

Alternative supports for PEM Fuel Cell Catalysts

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Abstract

Carbon corrosion is one of the main issues in the development of degradation resistant high surface area catalysts for PEM (Polymer Electrolyte Membrane) fuel cells. In this work, new corrosion resistant substrates, like TiO₂ and TiOC, were tested as possible alternatives to Carbon. The use of a colloidal method to synthesize the catalyst enables us to use the same preparation procedure for all catalysts, independent of the substrate. We obtained a high Pt dispersion on TiOC supports - comparable to commercial Pt/C, whereas on TiO₂ substrates the electrochemically active surface area (ECSA) proved to be ten times smaller than for the TiOC substrate. This result might be interpreted due to a reduced conductivity of the support, leading to a lower Pt loading on the support. By using TEM in combination with ECSA measurements, the favorable dispersion of Pt on the TiOC support has been demonstrated. Oxygen reduction reaction (ORR) activities have been measured in 0.1M HClO₄ showing a specific activity (mA/m²_{Pt}) and mass activity (A/g_{Pt}) comparable to commercial available Pt/C. The corrosion resistant behavior of Pt/TiOC has been tested in a half-cell setup and compared with standard Pt/EC300 catalyst with equivalent ECSA and the same particle size.

Introduction & Experimental

Carbon corrosion

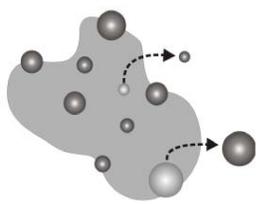


Significance in PEM fuel cell applications:

- Cathode carbon corrosion (start-stop potential cycles)
- Anode carbon corrosion (fuel H₂ starvation)

Consequences:

- Detachment of Pt NPs from the support material
→ electro-active surface area loss



Development of a corrosion resistant support for Pt nanoparticles

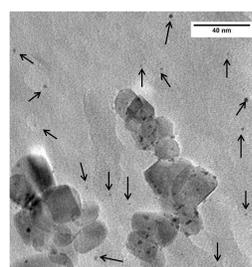
Application of TiO₂ and its carbon doped species as alternative substrate for Pt

- Synthesis
 - Heat treatment (HT) of TiO₂ in acetylene
 - Pt nanoparticles synthesis via ethylene glycol method, and physical deposition on the support material (C-EC300, TiO₂ and TiOC).
- Physical characterization
 - TEM validation of the particles size distribution and morphology
 - BET of the HT powder 14m²g⁻¹
- Electro-catalytic and Electrochemical characterization
 - Determination of the Specific and Mass Activity of the diverse systems (Pt/EC300, Pt/TiO₂ and Pt/TiOC) on the Oxygen Reduction Reaction (ORR)
 - Accelerated Stress Test (AST) treatments
 - Cyclic-voltammetry, 0.4-1.4V_{RHE} rate 500mVs⁻¹ 3600cv
 - Cyclic-voltammetry 1-1.5V_{RHE} rate 500mVs⁻¹ 12000cv
 - Potential steps 0.6-1V_{RHE}, holding time 3s-3s

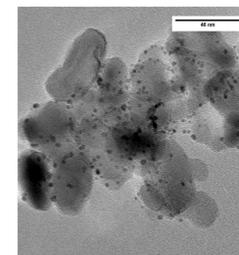
TEM characterization

10%Pt/TiO₂

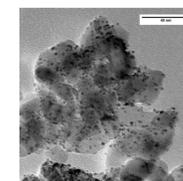
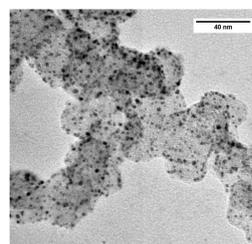
- Unsupported Pt NPs on the TEM grid



5%Pt/TiOC

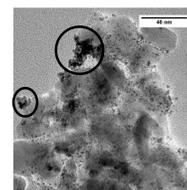


30%Pt/EC300



10%Pt/TiOC

- First signs of agglomeration



Electrocatalytic Activity

Cyclic-voltammetry of Pt/EC300 and Pt/TiOC

- Comparable pseudo capacitive currents
- Characteristic features of Pt NPs on both systems

