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Chemical Technology

Development of bi-metal catalysts for the oxygen reduction in the PEM fuel cell

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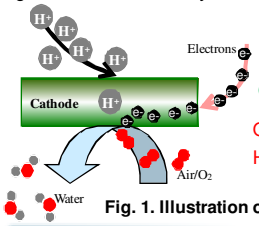
Introduction and motivation

Despite the large and growing interest of polymer electrolyte membrane fuel cell (PEMFC) as an energy converter, high cost, relatively insufficient activity and long-term stability of the catalyst materials remain major obstacles for commercialization. Platinum is still considered as the state-of-art for catalyst material in PEMFC. However, it exhibits a slow kinetics for oxygen reduction reaction (ORR) [1] that is mostly due to the strong bond of the oxygen molecules. Meanwhile, bi-metal catalyst such as PtNi, PtCo, PtFe have shown higher activity for ORR compared to Pt also in presence of methanol [2] The incorporation of transition metal alters the electronic d-band structure of Pt (ligand effect) and the Pt-Pt bond distance (compressive/tensile strain) that in some cases leads to a decrease of adsorption energy of oxygen molecule and consequently to higher activity for ORR. The ORR activity of the Pt alloy is also dependent on the type, concentrations of the second metal in the subsurface atomic layer [3]. A suitable bi-metal alloy should favor the "four electron" reduction step of oxygen as shown in the eq. (1). However, eq. (2) involves H_2O_2 intermediates step that is an unfavorable scenario for the catalyst and membrane. Therefore, we aims to explore various combination of second metals to form alloy of high active fuel cell catalysts.



The possible number of electrons involves on the oxygen reduction reaction (ORR) process:

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ($E^o = 1.229$ V) --- eq. 1

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ ($E^o = 0.695$ V)
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ ($E^o = 1.77$ V) --- eq. 2

Fig. 1. Illustration of oxygen reduction reaction (ORR) at platinum

Objectives

This project aims at the development of bi-metal Pt catalyst for the middle temperature fuel cell (100-150 °C, PEMFC and DMFC) cathode together with the research group of Prof. Dr. F. Schüth, Max-Planck-Institute in Mülheim. This project is part of an AiF/DFG cluster project.

The individual tasks of this project are:

KWI: Synthesis of high active Pt based bi-metal alloy with early and late transition metal elements • Optimization of carbon supported catalyst structure, particle size, dispersion, composition, stability through physicochemical characterization, electrochemical (rotating (ring) disk electrode - RDE/RRDE) and fuel cell testing • Investigation of new catalyst architecture (Core-Shell) • Study of influence on the thermal treatment.

MPI: Synthesis of high graphitized carbon supports alternative to Vulcan carbon (hollow spheres) • The encapsulation of the catalytic metals within the hallow spheres • Estimation of the physical shape, size, structure and chemical compositions.

Supply of high active catalysts for the cluster partners (TP3 & TP4)

Experimental

The Pt and Pt-M alloy catalysts, (M = Au, Cu, Ni, Co, Cr, V) were prepared by a conventional impregnation–formaldehyde (CH_3OH) reduction under reflux conditions. The experimental steps and conditions are shown in the flow chart (Fig. 2). The atomic weight ratio of the bi-metal Pt:M alloy was fixed to 60:40. In all cases, the total metal loading on carbon support was fixed to 20 wt.%. The thermal treatment was carried out in 10% H_2/Ar gas mixture at 10 ml min^{-1} flow rate.

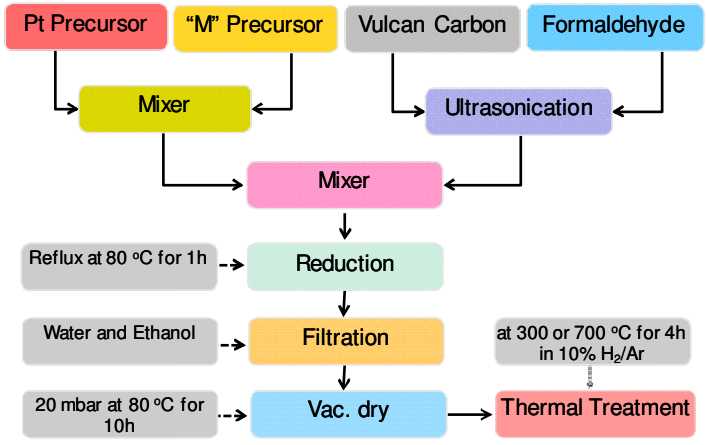


Fig. 2. A flow diagram of pre- and post-treatments on the bi-metallic catalysts preparation

Catalyst characterization

The amount of reduced metal was estimated on each bi-metal catalyst by thermo gravimetry (TGA) weight loss method. Figure 3 illustrates the TGA results and measurement conditions. Face-centered cubic (fcc) solid solution of alloy catalysts was revealed by XRD (Fig. 4). In the case of Pt-Au and Pt-Cu alloy, the Bragg reflection shifts to the left and right angles, respectively indicating that the changes in Pt atomic lattice strain is due to the incorporation of higher (Au) and lower (Cu) radii transition metal elements, respectively.

