

Porous Organic Polymer and its Composites for Electrocatalysis

(Electro Organic and Materials Electrochemistry Division, CSIR-Central Electrochemical Research Institute, India) ○Kathiresan Murugavel

Keywords: Porous Organic Polymers; Electrocatalysis; Water Splitting; Covalent Triazine Frameworks; Electrochemistry

Porous organic polymers (POPs) can be conveniently engineered and produced at the molecular level, known for their high surface area and ample porosity. The POPs have confined molecular spaces for photons, excitons, electrons and holes to interact, thereby providing great catalysis ability. Porous organic polymers can be further classified based on the monomeric repeating units such as triazine based POPs, etc. Among various types, triazine based porous organic polymers exhibit excellent chemical and thermal stability due to which they find numerous applications in chemical catalysis and electrocatalysis. Electrocatalysis highly relies on the ionic/electrical conductivity of a material and in this regard, bare POP sometimes lacks such essential characteristics. There are numerous strategies followed to improve the conductivity of POPs and they include composite formation, metal doping, carbonization, etc. Although these methods are very convenient, carbonization is usually adopted over composite formation. Latest studies have further shown that carbonization of doped porous organic polymers (POPs) with heteroatoms is an effective strategy to develop highly efficient 'N' and other heteroatom doped electrocatalysts. Simple carbonization of triazine/amine porous organic polymers yield N-doped amorphous carbon, which shows excellent electrocatalytic properties towards electrocarboxylation, hydrogen and oxygen evolution reactions. In addition, metal ions can be anchored onto the triazine/amine based POP via co-ordination or metal nanoparticles can also be anchored over the POP substrate. Carbonization of such derivatives typically yields metal oxide decorated N-doped porous carbon, and in most cases these materials [combining the best activity of both (metal oxide and porous carbon)] show better catalytic effect than their parent material.

Electrocatalytic activities of polymeric material towards water-splitting reactions, and electrocarboxylation is important as they form basis for fuel-cell applications and CO₂ utilisation respectively. Especially the organic-inorganic hybrid (metal anchored POP) with excellent long-term stability (acidic as well as basic conditions) and on par performance with that of benchmark noble metal water-splitting catalysts grasps industrial importance when it comes to large scale fuel cell applications. On the other hand, conversion of CO₂ to useful products is an efficient way to mitigate greenhouse gas (global warming). In this regard, indirect electrochemical reduction of CO₂ to useful organic products offers excellent route for the synthesis of fine chemicals and pharmaceutically important intermediates. In the case of indirect electrochemical reduction, the first one electron reduction is carried out over an organic substrate such as alkyl/aryl halides, aldehydes or ketones, alkenes.

Reduction of these substrates generates a radical species which is then coupled to CO₂ and subsequent one electron reduction yields corresponding carboxylate anion. Acidic work-up of this then yields the desired product. In this talk, we will focus on the various methods of preparation of POP based electrocatalysts, and further focus will be on their application towards water-splitting applications and CO₂ utilization. Although POP based catalysts exhibit excellent catalytic activities towards conversion of CO₂ to value added products, there are certain bottlenecks that hamper their efficiency such as moisture content, use of sacrificial anodes, etc. The talk will also focus on such bottlenecks.

