

Johnson Matthey Highlights

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

Exploring Fuel Cell Cathode Materials using *ab initio* High Throughput Calculations and Validation using Carbon Supported Pt Alloy Catalysts

M. Sarwar, J. L. Gavartin, A. Martinez Bonastre, S. Garcia Lopez, D. Thompsett, S. C. Ball, A. Krzystala, G. Goldbeck and S. A. French, *Phys. Chem. Chem. Phys.*, 2020, **22**, (10), 5902

The ORR activity and stability of elements (M) and platinum alloys (Pt₃M) was determined using a combined DFT and experimental approach. Carbon-supported alloy nanoparticles were measured within MEA environments, providing validation for the calculations. The reliability of descriptors and the stability of alloy surfaces under different adsorbate environments was assessed. It was predicted that segregation of M to the surface is likely under an oxygen atmosphere. Correlation was shown between the amount of base metal leached in the C-supported catalysts and the calculation segregation energies. Good correlation was also observed between computed O adsorption energies and ORR activity.

Isotopic Studies for Tracking Biogenic Carbon during Co-processing of Biomass and Vacuum Gas Oil

C. Mukarakate, K. Orton, Y. Kim, S. Dell'Orco, C. A. Farberow, S. Kim, M. J. Watson, R. M. Baldwin and K. A. Magrini, *ACS Sustain. Chem. Eng.*, 2020, **8**, (7), 2652

With the aim of tracking biogenic carbon in FCC units, ¹³C-labelled biomass was co-processed with vacuum gas oil (VGO) in both a Johnson Matthey zeolite catalyst (CP758) and an equilibrium catalyst (E-Cat). Biogenic C was shown to integrate into alkenes and aromatic hydrocarbons in both catalysts. It was also detected in cycloalkanes during experiments with E-Cat, however biogenic C was not observed in linear alkanes. Unexpectedly, small amounts of C from VGO were found in several partially deoxygenated biomass compounds. The work recognises the importance of utilising both biomass- and fossil-derived feeds in catalyst development. It also provides an understanding

of reaction mechanisms for co-processing bio-oil and VGO.

Thermal Runaway of a Li-Ion Battery Studied by Combined ARC and Multi-Length Scale X-ray CT

D. Patel, J. B. Robinson, S. Ball, D. J. L. Brett and P. R. Shearing, *J. Electrochem. Soc.*, 2020, **167**, (9), 090511

The key characteristics of thermal failure in a commercial lithium-ion battery were identified with the use of accelerating rate calorimetry (ARC). The effects of thermal failure on the electrode materials were then analysed using X-ray CT and SEM. Gas generation at elevated temperatures (>200°C) led to mechanical deformations in the cell architecture and the cathode particles reduced in size by a factor of two due to thermal runaway conditions. Surface deposits were detected on both cathode and anode materials. The relationship between heat generation within a cell during failure and electrode microstructure was analysed. The work has implications for the optimisation of electrode designs for safer battery materials.

Sized-Controlled ZIF-8 Nanoparticle Synthesis from Recycled Mother Liquors: Environmental Impact Assessment

M. García-Palacín, J. I. Martínez, L. Paseta, A. Deacon, T. Johnson, M. Malankowska, C. Téllez and J. Coronas, *ACS Sustain. Chem. Eng.*, 2020, **8**, (7), 2973

NaOH or NH₄OH were used to synthesise ZIF-8 nanocrystals from recycled mother liquors (**Figure 1**). Thermal stability, surface area, morphology and crystallinity were investigated. LCA was also implemented to examine the environmental effects associated with the product. The phase purity and nanometre size particles of the obtained ZIF-8 were considered when assessing the suitability of the synthesis methodology through different characterisation methods. The process was deemed sustainable, as the amount of solvent required for washing was significantly lower and phase pure ZIF-8 was obtained.

