of intercalation chemistry in the development of catalysts for the production of clean energy, conversion of molecules derived from biomass into value-added products, degradation of pollutants and environmental remediation, for the use in medicinal chemistry and for the preparation of polymeric composites are also reviewed in a critical way to summarise some of the most interesting and recent finds and advantages in the use of ILCs, but also to identify and discuss still open challenges and perspectives (C. Bisio *et al.*, <https://doi.org/10.1039/D4DT00757C>).

The third perspective article of this themed collection is related to an overview of the preparation, heterostructure and application of hybrid layered double hydroxides (LDHs) containing functional particles and to assess their performance in different applications spanning catalysis, electrochemical energy devices, protective and anti-corrosion coatings, polymer-based nanocomposites, and biomedical applications. Possible novel applications are also discussed together with the hybridization of LDHs with metal oxides, metals, carbons and carbonaceous materials, and other nanoporous materials. This perspective paper also gives an overview of heterostructures based on LDHs and other layered materials, such as MXenes, graphenes and layered silicates, including their synthesis, tunable properties and innovative applications (M. Ogawa, <https://doi.org/10.1039/D4DT00292J>).

Other contributions of the themed collection are related to the preparation

^aDipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, Viale Teresa Michel 11, 15121 Alessandria, AL, Italy.

E-mail: chiara.bisio@uniupo.it

^bCNR-SCITEC Istituto di Scienze e Tecnologie Chimiche “Giulio Natta”, Via C. Golgi 19, 20133 Milano, MI, Italy

^cInstitut Jean Lamour – UMR 7198 CNRS-Université de Lorraine, Groupe Matériaux Carbonés, Campus ARTEM – 2 Allée André Guinier, B.P. 50840, F54011, Nancy Cedex, France.

E-mail: sebastien.cahen@univ-lorraine.fr

^dInstitut de Chimie de Clermont-Ferrand, Université Clermont Auvergne, UMR CNRS 6296, Clermont Auvergne INP, 24 av Blaise Pascal, BP 80026, 63171 Aubière cedex, France. E-mail: fabrice.leroux@uca.fr

of intercalation materials and dehydration or swelling mechanisms of 2D compounds. In this respect, various synthetic parameters have been investigated to obtain nitrate or chloride LDHs using a one-pot synthesis procedure. Different morphologies are obtained according to the salt type (chloride or nitrate), reaction time, urea/(Al + Zn) molar ratio, and metal concentration. Moreover, the parameters affecting the morphology of the ZnAl in the different forms are studied (A. Di Michele, <https://doi.org/10.1039/D4DT01529K>).

Titanoniobate phases are an interesting family of materials for application in electrochemistry as both 3d and 4d transition metals exhibit a redox potential of about 1.6 V vs. lithium. A 2D-type structure of formula $A_xM_{2n}O_{4n+2}$ made of $2 \times n$ blocks with edge-sharing octahedra exemplified by $LiTiNbO_5$, that was obtained through a topotactic reaction between $HTiNbO_5$ and a eutectic composition of $LiOH$ and $LiNO_3$ is reinvestigated. The authors indeed revisit the family and synthesize a new layered titanoniobate, $Li_3Ti_5NbO_{14}$, whose structure is determined by 3D electron diffraction single-crystal analysis. The phase is found to reversibly insert 2 Li^+ ions with a discharge cut-off of 1.5 V vs. Li through a first-order transformation. This is scrutinized by operando X-ray diffraction cycling in galvanostatic mode, where it is shown that up to 4 Li^+ ions can be inserted when chemically reduced with *n*-butyllithium (A. Neveu *et al.*, <https://doi.org/10.1039/D4DT00208C>).

