

Electrochemical stability investigation of TiO_xN_y electro-catalyst produced by in-situ urea-based sol-gel method for PEM fuel cell application

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Despite, platinum supported on carbon (Pt/C) is the most used electro-catalyst for the Oxygen Reduction Reaction (ORR) in PEM fuel cells, problems such as sintering, dissolution of Pt in the electrolyte and oxidation of the carbon support during long-term operation are obstacles limiting the mass utilization of PEMFCs. The low abundance of Pt natural resources and its high cost are also limiting its utilization in high volume production of fuel cell cars (1, 2). Therefore, finding a new cheaper non-noble electro-catalyst with high activity and high stability in acidic condition becomes one of the most important topics in the PEMFC research. Development of transition metals oxy-nitride is an interesting approach for new electro-catalysts development for the ORR. Due to its high abundance, titanium oxy-nitride (TiO_xN_y) is one of the most appealing electro-catalysts for the ORR (3-6).

In this study, TiO_xN_y was prepared by a new in-situ urea-based sol-gel method. For comparison three other titanium oxide-nitrides were prepared using classical sol-gel method without urea. This electro-catalyst showed interesting activity for the ORR with an onset potential of ca. 0.75 volts vs. NHE. As well, exchange current density of the electro-catalyst prepared by in-situ urea-based sol-gel method was one order of magnitude higher than that of other electro catalyst obtained by another method. In addition, SEM pictures and BET surface area characterization showed a very small particle size (ca. 20-60 nm) with a BET surface area of ca. 93 m^2/g . This value is higher than those obtained on some titanium oxides (ca.45 m^2/g). The relatively high surface area of these electro-catalysts might be responsible for the improvement of their electro-catalytic performance for the ORR. The specific chemical composition of these electro-catalysts which led to an optimized ionization potential, work function and density of states of electrons might be the key success to identify excellent electro-catalysts for the ORR based on TiO_xN_y electrodes. The prepared electro-catalysts with different N/O ratios showed different properties from a semiconductor behavior in oxygen-rich materials to more conductive and stable electro-catalyst behavior in nitrogen-rich oxy-nitrides, respectively.

XRD and EDS results revealed that the in-situ urea-based sol-gel method might help to fabricate oxy nitride more active for the ORR than the conventional methods because it allows the insertion of more nitrogen, in the form of TiN phase, through the electro-catalyst structure. Considering the mass ratio of nitrogen, oxygen and titanium, EDS results show that the bulk electro-catalyst was prepared based on a 24 wt. % of nitrogen. However, results from XPS spectra showed only 11 % of nitrogen on the surface. Oxidation of the electrodes, specially, at a high anodic potential (ca. 1.5 volts vs. SCE) leads to a change of the surface chemical composition with a significant decrease of the nitrogen amount on the surface to 5 %. It affected the electro-catalytic properties of the electro-catalyst. Figure 1 shows the polarization curves of

the catalyst before and after oxidation at a high potential. Figure 2 shows the first five cycles of Cyclic Voltammetry (CV) curves of the electrode in H_2SO_4 0.5 M electrolyte at 25 °C between -2 to +2 V vs. SCE for 100 cycles with a scan rate of 100 mV/s. An important oxidation peak is seen around 1.5 volts vs. SCE. This might be related to the oxidation and/or dissolution of the electrode involving nitrogen and titanium. This is supported by evaluation of the dissolution of the Ti into the electrolyte using ICP-TOF-MS methods. Accordingly Ti concentration was measured after each oxidizing scans (up to +2 volts vs. SCE) by ICP-TOF-MS. Results are depicted in figure 3. Maximum dissolute titanium concentration was less than 45 $\mu\text{g}/\text{L}$ (~ 0.18 wt. %) after 100 cycles. This amount was less than 0.1 wt. % when there was no applied potential. In comparison, the concentration of the Pt dissolved in the same electrolyte with the same conditions is more than 57 $\mu\text{g}/\text{L}$ (more than 0.23 wt. %). Accordingly, the TiO_xN_y based electro-catalyst represents higher stability than the commercial Pt/C based electro-catalyst.

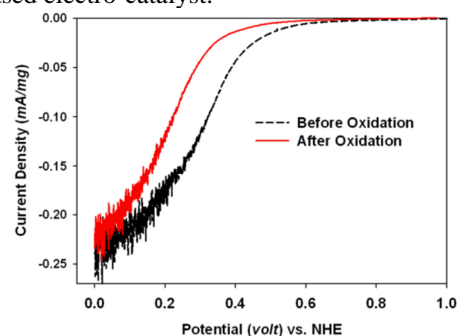


Figure 1. Polarization curves before and after oxidizing the catalyst of TiO_xN_y in 0.5 MH_2SO_4 at 25 °C

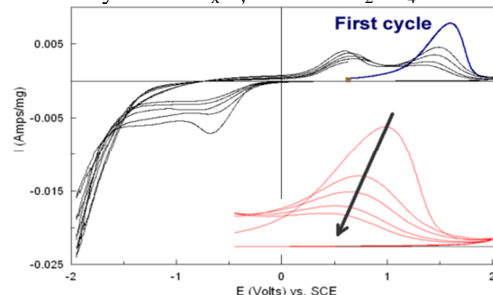


Figure 2. Cyclic Voltammetry with 100 mV/s scan rate of TiO_xN_y in 0.5 MH_2SO_4 at 25 °C

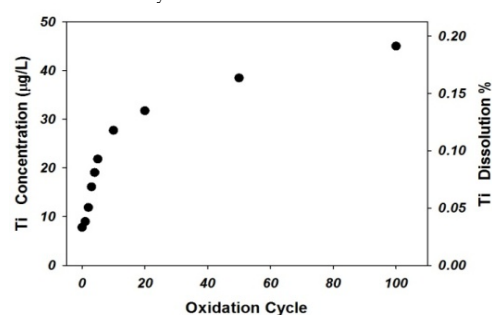


Figure 3. Ti concentration measured by ICP-TOF-MS in H_2SO_4 0.5 M at 25 °C

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