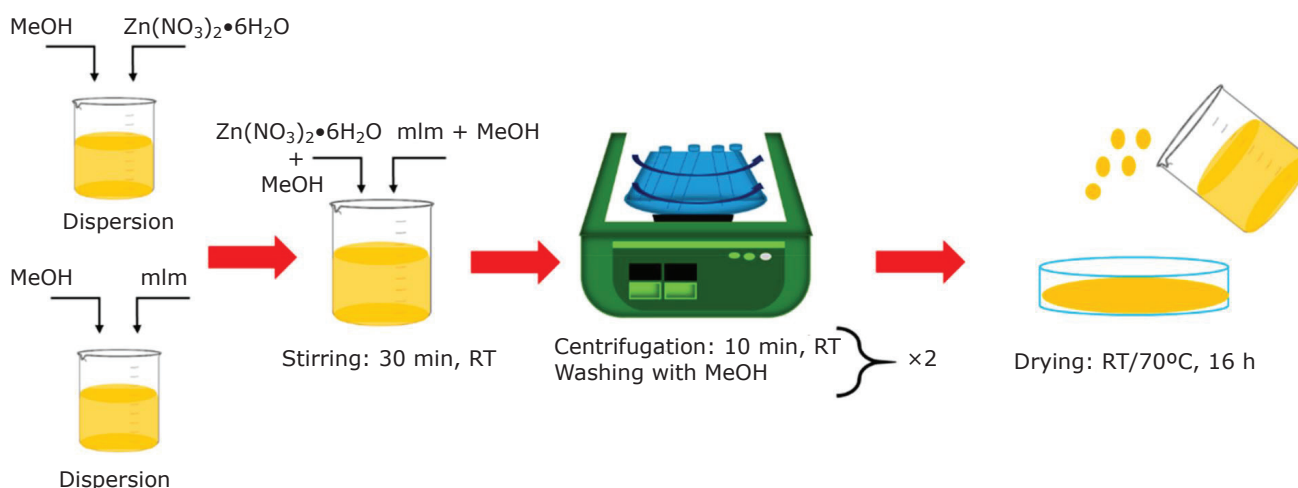


Fig. 1. Synthesis of ZIF-8. Reproduced with permission from M. García-Palacín et al., *ACS Sustain. Chem. Eng.*, 2020, **8**, (7), 2973. Further permissions related to the material should be directed to the ACS

New CCL|MPL Architecture Reducing Interfacial Gaps and Enhancing PEM Fuel Cell Performance

L. Daniel, A. Bonakdarpour, J. Sharman and D. P. Wilkinson, *Fuel Cells*, 2020, **20**, (2), 224

A novel architecture for fuel cell MEAs was presented to enable the reduction of gaps at the cathode catalyst layer (CCL) surface. This was achieved by deposition of the microporous layer (MPL) directly onto the catalyst coated membrane (CCM). Low temperature sintering of the MPL with the CCM was accomplished using a low bonding temperature Teflon. The altered structure improved electronic contact and minimised water pooling at the CCL|MPL interface, thus enhancing PEMFC performance. The water management improvements are of particular importance for thinner CCLs to achieve performance demand with low cathode catalyst loading MEAs.

Numerical and Experimental Studies of Gas Flow in a Particulate Filter

J. D. Cooper, L. Liu, N. P. Ramskill, T. C. Watling, A. P. E. York, E. H. Stitt, A. J. Sederman and L. F. Gladden, *Chem. Eng. Sci.*, 2019, **209**, 115179

Experimental measurements from MRI imaging were used to validate predicted gas flow fields in wall-flow particulate filters from one-dimensional (1D) and 3D numerical models. Through-wall and gas axial velocity were calculated at six flow rates and evaluated against predictions from a recent 1D model and an open source 3D CFD code. The 3D model outperformed the 1D model at high flow rates, however both models demonstrated good agreement at low flow rates. The 3D CFD predictions of gas velocity were validated and the calculated parameters were compared with existing literature correlations. With the correct descriptors, the 1D model velocity predictions were coincident with the 3D CFD predictions.

Investigation of the Oxygen Storage Capacity Behaviour of Three Way Catalysts Using Spatio-Temporal Analysis

C. Coney, C. Hardacre, K. Morgan, N. Artioli, A. P. E. York, P. Millington, A. Kolpin and A. Goguet, *Appl. Catal. B: Environ.*, 2019, **258**, 117918

Temperature profiles and gaseous species inside the channels of a commercial three-way monolith catalyst were investigated with *in situ* spatiotemporal mapping. This was achieved with the development of a transient lean-rich switching method alongside the spatially resolved capillary inlet MS (SpaciMS) technique. Carbon monoxide oxidation was used as a probe reaction. Reaction sequences in the monolith catalyst were clarified by the SpaciMS technique. The 3%Pd/Al₂O₃ catalyst demonstrated excess OSC-like behaviour, something previously unseen. The water gas shift reaction was shown to be insufficient to account for the excess CO conversion. It was hypothesised that, under rich conditions, a Pd(OH)_x surface species was acting in the same way as an oxygen storage component.

