

Synthesis and characterization of Pt-V on VulcanXC72 carbon for the PEM fuel cell cathode

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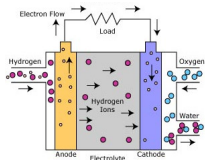
Motivation and objectives

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) that is mostly due to the strong bond of the oxygen molecules on Pt sites as well as a poor corrosion resistance depending on the particle size, support system, temperature and real current density. By alloying Pt with a transition metal such as Ni, Co, Cr dissociative adsorption of O₂ on Pt active sites is facilitated and activity enhancement for ORR can be achieved [1]. Also PtV has shown a higher mass activity for the ORR in phosphoric acid than pure Pt [2]. This work aims at the development of a bi-metal Pt₃V catalyst for the middle temperature polymer cathode fuel cell (100-150°C) and focuses especially on the study of the influence of the catalyst synthesis route on the PtV alloying level, particle size and electrochemical activity for ORR in 1 M H₂SO₄ in the absence and presence of methanol.

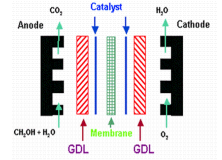
[1] M. Mukerjee et al., *J. Electroanal. Chem.* **357** (1993) 201-224
[2] T. He et al., *J. Electrochem. Soc.* **153** (9) (2006) A1637-A1643

Working Principle of PEM Fuel cells

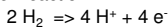
PEMFC



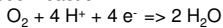
DMFC



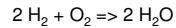
Anode Reaction:



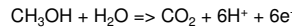
Cathode Reaction:



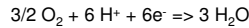
Overall Net Reaction:



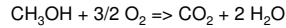
Anode Reaction:



Cathode Reaction:



Overall Net Reaction:



Synthesis of Catalysts

Pt-V bimetal catalysts were synthesized by three different routes:

- Non-polar method (Olei)
- Polar method with Formaldehyde
- Polar method with Sodium Borohydride

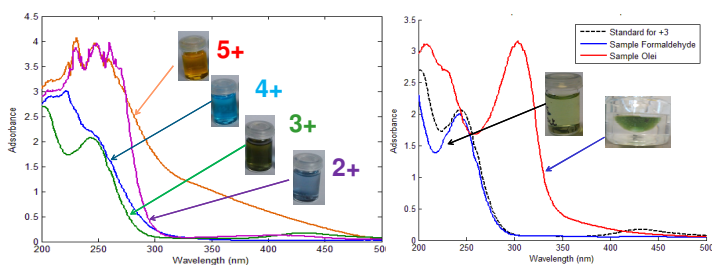
Synthesis Type →	Non-polar method	Polar method I	Polar method II
Parameters ↓			
Reducing Agent	Octadecene	Formaldehyde	Sodium Borohydride
Precursor for Pt	Platinum Acetylacetonate	Chloroplatinic Acid Hexahydrate	
Precursor for V	Vanadium Acetylacetonate	Ammonium Meta Vanadate and Vanadium (III) Chloride	
Temperature of reaction	200 °C	80 °C	Room temperature
Time of reaction	1 hour	1 hour	overnight
pH of reaction medium	Neutral	Acidic	Basic



Experimental setup used for catalyst synthesis

IR spectrum of Vanadium and Pt-V

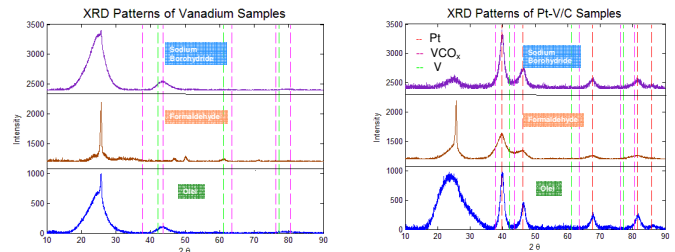
In order to identify the Vanadium oxidation state after co-precipitation of Pt and V, some reference solutions have been prepared and characterized by IR spectroscopy (left). By using the formaldehyde and Olei routes, PtV³⁺ has been clearly identified (right). In the latter case, peak shift is probably due to organic contamination.



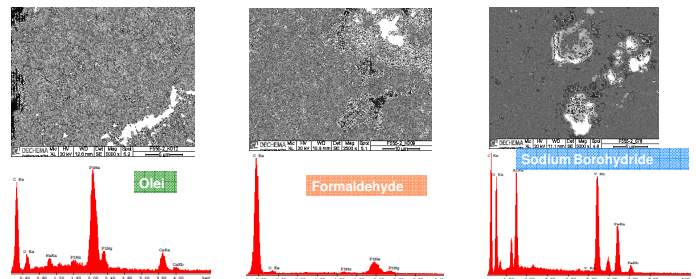
Absorption spectrum of Vanadium at different oxidation states

IR spectra of Pt-V issue from formaldehyde and Olei routes

XRD, SEM & EDX spectra of Vanadium and Pt-V/C

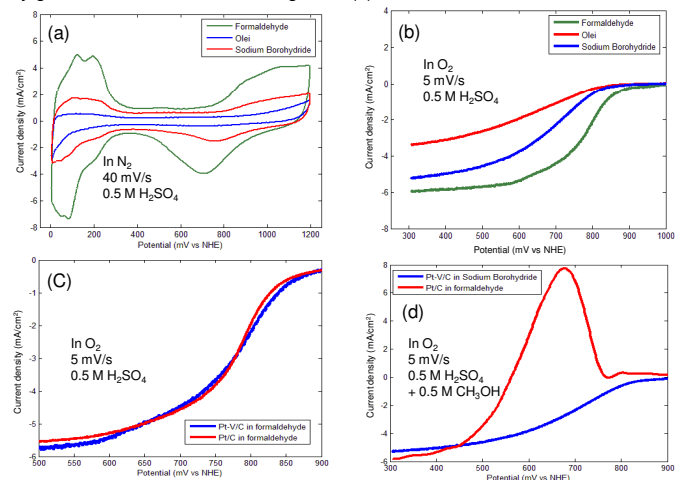


In the left patterns, V⁰ was detected at 2θ=62 (formaldehyde route). However, no V peak can be seen for this system on the right spectrum. From the XRD (2θ=44) and EDX spectra, PtVOx has been formed only by using the borohydride route. Small particles and good distribution with Olei and Formaldehyde routes, cluster of small particles due to strong reducing properties of NaBH₄ can be seen in SEM images.



Electrochemical performance of Pt-V/C toward ORR

The electrochemical investigations were performed with cyclic voltammetry in 0.5 M H₂SO₄ on a rotating disc electrode (diam. 8mm) under half-cell conditions at room temperature. For this purpose, about 80 μg of Pt-V/C (20wt% Pt, 10wt% Nafion) was fixed on the RDE and dried at 60 °C for 1h. Since Pt-V/C from formaldehyde behaves similar to Pt/C in presence and absence of oxygen (a) & (b), poor formation of V is concluded. No activity enhancement for ORR was detected in oxygen saturated electrolyte at Pt-V/C compared to Pt/C. However, Pt-V/C from NaBH₄ route exhibits a very good methanol tolerance during ORR (d).



Conclusions and Outlook

- The Formaldehyde route seems not to be adapted for V reduction.
- Cleaning procedure of organic surfactants after reduction in Oleic acid should be improved.
- Pt-V prepared by Sodium Borohydride route shows best performance for ORR in presence of methanol.
- Particle size of catalyst and oxidation state of Vanadium will be determined by TEM and XPS investigation, respectively.

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