

Johnson Matthey Highlights

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

Hierarchical Three-Dimensional Fe₃O₄@Porous Carbon Matrix/Graphene Anodes for High Performance Lithium Ion Batteries

S. Hao, B. Zhang, Y. Wang, C. Li, J. Feng, S. Ball, M. Srinivasan, J. Wu and Y. Huang, *Electrochim. Acta*, 2018, **260**, 965

A facile annealing of Mil-53(Fe) templates was used to synthesise a hierarchical 3D Fe₃O₄@porous carbon matrix (PCM) and Fe₃O₄@PCM/graphene and their electrochemical performances were tested as anode materials for Li-ion batteries. The Fe₃O₄@PCM/graphene electrode has a much better cycling performance with a high reversible capacity: up to 1000 mAh g⁻¹ after 500 cycles at 1 C, compared with Fe₃O₄@PCM. This enhanced performance can be attributed to the high conductivity and structure stability given by the special graphene based hierarchical 3D nanostructure.

Total Synthesis of (6 R,10 R,13 R,14 R,16 R,17 R,19 S,20 R,21 R,24 S,25 S,28 S,30 S,32 R,33 R,34 R,36 S,37 S,39 R)-Azaspiracid-3 Reveals Non-Identity with the Natural Product

N. T. Kenton, D. Adu-Ampratwum, A. A. Okumu, Z. Zhang, Y. Chen, S. Nguyen, J. Xu, Y. Ding, P. McCarron, J. Kilcoyne, F. Rise, A. L. Wilkins, C. O. Miles and C. J. Forsyth, *Angew. Chem. Int. Ed.*, 2018, **57**, (3), 805

A late stage Nozaki-Hiyama-Kishi coupling was used to form the C21–C22 bond with the C20 configuration unambiguously created from L-(+)-tartaric acid in a convergent and stereoselective total synthesis of an assigned structure of azaspiracid-3. Postcoupling steps included oxidation to an ynone, an amended Stryker reduction of the alkyne, global deprotection and oxidation of the ensuing C1 primary alcohol to the carboxylic acid. Mass spectrometry showed that there was a match between the synthetic

product and the naturally occurring azaspiracid-3 but there were chromatographic and spectroscopic differences between the two structures.

High Performance Mixed Matrix Membranes (MMMs) Composed of ZIF-94 Filler and 6FDA-DAM Polymer

M. Etxeberria-Benavides, O. David, T. Johnson, M. M. Łozińska, A. Orsi, P. A. Wright, S. Mastel, R. Hillenbrand, F. Kapteijn and J. Gascon, *J. Membrane Sci.*, 2018, **550**, 198

High performance mixed matrix membranes (MMM) comprising ZIF-94 filler and 6FDA-DAM polymer matrix were developed. Mixed gas tests (15CO₂:85N₂) at 25°C and 1–4 bar transmembrane pressure difference were carried out to assess the CO₂/N₂ separation performance. Adding ZIF-94 increased the CO₂ membrane permeability and maintained a constant CO₂/N₂ selectivity of ~22. At 40 wt% ZIF-94 loading the biggest increase in CO₂ permeability was observed, reaching the highest permeability at an equivalent selectivity to 6FDA-DAM MMM in the literature. For the first time non-hazardous solvents (THF and methanol) instead of DMF were used to synthesise ZIF-94 MOF crystals with particle size smaller than 500 nm in a scalable process. SEM, AFM and nanoscale IR imaging by s-SNOM were used to characterise the membranes.

Origin of Phase Inhomogeneity in Lithium Iron Phosphate during Carbon Coating

Y. Liu, J. Wang, J. Liu, M. N. Banis, B. Xiao, A. Lushington, W. Xiao, R. Li, T.-K. Sham, G. Liang and X. Sun, *Nano Energy*, 2018, **45**, 52

A non-conductive Fe₂P₂O₇ phase was found to be formed on LiFePO₄ during the carbon coating process. This phase formation depends on particle size, temperature and annealing atmosphere. The changes were directly linked to the change of the

reducing potential. Improved understanding of the parameters required during carbon coating will help to control the phase purity of carbon coated LiFePO_4 and achieve better electrochemical performance.