In their article, Mir *et al.* developed lithiated iron hydroxysulfides $LiOHFeS$ formed under hydrothermal conditions from Fe and S in a solution of $LiOH$, described as a lamellar material with alternating $Li_2(OH)_2$ and Fe_2S_2 layers. By varying the $LiOH$ concentration, it is possible to obtain high non-stoichiometry of the Li/Fe ratio resulting in the formulation $Li_{1-x}Fe_x(OH)_{1-x}O_xFeS$, presenting the two kinds of non-stoichiometries. For $x = 0$ and with the insertion of a Li ion, an original mechanism is depicted that is associated with the reduction of the hydroxyl into hydrogen according to $LiOHFeS + Li^+ + e^- \rightarrow Li_2OFeS + \frac{1}{2}H_2$. Supported by a

Mössbauer study, the lithiated material cycles reversibly through the redox Fe^{3+}/Fe^{2+} between $Li_2OFe^{2+}S$ and $LiOFe^{3+}S$ compositions making it of interest as a negative electrode material in LIBs (C. Mir *et al.*, <https://doi.org/10.1039/D4DT00405A>).

The development of neutron science has been accompanied with more and more experiments using powerful neutron sources for the characterization of advanced materials. Nevertheless, the use of cold neutrons remains conditioned with the availability of reflectors efficient for both fast and slow cold neutrons. To bridge the gap, the elaboration of ideal reflectors is restricted to only a few elements, where carbon and fluorine remain the best candidates. Starting from literature data, the synthesis of an ideal $(C_2F)_n$ phase is realized by the optimization of fluorination conditions of graphite foils where the intercalation of fluorine bonded to graphene layers leads to an optimal interplanar distance of 0.9 nm (K. Henry *et al.*, <https://doi.org/10.1039/D4DT00794H>).

If intercalation reactions presented in the two perspective papers of this collection deal mainly with two-dimensional hosts, intercalation reactions in 3D materials cannot be omitted. For instance, considering anodes for LIB and NIB technologies, intercalation occurs mostly in lamellar carbon-based materials. However, 3D titanium dioxide, largely studied in the literature for numerous applications, is an interesting material. An original synthesis where TBOT acts as both carbon and TiO_2 precursor leads to a $TiO_2@C$ composite where carbon enhances the intercalation reaction in anatase interstitial sites for improving the electrochemical performance of titanium dioxide (T. Soudant *et al.*, <https://doi.org/10.1039/D4DT00459K>).

Some articles focus on dehydration and swelling mechanisms in 2D materials. The dehydration process of Na and K birnessites is studied using a multi-technique approach. The combination of experimental and computational techniques provided insights on the complete dehydration mechanism of birnessite prepared under ambient con-

ditions (RH ~ 50%) and evidenced that dehydration occurs in two successive stages. The first one is related to a gradual loss of water from the interlayer space, thus leading to a material in which each cation is hydrated by two water molecules, whereas upon further dehydration, completely dehydrated domains characterised by an interlayer distance 10 to 20% shorter than that of birnessite under ambient conditions appear (E. André *et al.*, <https://doi.org/10.1039/D4DT00588K>).

Osmotic swelling and delamination mechanisms of montmorillonite clays with monovalent and divalent inorganic interlayer cations are studied in organic solvents. The conditions for the swelling and delamination of inorganic homoionic smectites in water-polar organic mixed solvents are studied, and the obtained results indicate that osmotic swelling of inorganic homoionic smectites together with the delamination of clay crystallites to single layers is a general phenomenon in water-polar organic mixed solvents, whereas the interlayer inorganic cations are exchanged for organic ones for delaminating the clay mineral in organic solvents (T. Nakato, <https://doi.org/10.1039/D4DT00192C>).

Other articles deal with the study of specific properties of intercalation compounds. Some mesoionic triazolium scaffolds of two sulfonated organic molecules are co-intercalated in between LDH sheets by applying the so-called size-matching interlayer space (SMIS) approach, that consists of selecting a "passive" spacer whose length is close to that of the photoactive molecule. The authors demonstrate an efficient insertion rate when adopting SMIS since the targeted amount does correspond to the experimental interleaved guest uptake. It is found that the LDH host is able to restore in the solid state a strong luminescence like that observed in very dilute solutions of non-aggregated photo-active molecules. The hybrid LDHs are stable in temperatures up to 100 °C; however, the photoluminescence decreases after prolonged times at 200 °C (G. Zerbib *et al.*, <https://doi.org/10.1039/D4DT00573B>).

