

Johnson Matthey Highlights

A selection of recent publications by Johnson Matthey R&D staff and collaborators

Factors Affecting the Nucleus-Independent Chemical Shift in NMR Studies of Microporous Carbon Electrode Materials

L. Cervini, O. D. Lynes, G. R. Akien, A. Kerridge, N. S. Barrow and J. M. Griffin, *Energy Storage Mater.*, 2019, **21**, 335

The factors influencing the nucleus-independent chemical shift (NICS) of aqueous electrolyte species adsorbed on polymer-derived activated carbon were investigated in this systematic study. The observed NICS was found to be influenced by the carbon structure and the behavioural and chemical properties of the electrolyte species. Measurement of these effects demonstrates differences in the adsorption behaviour of different ions in the absence of an applied potential. For instance, as pore size decreases, so does the local concentration of spontaneously adsorbed alkali ions. This research could potentially enable greater understanding of the mechanism of charge storage in capacitive devices at the molecular level.

Fe³⁺ Reduction During Melt-Synthesis of LiFePO₄

P. Sauriol, D. Li, L. Hadidi, H. Villazon, L. Jin, B. Yari, M. Gauthier, M. Dollé, P. Chartrand, W. Kasprzak, G. Liang and G. S. Patience, *Can. J. Chem. Eng.*, 2019, **97**, (8), 2196

5 kg batches of LiFePO₄ (LFP) were melt synthesised in an induction furnace from coarse Fe₂O₃ (509 µm). Graphite from the crucible was an effective reducing agent. The Fe²⁺ content and reaction kinetics were improved *via* the addition of metallic Fe, which is also shown to improve the lifetime of the graphite crucible. To avoid agglomeration of the Fe powder due to the presence of a eutectic in the LiPO₃-Fe-Fe₂O₃ system, a pre-mixing step is required. A Fe²⁺ content of 0.325 g g⁻¹ was observed when fine Fe³⁺ (142 µm) was used with CO as the reducing agent at half the holding period at 1150°C, which

can be attributed to improved contact between the suspended Fe³⁺ and the CO reducing gas.

Chemical Speciation and Mapping of the Si in Si Doped LFP Ingot with Synchrotron Radiation Technique

M. Norouzi Banis, Z. Wang, S. Rousselot, Y. Liu, Y. Hu, M. Talebi-Esfandarani, T. Bibienne, M. Gauthier, R. Li, G. Liang, M. Dollé, P. Sauriol, T.-K. Sham and X. Sun, *Can. J. Chem. Eng.*, 2019, **97**, (8), 2211

The performance of lithium-ion batteries is significantly affected by small changes to the structure of LFP. The authors aimed to understand the effect of silicon-doped LFP prepared using a melt-synthesis process by utilising XAS and XRF mapping as characterisation methods. By using these methods, the non-uniform nature of prepared ingot samples could be better evaluated. With comparison to SiO₂ and amorphous glass phases formed as impurities in Si containing undoped samples, the XAS of Si-doped LFP indicate subtle changes in the local structure surrounding the dopants. Studies of this kind on the structure of modified LFP will help with the design of materials for Li-ion batteries.

Visualization of the Secondary Phase in LiFePO₄ Ingots with Advanced Mapping Techniques

Y. Liu, M. N. Banis, W. Xiao, R. Li, Z. Wang, K. R. Adair, S. Rousselot, P. Sauriol, M. Dollé, G. Liang, T.-K. Sham and X. Sun, *Can. J. Chem. Eng.*, 2019, **97**, (8), 2218

The electrochemical performance of LFP in lithium-ion batteries is influenced by impurity phases. Detection of such impurity phases is essential to improve the quality of LFP as a cathode material. The origin of the impurity and secondary phases can be understood through visualisation of the impurity and secondary phase distributions

immersed in the bulk LFP crystal. EDS and Raman techniques were used to observe the low melting lithium phosphate phase in the LFP ingot. Further exploration into the LFP materials after carbon coating was achieved through micro XRF mapping. This technology has high sensitivity, which ensured that the secondary phases were clearly defined.

