

Nitrogen-graphitized ceramic oxides (NGCO) as support for alcohol oxidation catalysts

Wan-Ying Lin, Huang-Yu Lee, Peter P. Chu*
 Department of Chemistry, National Central University, Jung-Li, Taiwan 32054
 Tel: (03)4227151 ext.65912; Email: ppjchu@gmail.com

A novel catalysts support based on nitrogen-containing graphite coated on ceramic oxide is reported. The nitrogen-graphitized ceramic oxide (NGCO) were prepared by coating a thin layer of conducting polymer (e.g. polyaniline) first on ceramic oxides (TiO_2 , SiO_2 , and ZrO_2) followed by graphitization at 900°C under N_2 atmosphere. The thin layer of N-containing graphene over-coating the ceramics served several functions. First it establishes fluent electron conducting pathway, second it served to store fuel (methanol/ethanol, and other reaction intermediates) and leads more complete electrochemical reaction, and third, it act as a stable anchorage for metal nano-catalysts. The intensity ratio of D- and G-band ($I_{\text{D}}\text{-band}/I_{\text{G}}\text{-band}$) derived from Raman scattering is indicative of the degree of graphitization after pyrolyzing PANi, and they are summarized in Table 1, for comparison. Note that the $I_{\text{D}}/I_{\text{G}}$ ratio decreases with increasing carbon content (by varying PANi content), indicates that samples with thinner carbon layer forms more ordered carbon structure during graphitization.

Surface topography mapping shows the Pt nanoparticle is better dispersed on NGCO compared to that on XC-72 or other graphite based carbons, with a stable particle size of $\sim 3\text{-}4$ nm. Electrochemical studies show Pt supported on NGMO worked as highly efficient catalysts for alcohol (Methanol and ethanol) oxidation. As shown in Fig.1, Pt support on both TiO_2 and PANI- TiO_2 yield negligible activity (Figure 1a, and Figure 1b), as the support lacks electronic conductivity. Of the other two catalysts systems display activity; Pt/NG- TiO_2 catalyst shows a higher methanol oxidation activity (Figure 1c) than E-TEK (Figure 1d). Judging from forward and backward peak current densities, Pt/NG- TiO_2 also exhibited distinctively higher electro-oxidation activity compared to the other two supports without nitrogen-graphitization (Figure 1a, 1b). Furthermore, the Pt/NG- TiO_2 exhibited a mass current density of 265A/g Pt , which is higher compared to that of E-TEK (233A/g Pt) measured under the same condition. Apparently, the ceramic TiO_2 modified with conducting polymer with subsequent nitrogen-graphitized can deliver superior or comparable catalytic activity compared to carbon-based support used in the conventional art. This is likely due to the increase the electron conductive and the assist of metal particles disperse by nitrogen elements on TiO_2 surface. Notice that single metal element Pt catalysts is not CO tolerant as Pt/Ru binary catalyst, thus the CO-adsorption peak appeared in the reverse scan in all samples.

The topology of the Pt nanoparticle on NGMO and its methanol oxidation activity varies with ceramic oxides. SiO_2 , and ZrO_2 were also used to prepare the nitro-containing graphitized carbon support. The NGMO using SiO_2 nano-particle appears to deliver the best electrochemical performance (as shown in Fig. 2). The Pt particle size is the primary factor responsible for the improvement, but the ceramic oxide is found to also play a role during reaction. The Pt/NGMO system also displayed much better life-time durability and negligible carbon corrosion, when compared to that of Pt/ metal oxide or Pt/XC-72.

The many functions of nitrogen-containing graphitized carbon which are responsible for the improved electro-chemical reaction and stability will be discussed.

Table.1 graphitization of TiO_2

sample	degree of graphitization $I_{\text{D}}\text{-band}/I_{\text{G}}\text{-band}$ [a.u.]
PANI- $\text{TiO}_2(1:10)$	3.4
PANI- $\text{TiO}_2(1:1)$	3.2
NG- $\text{TiO}_2(1:1)$	0.25

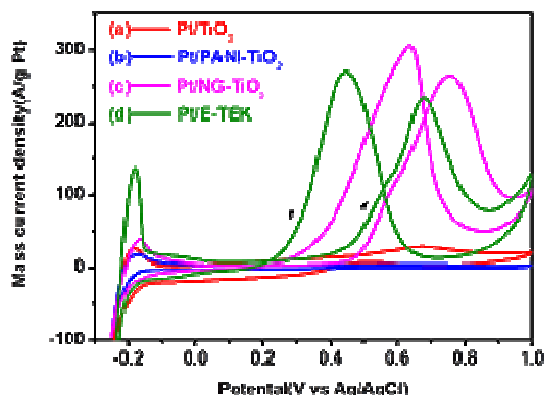


Fig.1 Cyclic voltammograms of methanol electro-oxidation for Pt on different TiO_2 -based supports compared with that of E-TEK in $0.5\text{M H}_2\text{SO}_4 + 1\text{M CH}_3\text{OH}$ at room temperature. Scan rate: 50 mVs^{-1}

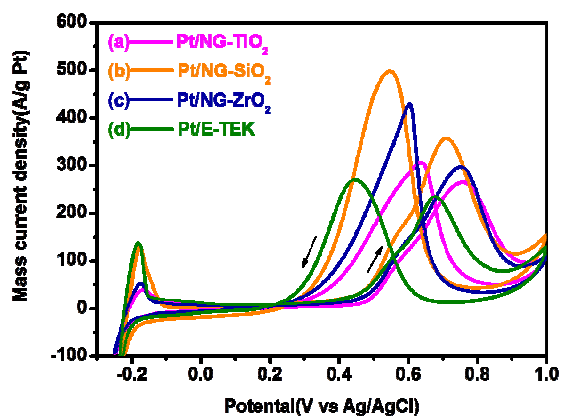


Fig.2 Cyclic voltammograms of methanol electro-oxidation for (a) Pt/NG- TiO_2 , (b) Pt/NG- SiO_2 , (c) Pt/NG- ZrO_2 , (d) Pt/E-TEK in $0.5\text{M H}_2\text{SO}_4 + 1\text{M CH}_3\text{OH}$ at room temperature. Scan rate: 50 mVs^{-1}