Efficient Non-dissociative Activation of Dinitrogen to Ammonia over Lithium-Promoted Ruthenium Nanoparticles at Low Pressure

J. Zheng, F. Liao, S. Wu, G. Jones, T.-Y. Chen, J. Fellowes, T. Sudmeier, I. J. McPherson, I. Wilkinson and S. C. E. Tsang, *Angew. Chem. Int. Ed.*, 2019, **58**, (48), 17335

A suitable catalyst has yet to be developed to decentralise ammonia synthesis for energy storage or fertiliser production without carbon emissions. It is widely known that Ru catalysts are promoted by heavier alkali dopants. However in this study, and despite its poor electron donating ability, Li demonstrated the highest rate through surface

polarisation. Due to this excellent promotion rate, Ru-Li catalysts were shown to be suitable for ammonia synthesis, surpassing industrial Fe counterparts by 195-fold. Further investigations revealed new insights in activating N₂ by metallic catalysts. It was demonstrated that Ru-Li catalysts hydrogenate end-on adsorbed N₂ stabilised by Li⁺ on Ru terrace sites to ammonia in a stepwise manner.

Understanding the Dynamics of Fluorescence Emission during Zeolite Detemplation Using Time Resolved Photoluminescence Spectroscopy

N. Omori, A. G. Greenaway, M. Sarwar, P. Collier, G. Valentini, A. M. Beale and A. Candeo, *J. Phys. Chem. C*, 2020, **124**, (1), 531

Time resolved photoluminescence spectroscopy (TRPS) was used to characterise photoluminescence (PL) arising from synthesised chabazite framework zeolites at three separate phases of the detemplation process. Within a zeolite framework, the steric confinement effects of organic structure directing agents (OSDAs) were demonstrated using temporal resolution. A signature region for determining the presence of the template was established. Gated spectra comparisons between uncalcined and partially calcined zeolites revealed the presence of the template together with template-derived combustion products. TRPS had the capacity to track depletion of OSDA and establish a characteristic PL spectrum for a clean zeolite, and the sensitivity to show residual organic material remained in a zeolite after an extended thermal detemplation process.

Interstitial Boron Atoms in the Palladium Lattice of an Industrial Type of Nanocatalyst: Properties and Structural Modifications

T. Chen, I. Ellis, T. J. N. Hooper, E. Liberti, L. Ye, B. T. W. Lo, C. O'Leary, A. A. Sheader, G. T. Martinez, L. Jones, P.-L. Ho, P. Zhao, J. Cookson, P. T. Bishop, P. Chater, J. V. Hanna, P. Nellist and S. C. E. Tsang, *J. Am. Chem. Soc.*, 2019, **141**, (50), 19616

B atom properties, positions and structural modifications to the Pd lattice of an industrial interstitial B doped Pd nanoparticle catalyst system were studied using a combination of techniques. Short-range disorder was introduced with B incorporation into the Pd lattice, however the overall fcc lattice was maintained. Different types of structural disorder and strain were shown to

be introduced into the nanoparticle history, and these distortions contributed to the appearance of local HCP structured material in localised regions. The characterisation of industrial metal nanocatalysts provides important guidance to the structure-activity relationship of the system and this was achieved by using new toolsets across length scales from macro- to microanalysis.

Electrochemical Measurement of Intrinsic Oxygen Reduction Reaction Activity at High Current Densities as a Function of Particle Size for Pt_{4-x}Co_x/C (x = 0, 1, 3) Catalysts

C. Zalitis, A. Kucernak, X. Lin and J. Sharman, *ACS Catal.*, 2020, **10**, (7), 4361

The performance of a range of catalysts with the initial composition Pt_{4-x}Co_x/C was compared using a newly developed electrochemical technique. The current densities for the Pt/C catalysts were shown to increase by up to 80-fold when moving from the typical 0.9 V to 0.65 V. As demonstrated using a kinetic model, at low current densities (~0.9 V vs. RHE) the dealloyed catalysts had greater mass activity while at high current densities (~0.65 V vs. RHE) they were no longer as active as 2.1 nm particle Pt catalysts. The study predicted that a catalyst composed of 3.8 nm CoPt@Pt_{1ML} particles at 0.65 V would have optimum mass activity performance.

Spatially-Resolved Investigation of the Water Inhibition of Methane Oxidation Over Palladium

C. Coney, C. Stere, P. Millington, A. Raj, S. Wilkinson, M. Caracotsios, G. McCullough, C. Hardacre, K. Morgan, D. Thompsett and A. Goguet, *Catal. Sci. Technol.*, 2020, **10**, (6), 1858

SpaciMS and steady state furnace temperatures of 400–450°C were used to assess the spatial effects of temperature and 0–10% H₂O feed concentrations on complete methane oxidation reactions on a 3%Pd/Al₂O₃ wash-coated monolith. Within a central monolith channel, 12 sets of experimental profiles were obtained and used to screen a series of postulated global kinetic models. With the aim of improving confidence in parameter estimation, a 1D heterogenous single channel reactor model was incorporated. A number of global kinetic models were hypothesised and the Akaike information criterion (AIC) was used to differentiate between them. The best statistical fit was a newly derived two site model.