The Role of Catalyst Support, Diluent and Co-Catalyst in Chromium-Mediated Heterogeneous Ethylene Trimerisation

M. J. Lamb, D. C. Apperley, M. J. Watson and P. W. Dyer, *Top. Catal.*, 2018, *in press*

Initiator systems for the oligomerisation or polymerisation of ethylene were made by consecutive treatment of an already calcined solid oxide support (SiO_2 , $\gamma\text{-Al}_2\text{O}_3$ or mixed $\text{SiO}_2\text{-Al}_2\text{O}_3$) with solutions of $\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_3$ (0.71 wt% Cr) and a Lewis acidic alkyl Al-based co-catalyst (15 molar equivalents). The impact of the oxide support, calcination temperature, co-catalyst and reaction diluent on both the productivity and selectivity of the immobilised Cr initiator systems were studied. The top performing combination ($\text{SiO}_2\text{-600}$, modified methyl aluminoxane-12 {MMAO-12}, heptane) created a mixture of hexenes (61 wt%, 79% 1-hexene) and polyethylene (16 wt%) with an activity of $2403 \text{ g}_{\text{Cr}}^{-1} \text{ h}^{-1}$. Two competing processes are proposed to explain the results: trimerisation *via* a supported metallacycle-based mechanism and polymerisation through a classical Cossee-Arlman chain-growth pathway.

Using a Freeman FT4 Rheometer and Electrical Capacitance Tomography to Assess Powder Blending

G. Forte, P. J. Clark, Z. Yan, E. H. Stitt and M. Marigo, *Powder Technol.*, 2018, *in press, corrected proof*

A Freeman FT4 powder rheometer and electrical capacitance tomography (ECT) were used to measure the influence of segregation or mixing on flow properties as well as powder mixing and mixedness. Two powders with different properties such as particle size, density, basic flowability and electrical permittivity were used in two different initial arrangements: (a) a heavier, smaller powder at the top which would be expected to mix readily; (b) the inverse which would be expected to resist the axial blending mechanism in the FT4. During 30 cycles of the FT4 impeller passing into and back out of the powder layer, the torque and thus flow energy were tracked. Simultaneous ECT measurements using a two plane sensing system were taken. Mixing was clearly shown for (a) and the absence of blending for (b) using reconstructed tomograms and the basic average permittivity data.

Hydrogenation and Reductive Amination of Aldehydes using Triphos Ruthenium Catalysts

F. Christie, A. Zanotti-Gerosa and D. Grainger, *ChemCatChem*, 2018, **10**, (5), 1012

Triphos- $\text{Ru}(\text{CO})\text{H}_2$, **1**, a stable and accessible Ru dihydride complex, has been found to catalyse aldehyde hydrogenation under neutral conditions. It shows high activity and can be used without solvent. It has good activity at low catalyst loadings for the reductive amination of aldehydes under mildly acidic conditions. Challenging chemoselectivity examples are presented where C-halogen groups, alkene or ketone functionality are not reduced. Improved chemoselectivity and activity are obtained by using the pre-formed complex, **1**, compared to *in situ* formed catalysts from Triphos and $\text{Ru}(\text{acac})_3$ especially at low reaction temperatures.

Microstructural Analysis and Transport Resistances of Low-Platinum-Loaded PEFC Electrodes

F. C. Cetinbas, X. Wang, R. K. Ahluwalia, N. N. Kariuki, R. P. Winarski, Z. Yang, J. Sharman and D. J. Myers, *J. Electrochem. Soc.*, 2017, **164**, (14), F1596

Microstructural characterisation and polarisation data analysis were carried out for PEFC cathodes with low pgm loadings. 3D pore morphology and ionomer distribution were resolved using nano-CT. A model accounts for energy, charge and mass transport and the effect of liquid water flooding. Flooding in the electrode was shown to contribute significantly to transport losses especially at high operating pressures while the pressure-independent resistance at the catalyst surface due to transport through the ionomer film is significant at low temperatures and low catalyst loading. The importance of electrode roughness (electrochemically-active surface area/geometric electrode area) in determining the mass transport losses is also highlighted.

CO Oxidation and Site Speciation for Alloyed Palladium–Platinum Model Catalysts Studied by *in Situ* FTIR Spectroscopy

N. M. Martin, M. Skoglundh, G. Smedler, A. Raj, D. Thompsett, P. Velin, F. J. Martinez-Casado, Z. Matej, O. Balmes and P.-A. Carlsson, *J. Phys. Chem. C*, 2017, **121**, (47), 26321

Transient CO oxidation over a series of bimetallic Pd-Pt catalysts with different Pd:Pt molar ratios was studied using *in situ* FTIR. The catalysts contained both alloyed PdPt nanoparticles with particle sizes 25–35 nm and monometallic Pd nanoparticles below 10 nm. In the absence of O_2 , adsorbed carbonyl species formed on both Pd and Pt. CO adsorbed linearly on top of Pt and in bridged configurations on Pd. It was shown that adding Pd to Pt/ Al_2O_3 shifted the CO-poisoned state to lower temperatures, therefore increasing the temperature range for low-temperature CO oxidation (**Figure 1**).

