

Electrocatalytic Conversion of Inert Inorganic Molecules: Oxygen, Carbon Dioxide and Dinitrogen

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There has been growing interest in the environmentally friendly alternative energy sources and methods of formation of fuels and utility chemicals. In this respect, low-temperature electrochemical approaches comprising modern fuel cell technology, electrolytic methods, that include conventional and visible-light-induced photoelectrochemical systems, seem to be very promising. With reference to hydrogen-oxygen fuel cells special attention has been paid to development of both noble-metal-free and low-platinum-content electrocatalytic materials for the efficient oxygen reduction with the ultimate goal of lowering formation of undesirable H_2O_2 intermediate. The progress in this subject is greatly hindered by the high cost and scarcity of the state-of-the-art platinum-based materials which are regarded as the most effective cathode catalysts. An important strategy addressed here is hybridization, activation, and stabilization of carbon-supported low-content Pt-catalysts by functionalization with certain nanostructured or substoichiometric metal oxides (e.g., CeO_x or $\text{H}_x\text{WO}_{3-y}$), both in simple or mixed forms. Among important issues are not only improvement of the catalysts' performance and ability to decompose undesirable hydrogen peroxide intermediate, but also the need to increase their stability.

Regarding the continuously rising levels of atmospheric carbon dioxide, the development of advanced technologies permitting the CO_2 utilization is highly desirable. In principle, conventional electrocatalytic and visible-light-induced photoelectrochemical approaches are well-suited for the reduction of carbon dioxide and possible generation of carbon-based fuels or chemicals. But electroreduction of CO_2 requires large overpotentials and suffers from the competitive hydrogen evolution. To overcome the problem, highly specific and selective catalysts would be required to drive effectively conversion (reduction) of carbon dioxide (and water) into fuels, syn-gas or utility chemicals. Having in mind our recent electrocatalytic results with copper-substituted polytungstates (or polyoxometallate-network-stabilized copper oxo assemblies) and regarding successful utilization of the Cu_2O films over-coated with WO_3 nanowires for both electrochemical and photoelectrochemical reduction of carbon dioxide in near-neutral media, we have pursued research along this line and proposed a hybrid catalytic system composed of copper sites immobilized in tungsten(VI) oxide nanostructures exhibiting improved high selectivity toward CO_2 -reduction relative to the competitive hydrogen evolution in acid medium ($0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$).

Formation of ammonia is one of the most important chemical synthetic processes. Under industrial conditions, ammonia is primarily been synthesized from nitrogen and hydrogen via the Haber-Bosch process which requires pressurizing and heating, despite utilization of catalysts. Consequently, development of low-temperature synthetic methodology is tempting both from the practical and fundamental reasons. An ultimate goal for electrochemistry is to generate NH_3 from N_2 at temperatures lower than 100°C , atmospheric pressure, and with use of new generation of catalysts. Currently, most of electrochemical approaches to drive N_2 -fixation suffer from slow kinetics due to the difficulty of achieving the appropriate adsorption and activation of dinitrogen molecule leading to cleavage of the strong triple $\text{N}\equiv\text{N}$ bond. Our recent studies, clearly demonstrate that coordinatively stabilized iron catalytic sites, e.g. iron-centered heme-type porphyrins or iron phosphide, FeP and Fe_2P phases, have been found to act as efficient catalysts for the formation of NH_3 in alkaline and semi-neutral media.

Development of durable, specific and reasonably efficient low-cost catalysts for electroreduction of O_2 , CO_2 and O_2 remains a great challenge for electrochemical science and technology. Present trends and future possibilities will be addressed.