

Manufacturing and stabilization of PtCo/C cocatalysts for PEM Fuel Cells

Christoph Grimmer¹, Alexander Schenk¹, Birgit Pichler¹,
Markus Perchthaler², Viktor Hacker¹

¹Graz University of Technology
Inffeldgasse 25/II/C, 8010 Graz, Austria

²elcomax GmbH
Bayerwaldstraße 3, 81737 Munich, Germany

The usage of platinum as electrocatalyst is responsible for approx. 30 % of the manufacturing costs of the proton exchange membrane fuel cell (PEMFC) [1]. Reducing the platinum loading, especially on the cathode side, is therefore crucial for this promising technology to be commercially successful. One strategy of increasing the activity towards the oxygen reduction reaction (ORR) and reducing the platinum loading is the appropriate combination of platinum with first row transition metals such as Fe, Ti, Ni, Fe or Co [2]. To date these new materials are not utilized in PEMFCs because of insufficient stability and missing big scale manufacturing processes. In this paper we present a straightforward and scalable PtCo/C cocatalyst preparation method with stability increasing post-preparation treatments.

Platinum cobalt cocatalysts supported on high surface carbon (PtCo/C) were prepared by impregnation of gas diffusion electrode (GDE) sheets with a precursor solution containing hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), nonionic surfactants, a mixture of 2-propanol and ultrapure water as solvent and ethylene glycol as reducing agent. After a short drying step the reduction was initiated by a mild thermal treatment in inert atmosphere. Post-preparation treatments with activity and stability increasing effect were performed (see Figure 1) [3]. By acid leaching and annealing steps and combinations of both the activity as well as the stability could be increased significantly.

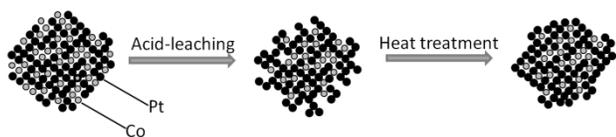


Figure 1. Proposed mechanism of post-preparation treatment

For electrochemical ex-situ characterization 2 cm² of the GDE are suspended in 2-propanol and treated with an ultrasonic bath to form a homogeneously dispersion. A defined aliquot of this dispersion is dispensed on the glassy carbon rotating disk electrode (RDE). A standard 3-electrode-configuration, perchloric acid as electrolyte and a reversible hydrogen electrode (RHE) are used. The activity towards the ORR in terms of specific activity (mA/cm²) and mass activity (A/mg Pt) is measured by cyclic voltammetry in the potential range of 0.050 and 1.055 V_{RHE} in oxygen saturated electrolyte at a rotating speed of 1600 rpm.

In order to determine and compare the stability of the prepared PtCo/C cocatalysts to standard Pt/C catalysts an accelerated stress test (AST) protocol was defined. The working electrode is cycled between 0.5 and

1.4 V_{RHE} at a scan rate of 500 mV s⁻¹ in nitrogen saturated electrolyte. Each 555 cycles the loss of electrochemical active surface area (ECSA) is determined.

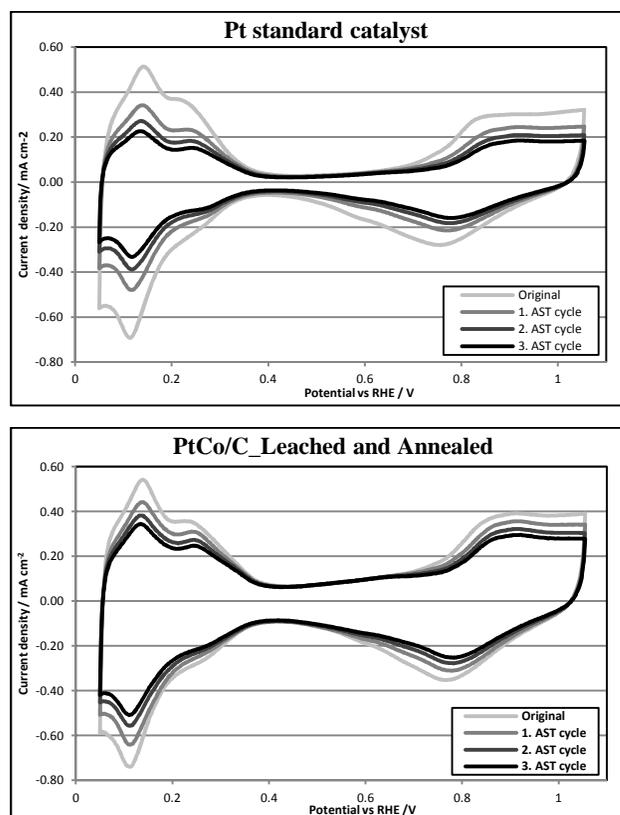


Figure 2. CV results of a Pt/C standard catalyst and a stabilized PtCo/C cocatalyst with a stoichiometric ratio of Pt:Co 1:5.

Table 1. ECSA results during ASTs.

	Pt/C		PtCo/C	
	ECSA cm ² /mg	Loss %	ECSA cm ² /mg	Loss %
Original	303		337	
1. AST cycle	193	36	302	11
2. AST cycle	149	51	261	22
3. AST cycle	120	61	234	31

Figure 2 and Table 1 show the effect of the post-preparation treatment on PtCo/C cocatalysts. Compared to Pt/C standard electrocatalysts and to non-treated PtCo/C catalysts the loss of ECSA during ASTs decreased by approx. 50 %.

[1] B. Fang, B.N. Wanjala, J. Yin, R. Loukrakpam, J. Luo, X. Hu, J. Last, C.-J. Zhong, International Journal of Hydrogen Energy 37 (2012) 4627.

[2] V.R. Stamenkovic, B.S. Mun, M. Arenz, K.J.J. Mayrhofer, C. a Lucas, G. Wang, P.N. Ross, N.M. Markovic, Nature Materials 6 (2007) 241.

[3] A. Schenk, C. Grimmer, M. Perchthaler, A. Stadlhofer, V. Hacker, 63rd Annual Meeting of the International Society of Electrochemistry. Prague, Czech Republic at: 21.08.2012.