Melt-Synthesis of LiFePO_4 Over a Metallic Bath

H. Villazon, P. Sauriol, S. Rousselot, M. Talebi-Esfandarani, T. Bibienne, M. Gauthier, G. Liang, M. Dollé and P. Chartrand, *Can. J. Chem. Eng.*, 2019, **97**, (8), 2287

An Fe^{3+} precursor was used to study silver and tin charged metallic baths for purification of the melt-synthesis of LFP. Samples prepared by the Sn bath delivered up to 156 mAh g^{-1} of LFP, whilst Ag bath samples delivered 161 mAh g^{-1} of LFP. XRD patterns of the Ag LFP samples were also cleaner than those produced by the Sn bath. Ag oxides and Ag compounds were not present. It is suggested that future studies should focus on investigating Ag baths as a potential contaminant trap for the melt-synthesis of LFP.

Synthesis of ZIF-8 Based Composite Hollow Fiber Membrane with a Dense Skin Layer for Facilitated Biogas Upgrading in Gas-Liquid Membrane Contactor

Y. Xu, X. Li, Y. Lin, C. Malde and R. Wang, *J. Membr. Sci.*, 2019, **585**, 238

A composite hollow fibre membrane with an aminosilane-modified zeolitic imidazolate framework-8 (mZIF-8) based dense skin layer was designed and synthesised. The ZIF-8 nanocrystals were modified by the introduction of (3-aminopropyl)triethoxysilane. This enabled the ZIF-8 nanocrystals to bond with PDMS chains for further hydrophobicity enhancement, with a contact angle of 130° . This was competitive in comparison to the control membrane. The mZIF-8 based composite membrane also demonstrated enhanced biogas upgrading performance and long-term stability. Biogas upgrading performance in gas-liquid membrane contactor applications could be improved by using mZIF-8 based composite hollow fibre membranes.

Hydrogen Production from Sucrose via Aqueous-Phase Reforming

L. I. Godina, H. Heeres, S. Garcia, S. Bennett, S. Poulston and D. Yu. Murzin, *Int. J. Hydrogen Energy*, 2019, **44**, (29), 14605

Hydrogenation and aqueous phase reforming techniques were used to produce hydrogen from commercial sucrose. The aqueous sucrose solution was hydrogenated in a trickle bed reactor over 5 wt% Ru/C to produce a technical sorbitol/

mannitol mixture. The mixture was compared to a commercial sorbitol in aqueous phase reforming over a Pt/C catalyst. The mixtures demonstrated similar selectivity towards the gas-phase products and little difference in the distribution of products retained in the liquid phase. The Pt/C catalysts displayed low efficiency regarding hydrogen production at an industrial level. It is suggested that future work should focus on increasing the amounts of hydrogen generated per mole of converted sugar alcohols.

Crystal Chemistry and Antibacterial Properties of Cupriforous Hydroxyapatite

A. Bhattacharjee, Y. Fang, T. J. N. Hooper, N. L. Kelly, D. Gupta, K. Balani, I. Manna, T. Baikie, P. T. Bishop, T. J. White and J. V. Hanna, *Materials*, 2019, **12**, (11), 1814

Solid-state and wet chemical processing were used to produce copper-doped hydroxyapatite with the composition $\text{Ca}_{10}(\text{PO}_4)_6[\text{Cu}_x(\text{OH})_{2-2x}\text{O}_x]$ ($0.0 \leq x \leq 0.8$). The impact of synthesis route and mode of crystal chemical incorporation of Cu on the antibacterial efficacy against *Escherichia coli* and *Staphylococcus aureus* strains was investigated. Studies revealed that the substitution site of Cu into the hydroxyapatite framework is mainly controlled by the synthesis method and heat treatment process. Finer particle sizes and greater specific surface areas were observed in the wet chemical material, thus leading to superior efficacy. In comparison to undoped hydroxyapatite, Cu-doping increases antibacterial efficiency by 25% to 55%.

A Robust and Precious Metal-Free High Performance Cobalt Fischer-Tropsch Catalyst

P. R. Ellis, D. I. Enache, D. W. James, D. S. Jones and G. J. Kelly, *Nature Catal.*, 2019, **2**, (7), 623

Synthetic transportation fuel production commonly uses slurry-phase Fischer-Tropsch catalysis. However, due to the hydrothermal and mechanical reaction conditions of such processes, the catalyst used is exposed to extreme stress. Therefore, the authors demonstrate the synthesis, characterisation and catalytic performance of a robust cobalt-based Fischer-Tropsch catalyst. An inert alpha alumina support and an appropriate cobalt addition were combined to form a mechanically and hydrothermally stable material, which is easy to reduce without precious metal additives. The material demonstrated excellent selectivity and good activity in slurry-phase testing over 1000 h.