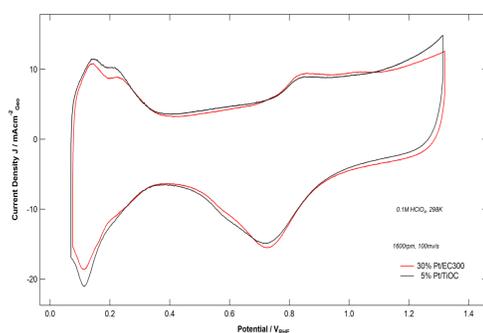


Table 1. Specific and Mass Activities

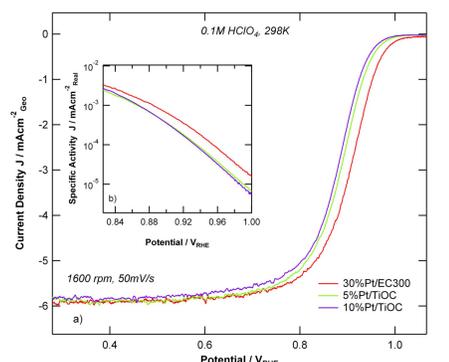
Catalyst	Rf	*ECSA (m ² g ⁻¹)	<i>i</i> _s (0.5V) (mAcm ⁻² _{Pt})	<i>i</i> _m (0.5V) (A/mg _{Pt})
30%Pt/EC300 720m ² g ⁻¹	11	80	0.54	0.9
10%Pt/TiO ₂ 50m ² g ⁻¹	2.3	17	0.33	0.024
10%Pt/TiOC 14m ² g ⁻¹	8.5	61	0.385	0.39
5%Pt/TiOC 14m ² g ⁻¹	10.8	78	0.39	0.64

Electro-catalytic behaviour

- Comparable ESCA for 30%Pt/EC300 and 5%Pt/TiOC
- Lower ECSA for 10%Pt/TiO₂
 - Pt NPs less likely stick on the TiO₂ support
 - The semiconducting nature of the support plays a rate limiting role on the electron transfer process
- 10%Pt/TiOC lower ECSA, first signs of agglomeration

ORR activity

- Comparable behaviour for all the measured systems
- Pt/TiOC slightly less active
- No strong kinetic hindrance for Pt/TiOC
- Tafel-plot shows the same reaction pathway for all the investigated systems

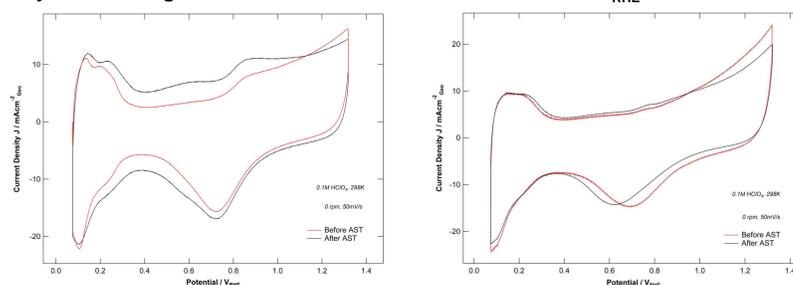


Degradation Studies: Accelerated Stress Test (AST) Treatments

Table 2. Summary of the ECSA loss, determined by CO stripping, of the respective catalyst due to the AST treatment

Catalyst	AST treatment	Pt wt% loading	Initial ECSA (m ² /g)	ECSA after deg (m ² /g)	% area loss
Pt/EC300	0.4-1.4V _{RHE} 500mVs ⁻¹ 3600cv	30%	83.5	32.4	61.2
Pt/TiOC	0.4-1.4V _{RHE} 500mVs ⁻¹ 3600cv	5%	92.6	50	46
Pt/EC300	1-1.5V _{RHE} 500mVs ⁻¹ 12000cv	30%	79.4	64.4	18.7
Pt/TiOC	1-1.5V _{RHE} 500mVs ⁻¹ 12000cv	5%	81.1	75	7.5
Pt/EC300	0.6-1V _{RHE} 3s-3s 9000cv	30%	84.4	51.9	38.5
Pt/TiOC	0.6-1V _{RHE} 3s-3s 9000cv	5%	94	52.6	44

Cyclic voltammograms before and after AST treatment: 1-1.5V_{RHE} 500mVs⁻¹ 12000CVs



- 30%Pt/EC300
- Corrosion of the Carbon support
- Widening of the double layer region
- Formation of the quinone peak

- 5%Pt/TiOC
- No widening of the double layer region
- Shift in Pt reduction peak

References

- Y. Wang *et al.*, *Chem. Mater.*, 2000, 12, 1622-1627
- R. Hahn *et al.*, *Angew. Chem. Int., Ed.*, 2009, 48, 7236-7239
- A. Ohma *et al.*, *ECS Transactions*, 2011 41 (1) 775-784