Relatively low-cost and low-toxicity, as well as being environmentally compatible, manganese dioxides are interesting positive electrode materials in asymmetric MnO₂/C supercapacitors. The authors of one paper combine such pseudocapacitive properties with the conductive properties of lamellar cobalt (oxy)hydroxides, and this in a single lamellar material, reminiscent of the asbolane-type structure well-known by mineralogists and geologists but not often reported in materials science. The heterostructure is built from the reaction between the birnessite, a layered δ-MnO₂, and cobalt nitrate, and an analysis by electronic transmission microscopy confirms the presence of two interlocking hexagonal sublattices. Enhanced performance up to 180 F g⁻¹ at moderate current densities is obtained, much higher compared to that of either the pristine birnessite or the sum of the constituents birnessite and Co(OH)₂, underlining the benefit of the assembly in providing larger charge transfer and to improve the diffusion of migrating species within the material, most probably due to the protonic conduction supplied by Co(OH)₂ moieties (T. Tailliez *et al.*, <https://doi.org/10.1039/D3DT03342B>).

Atomic layer fluorination (ALF) is used to produce an efficient protecting fluorinated layer at the surface of the material. A well-known positive electrode material for LIBs, Li(Ni_{0.80}Co_{0.15}Al_{0.05})O₂ (NCA), is used and exposed to vapours of xenon difluoride. It is found that the atomic fluorine diffuses into the first few nanometres of the particles and that the relative quantity of F atoms is very low and the NCA structure stays fully intact. However, the electrochemical performance in terms of cyclability, polarization and rate capability is improved and *operando* infrared spectroscopy and *post mortem* gas chromatography underline that the electrolyte reacts with the fluorine layer forming an electrode–electrolyte interphase (Y. Charles-Blin *et al.*, <https://doi.org/10.1039/D4DT00600C>).

Three-dimensional materials such as zeolites are also discussed in the collection. The magnetic, electric and optical properties of Li–Na alloys, Na–K alloys,

and Rb clusters in sodalite crystals are investigated by using a multi-technique approach. While Na–K alloy zeolites demonstrated anti-ferromagnetic properties, the Rb sample showed a non-magnetic metallic state, probably in relation to weak Coulomb repulsion between electrons and larger electron transfer energy between neighbouring clusters. The physical properties of the materials are reviewed in terms of electron correlations and polaron effects (T. Nakano *et al.*, <https://doi.org/10.1039/D4DT00562G>). Low-silica zeolite X loaded with potassium is also studied giving particular emphasis to the determination of the hyperfine couplings between the paramagnetic moment and nuclei in the metallic phase of the zeolite. ²³Na and ²⁷Al NMR spectra at different temperatures of the low-silica X zeolite loaded with potassium for saturation levels are used to estimate the hyperfine coupling constants of the studied zeolites (M. Igarashi, <https://doi.org/10.1039/D4DT00599F>).

Several papers are related to the use of layered materials for agricultural purposes. Montmorillonite-containing bentonite natural clays functionalized with linear aliphatic aldehydes by the incipient wetness deposition method are proposed as a sustainable approach against the olive tree pest. It is shown that these compounds can be positively used to induce an interference effect and biocidal activity against the olive tree infestations of *Bactrocea oleae*. The long-lasting inhibition effects reside in the positive effects provided by the preparation process and in the formation of non-covalent interactions between the aldehyde molecules and the layered solid, making the final materials robust against weathering and leaching of the active ingredient, but, at the same time, allowing a smooth and constant release of the active principle in the atmosphere (S. Econdi *et al.*, <https://doi.org/10.1039/D4DT00705K>).