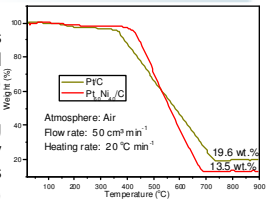


Fig. 3. Estimation of metal loading by TGA weight loss

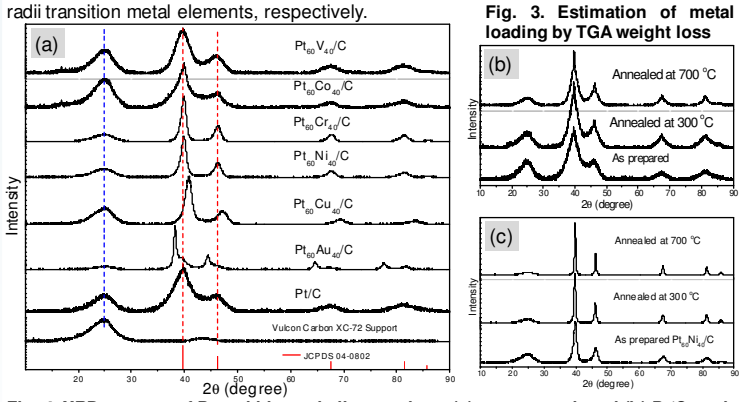


Fig. 4. XRD patterns of Pt and bi-metal alloy catalysts (a) as prepared; and (b) Pt/C, and (c) $Pt_{60}Ni_{40}$/C after annealing at 300 and 700 °C in H_2/Ar atm

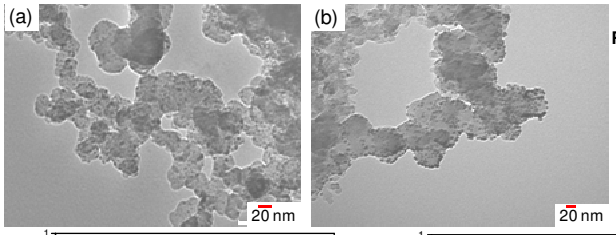


Fig. 5. Representative TEM image of (a) 3-5 nm Pt, and (b) 10-15 nm Pt-Ni particles deposited on the carbon support

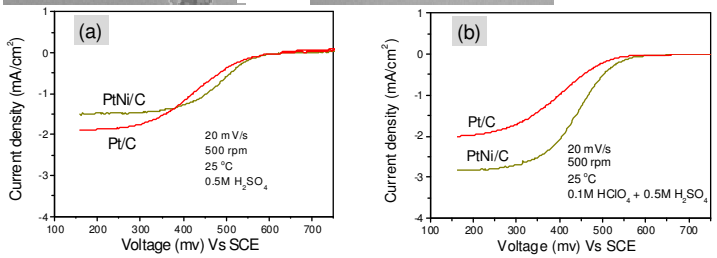


Fig. 6. The RDE results on Pt/C and $Pt_{60}Ni_{40}$/C catalyst with (a) 0.5 M H_2SO_4, (b) 0.1 M $HClO_4$ + 0.5 M H_2SO_4

The voltammogramm of ORR at $Pt_{60}Ni_{40}$/C clearly shows about 70 mV less overpotential at 50 $mAcm^{-2}$ compared to that of pure platinum catalyst in a perchloric acid containing electrolyte solution.

Summary and outlook

A series of Pt based nano alloys were formed by metal precursors reduction in formaldehyde. Pt based alloys phase formation was confirmed by XRD. A nominal yield of metal reduction between 68 to 99% was achieved from the formaldehyde method. Thermal treatments catalysts obviously increase the particle size that is evidenced from reduction on the diffraction peak width. A homogenous distribution of the Pt-Ni alloy nano particles were observed by TEM investigations. Electrochemical measurements reveal a higher activity of Pt-Ni for ORR compared to that of pure Pt.

Further works:

- The other method/reductant will be conducted to synthesize the bi-metal alloys and their performances will be compared with these results
- Influence of the thermal treatment of Pt-M on ORR activity and chemical stability
- Alternative support materials (supplied by MPI) will be tested
- Ultimately, the activity of alloy catalyst for ORR will be tested in a gas diffusion electrode (GDE) cell

Literature

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