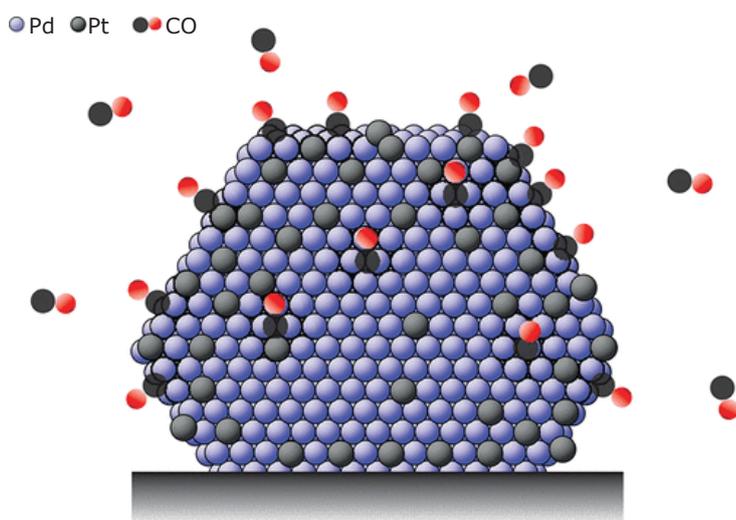


Fig. 1. Reprinted with permission from N. M. Martin, M. Skoglundh, G. Smedler, A. Raj, D. Thompsett, P. Velin, F. J. Martinez-Casado, Z. Matej, O. Balmes and P.-A. Carlsson, *J. Phys. Chem. C*, 2017, **121**, (47), 26321. Copyright 2017 American Chemical Society

Renewable Acrylonitrile Production

E. M. Karp, T. R. Eaton, V. Sánchez i Nogué, V. Vorotnikov, M. J. Bidy, E. C. D. Tan, D. G. Brandner, R. M. Cywar, R. Liu, L. P. Manker, W. E. Michener, M. Gillespy, Z. Skoufa, M. J. Watson, O. S. Fruchey, D. R. Vardon, R. T. Gill, A. D. Bratis and G. T. Beckham, *Science*, 2017, **358**, (6368), 1307

Acrylonitrile (ACN), presently derived from propylene and used as a commodity chemical for the production of plastics and fibres, is a candidate for displacing petroleum feedstocks with biomass. The starting material in this work is 3-hydroxypropionic acid (3-HP) produced *via* microbes from sugars. A TiO₂ catalyst is used to dehydrate and nitrilate using NH₃. Yields are over 90% and could be scaled up to 98%. Hazards are reduced as the process is endothermic and the production of HCN is avoided.

Application of Surrogate Modelling to the Optimisation of Kinetic Parameters in an Emissions Control Catalyst Model Using Vehicle Drive Cycle Data

J. E. Etheridge, G. John and T. C. Watling, *Emission Control Sci. Technol.*, 2017, **3**, (4), 310

Surrogate modelling was used to optimise kinetic parameters in a vehicle emissions control catalyst model using engine or vehicle test data. This approach reduces the time needed for optimisation by reducing the number of evaluations of the

detailed model. It approximates the behaviour of the full model; accuracy is sacrificed for speed of evaluation. A few runs of the detailed model are used to train the initial surrogate, then the surrogate model is used in place of the detailed model with a simplex optimisation method. The kinetic parameters are evaluated with the full model and the surrogate model can be updated with the new information.

A Study of the Soot Combustion Efficiency of an SCR[®] Catalyst vs a CSF During Active Regeneration

L. Cumarantunge, A. Chiffey, J. Stetina, K. McGonigle, G. Repley, A. Lee and S. Chatterjee, *Emission Control Sci. Technol.*, 2017, **3**, (1), 93

A Pt-based catalysed soot filter (CSF) was found to have a significantly higher soot combustion efficiency compared to a Cu-SCR catalyst-coated soot filter (SCR[®] catalyst) under typical active regeneration conditions at 550–600°C. There was sufficient NO₂ production capacity in the CSF and the impact of NO₂ to the overall soot combustion efficiency under active regeneration conditions was significant. It is thought that NO₂ produced *in situ* in the CSF is quickly reacted with soot to drive the thermodynamic equilibrium of the NO oxidation. This leads to significantly higher soot combustion efficiency in the Pt-coated CSF compared to the SCR[®] catalyst or an uncoated filter.