Proton Chelating Ligands Drive Improved Chemical Separations for Rhodium

H. Narita, R. M. Nicolson, R. Motokawa, F. Ito, K. Morisaku, M. Goto, M. Tanaka, W. T. Heller, H. Shiwaku, T. Yaita, R. J. Gordon, J. B. Love, P. A.

Tasker, E. R. Schofield, M. R. Antonio and C. A. Morrison, *Inorg. Chem.*, 2019, **58**, (13), 8720

In comparison to all elements used for technological applications, rhodium extraction has the worst carbon footprint and, unlike other elements, there are also no commercial extractants for Rh. Solvent extraction could improve current practices; however, the chemical separation stage is complicated by the presence of mixed speciation states following acid chloride leaching. Using a variety of experimental and computational techniques, the dianion $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ was shown to transfer to the organic phase in a process involving the formation of an outer-sphere assembly with the diamidoamine reagent *N-n*-hexylbis(*N*-methyl-*N*-*n*-octylethylamide)amine (**Figure 1**). The detailed knowledge gained from this work will be beneficial to the design of Rh extractants and has implications for sustainable metal extraction from both recycling and traditional mining.

High-Selectivity Palladium Catalysts for the Partial Hydrogenation of Alkynes by Gas-Phase Cluster Deposition onto Oxide Powders

P. R. Ellis, C. M. Brown, P. T. Bishop, D. Ievlev, J. Yin, K. Cooke and R. E. Palmer, *Catal. Struct. React.*, 2018, **4**, (2), 1

The bulk and fine chemical industries rely on the selective hydrogenation of alkynes, with good selectivity to the desired product being of particular importance. In this study, a gas-phase cluster deposition method onto conventional support powders was used to prepare palladium catalysts. These catalysts are shown to be as active and selective as those prepared *via* conventional methods such as impregnation. Good selectivity was observed for both support materials used. The catalysts prepared by gas-phase cluster deposition are shown to contain less-active interfacial sites.

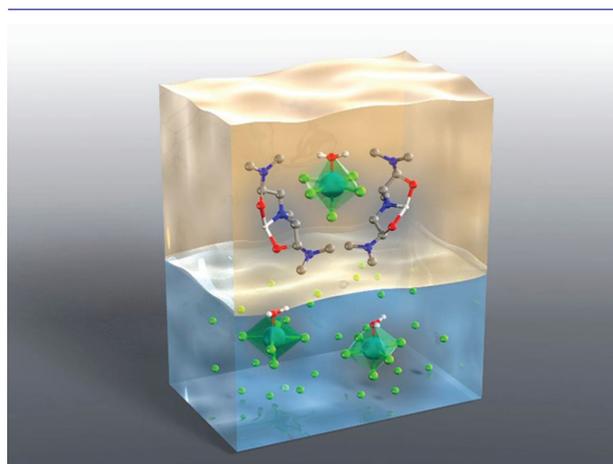


Fig. 1. Reprinted with permission from H. Narita *et al.*, *Inorg. Chem.*, 2019, **58**, (13), 8720. Copyright 2019 American Chemical Society

Low-Temperature Studies of Propene Oligomerization in ZSM-5 by Inelastic Neutron Scattering Spectroscopy

A. P. Hawkins, A. Zachariou, P. Collier, R. A. Ewings, R. F. Howe, S. F. Parker and D. Lennon, *RSC Adv.*, 2019, **9**, (33), 18785

Inelastic neutron scattering (INS) spectroscopy was used to study the reaction between propene and an activated sample of ZSM-5 at 140 K, 293 K and 373 K. The formation of linear alkyl species is observed when propene oligomerises within the zeolite at 293 K, with no evidence to show branched product formation. This selective formation is attributed to confinement within the zeolite pore structure. The reaction at 373 K yielded the same spectrum as that observed at 293 K, suggesting that oligomerisation process is complete at 293 K. The influence of zeolite crystallite size on the product composition in technically relevant olefin oligomerisation reactions was considered.