OBJECTIVE

Among the different types of fuel cells direct methanol fuel cells (DMFCs) are recognized to be a promising power source for portable electronic devices and electric vehicles. Methanol is an efficient fuel, due to its low molecular weight, simplest structure, and very high energy density \((6.1 \text{ kWh kg}^{-1})\) and can be obtained from natural gas, coal and biomass. However, commercialization of these fuel cells has been facing serious difficulties due to sluggish kinetics of the ORR and MOR and crossover of the methanol molecule from the anode to cathode through polymer electrolyte membrane. Pt-based metals and alloys are the most active electrocatalysts for both MOR and ORR in acid/alkaline solutions. But, its high cost, limited resource and poisoning by the methanol oxidation intermediates, particularly by CO molecule do not allow it to be used at commercial level. So, considerable interest has been shown during recent years toward development of suitable electrode materials which can be used as efficient anodes (methanol oxidation) and cathodes (oxygen reduction) in DMFCs involving alkaline or acidic electrolytes and, at the same time, they are low cost, more poisoning tolerant and stable than Pt.

Efforts have been made in search of efficient and robust catalysts based on abundant non-Pt metals, catalytic activities of which toward the MOR/ORR are comparable to or greater than Pt. To improve the kinetics of MOR and increase the range of metals other than Pt as catalysts, the study of electrocatalysis of the MOR is recently resorted to in alkaline solutions. Among non-Pt metal catalysts investigated, Pd is considered as an efficient and a potential substitute for Pt. Also, Pd exhibits inert behavior towards alcohol oxidation in acidic medium (like \(\text{H}_2\text{SO}_4\)) so it can be used as methanol tolerant cathode materials also. One of the ways for improving the electrode kinetics of the MOR as well as ORR in DMFCs is to use the Pd-based alloys/composites in highly dispersed form on high surface area substrates. For the purpose, different carbon materials such as carbon nanopowder (NC), carbon nanofibers, multiwalled carbon nanotubes (MWCNTs) and graphene nano sheets (GNSs) have been used as support materials.
It is known that transition metal mixed oxides in alkaline solution produce surface adsorbed OH radical from the electrochemical discharge of OH⁻ ion under anodic potential conditions. The adsorbed OH radical, so obtained, might promote the dehydrogenation of adsorbed alcohol and also oxidation of CO into CO₂. Considering these facts, novel hybrids comprising of Palladium, Graphene and a mixed valence spinel oxide have been synthesized and investigated as bifunctional catalysts for methanol electrooxidation and oxygen electroreduction in 1M KOH at 25°C. Transition metal mixed oxides chosen for the study were MCo₃O₄ (M=Mn, Co, Ni) and MMn₂O₄ (M=Mn, Co, Fe, Cu). The purpose of using complex oxide as ingredient in the hybrid catalysts has been to increase the concentration of OH⁻/OH radical on the catalyst surface so as to reduce the CO poisoning effect and enhance the methanol oxidation. In fact, the addition of a controlled amount of an oxide into the Pd/GNS matrix greatly improved the poisoning tolerance, stability and also electrocatalytic activity of the catalyst both for MOR and ORR in 1M KOH greatly.

All novel hybrid catalysts have been characterized by X-ray diffraction, Transmission electron microscopy, X-ray photoelectron spectroscopy, Cyclic voltammetry, Linear sweep voltammetry, CO stripping voltammetry and Chronoamperometry. Detailed results obtained are presented and discussed in the present dissertation.