Slow-release fertilisers (SRFs) based on LDHs are also proposed. In particular, a study of the mechanism governing phosphate release from an MgAl LDH is proposed by Jourdain *et al.* (A. Jourdain *et al.*, <https://doi.org/10.1039/D4DT00601A>) is

carried out by modifying the experimental conditions such as the pH, solid/liquid ratio, the concentration of carbonates and the ionic strength, and by analysing the intercalated species and/or interstratification/contamination from carbonate anions. Moreover, the potential phosphate recovery by LDHs and the development of LDH-based SRFs is also discussed.

Another article, also related to agricultural use of intercalated compounds, reports the development of hybrid membranes formed by synthetic hectorite (LAPONITE®) and polymers in the pre-treatment of garlic bulbils (*Allium sativum* L.) exposed to the pathogen *Stromatinia cepivora*, which causes white rot. The hybrid membranes are studied by a multi-technique approach to confirm the presence of fungicides. The experiments carried out indicated that the use of these membranes can be positively used to mitigate the white rot occurrence. Moreover, the use of these hybrids, based on the associated use of polymeric membranes in the pretreatment of garlic bulbils, can be used to reduce the concentrations of fungicidal active ingredients currently used to mitigate white rot disease (L. Alves de Melo Bessa *et al.*, <https://doi.org/10.1039/D4DT00301B>).

Different contributions discuss environmental remediation of modified porous and layered solids. Cylindrical-shaped mesoporous silica monoliths functionalized with an organic ligand are prepared and tested for the recovery of paramagnetic metal ions from aqueous solutions. The real-time ¹H-NMR relaxometry technique is used to follow the metal capture process over time and under simple experimental conditions, thus obtaining information about the uptake mechanism and related kinetic parameters. The possibility to regenerate and reuse the silica-based monoliths is also studied. The authors of one paper demonstrate that the functionalised monoliths are interesting materials for metal-ion sequestration from aqueous media, being easier to use and handle when compared to conventional powder systems (G. Ancora *et al.*, <https://doi.org/10.1039/D4DT00388H>).

LDHs and especially hydrotalcite composition Mg_2Al are known to convert into layered double oxides (LDOs) at medium temperatures, usually presenting a high surface area in comparison to the pristine LDH and able to reconstruct back to LDH by trapping anions. Here the authors of one paper focus on the capture of CO_2 by LDOs by varying the thermal treatment with a rapid ramp rate preferred since it significantly increases the surface area as well as the hydroxyl presence, the effect of which is to boost the CO_2 capture efficiency. The surface reactivity of the LDOs is studied by probe molecule adsorption with ammonia for the acid sites and CO_2 for the Lewis basic sites and completed with temperature-programmed desorption (TPD) techniques. Additionally, a fixed temperature of 400 °C for a prolonged time of 2 h to avoid the presence of too many strong acid sites is found to optimize the efficiency further, altogether underlining the intricate relationship between surface functionality and its associated CO_2 capture efficiency (D. W. Justin Leung *et al.*, <https://doi.org/10.1039/D4DT00270A>).

In the domain of human health, and in particular regarding the ever-growing field of theragnostics that integrates diagnostic and therapeutic approaches, layered rare-earth hydroxides (LRHs) are promising candidates due to their drug-uptake ability, as well as being phosphorescent upon release. The authors of one paper focus on layered terbium hydroxide (LTbH) since it is biocompatible, as verified by *in vitro* cell viability assays, but it lacks interest due to its initial large particle size distribution. Adopting a hydrothermal synthesis that can be generalized to other rare-earth elements, they succeed in reaching a size range appropriate for possible *in vivo* applications. By combining Gd and Tb in the same LRH, the material acts as a multi-modal medical imaging probe since it appears as a negative magnetic resonance imaging (MRI) contrast agent and also emits enhanced fluorescence by minimizing Tb^{3+} self-quenching due to the substitution with Gd^{3+} cations (M. Strimaite *et al.*, <https://doi.org/10.1039/D4DT00371C>).

