# Solving the Energy Waste Roadblock

The burning of coal and gas for electricity generation is the major contribution to the rapidly increasing concentration of carbon dioxide ($CO_2$) in our atmosphere, constituting globally the most significant waste product from the production of energy. The effects of this atmospheric change are well established, but technologies for reducing our dependence on fossil fuels have not been developed rapidly enough to avoid very significant changes to our climate and oceans. Economic methods for capturing, storing and using $CO_2$ need to be identified and explored.

**This project addressed two distinct challenges:**

1. The exhaust gas from a coal- or gas-burning power station is a mixture of many gaseous and solid components. Separation of $CO_2$ from other gasses is energy intensive and a major obstacle to the commercial use of 'carbon capture' technologies. Development of new materials to carry out this separation efficiently is critical to the cost-effective application of this method.
2. Separated $CO_2$ is generally regarded as a waste product to be disposed of underground. However, the availability of alternate energy sources and clever catalytic chemistry may allow waste $CO_2$ to be converted into useful products, either as an energy carrier (eg methane, ethanol) or as a chemical feedstock (eg acetic acid).

We focused on a particular 'family' of materials known as "metal-organic frameworks" – MOFs, which has emerged in the past two decades as a highly promising source of functional materials for a very wide range of applications. MOFs are composed of metal atoms bridged by organic molecules in a highly porous network or scaffold. Having a known, regular and modular structure at a molecular level gives chemists an unprecedented opportunity to tailor and understand the properties of these materials. Two of their most promising areas of application are in separation of gases and in catalysis.

We assembled a highly multidisciplinary research team of 19 lead researchers from seven institutions: The University of Sydney, The University of Melbourne, Monash University, The University of New South Wales, The University of Adelaide, CSIRO and ANSTO. The team brought together synthetic chemists experienced in materials design and preparation, theoretical chemists able to model and predict gas interactions at the molecular scale, and chemical engineers who are fabricating membranes and designing scale-up strategies for pilot plants. This depth of expertise was augmented by a dozen early-career researchers and over 20 postgraduate research students. We also partnered with major national facilities at ANSTO and the Australian Synchrotron to measure and characterise the structure and properties of our materials.

After four years of collaborative research, we now have a very substantial library of candidate materials, the capacity to produce some of these at kilogram scale, and world-leading expertise in incorporating MOFs into separation membranes. We have developed a number of successful strategies for the design and synthesis of porous MOFs for separation, and these strategies have been refined and extended to optimise materials performance.

For a decade a persistent challenge to scientists in this field has been effectively scaling-up synthesis of MOFs from milligram and gram scale in the laboratory, to kilogram and tonne scales required by

industry. Over the course of this project CSIRO has become a world-leader in this field, having developed a flow reactor capable of producing many kilograms per hour, and leading to a spin-off company MOFWORX.

The most promising gas separation technology in which to use MOFs was identified to be mixedmatrix membranes, in which nano-sized particles of the active material are incorporated into very thin polymer membranes. We started with proof-of concept flat membranes at the laboratory scale, which have been thoroughly characterised for their separation properties and resistance to the various toxic and corrosive gasses found in flue gas. We continued on to more complex membranes suited to industrial-scale separations: hollow-fibre membranes, and spiral wound membranes.

Very substantial contributions have also been made to the fundamental science of MOFs and related materials, indicated by over 85 refereed publications over 4 years, many in leading journals. Particular advances were made in understanding the interactions and behaviour of carbon dioxide molecules within the pores of MOF materials, using both advanced structural studies and computational modelling. This body of work supports ongoing international research in this field.

The catalysis of $CO_2$ to form higher-value products is an internationally active field of research. For the first time we have established a materials design approach to incorporate known catalytic complexes into open-framework MOF-type materials. Distinct families of catalytic materials were designed and tested for photocatalytic, electrocatalytic and more conventional gas-phase systems, each leading to advances in the field. The structural complexity required to incorporate active sites led to reduced stability, but work is continuing in this challenging area. In a further advance we found that when the pores in certain MOFs are loaded with catalytically active metal salts and heated, they decompose to form very active nano-structured catalytic materials, which perform considerably better in gas phase reduction of $CO_2$ than commercial catalysts.

Our Industry Advisory Board and existing relationships with commercial partners helped direct our goals towards commercial applications. While the bulk of our outcomes have support the fundamental science and developed the broad platform technology of open framework materials, several patents have been or are in the processes of being filed, and we anticipate the first commercial products will begin to emerge within 18 months, initially in niche applications.