The themed collection also contains contributions related to the development of materials for corrosion protection. New formulations based on α -zirconium hydrogenophosphate (α -ZrP) are obtained by intercalation of the corrosion inhibitor 2-aminobenzimidazole (ABIM) and characterized to determine their chemical composition and morphology. These pigments are put in contact with zinc to determine the corrosion behavior of the metal using electrochemical measurements. In the NaCl corrosive environment, ABIM molecules are released by an exchange reaction with Na^+ ions to form $Zn^{2+}/ABIM$ compounds, thus modifying and reinforcing the corrosion product layer on zinc. When the ABIM-ZrP particles are incorporated into an alkyd-polymer coating, an efficient barrier to gases and water is formed and this ensures efficient corrosion protection, even after 30 days of immersion in the corrosive electrolyte (I. Bouali *et al.*, <https://doi.org/10.1039/D4DT00476K>).

Finally, other research articles deal with the use of intercalation compounds for electrochemical applications. Cathodes using fluorinated multi-metallic materials are promising alternatives for lithium-ion batteries (LIBs) and LDH templates can support high substitution of their divalent and trivalent cations to achieve compositions of interest. The authors of one paper choose a precise composition containing Cu^{2+} , Co^{2+} , Fe^{3+} and Al^{3+} ions, which leads to an intimate composite blend after fluorination. The temperature of the reaction is important and original phases are observed at intermediate temperatures and after hydration. The redox activity and the associated mechanisms of the transition-metal fluorides are scrutinized by cyclic voltammetry coupled to *operando* Raman spectroscopy, underlining a first insertion process followed by some possible conversions. The authors remark on the versatility of LDHs as an intra-layer toolbox generating electroactive cations disposed in an intimate inorganic layered mosaic (A. Rouag *et al.*, <https://doi.org/10.1039/D4DT00504J>).

Since fluorine led to higher potentials compared to oxygen ligands due to the

larger ionicity of the bonds, the authors of one paper study the insertion of fluorine into $LiFePO_4$, an interesting candidate for a positive electrode material in Li batteries. This is performed under molecular fluorine F_2 , which induces at low temperature a core delithiation of $LiFePO_4$ with LiF shells formed around the particles. At higher temperatures, it results in a mixture of α - FeF_3 and α - Li_3FeF_6 when LiF is consumed and $FePO_4$ converts into FeF_3 . Interestingly, the authors report the latter mixture converts into $LiFePO_4F$ after thermal treatment under N_2 , and such conversion is also verified to form the triphylite form of $NaFePO_4$. However, the first attempts in using these materials as electrode materials fail to meet performance expectations, while a large hysteresis seems to indicate the electrochemical process of Li insertion and de-insertion is rather difficult. A better understanding of these limitations is required for future improvement with adapted formulation engineering (K. Lemoine *et al.*, <https://doi.org/10.1039/D4DT00603H>).

In the search for new redox-active materials, the authors of one paper study computationally the evaluation of the HOMO–LUMO gaps present in the heterocyclic *N*-oxides class of compounds and, in particular, the derivatives of quinoxaline 1,4-di-*N*-oxides and phenazine *N,N'*-dioxides. Indeed, understanding structure–property relationships, as well as predicting redox potentials of crucial interest, is possible through molecular and crystalline DFT calculations combined with an accurate electronic structure analysis, thus helping in classifying the potential application of an organic molecule such as pyrazine *N,N'*-dioxide, PZDO, as a negative electrode material with a potential of about 1.4 V vs. Li^+/Li lower than the inorganic counterpart $Li_4Ti_5O_{12}$ (LTO) (F. Lambert *et al.*, <https://doi.org/10.1039/D4DT01144A>).

We hope this themed collection makes for enjoyable reading and can be a source of inspiration and future fruitful collaborations.

We wish to thank all the authors for their valuable contribution, the

reviewers for their work and relevant input, as well as all the members of the ISIC board for their fruitful and kind discussions.

We would also like to thank the editorial staff at *Dalton Transactions* for making this themed collection possible. We address a special acknowledgement

to Prof. Russell Morris, Dr Mike Andrews, Emily Cuffin-Munday, Dr Kate Tustain and Dr Helen Lunn for their precious support.