ABSTRACT. Two different methods were used to prepare bimetallic Pt$_3$Cr$_1$/C nanocatalysts from similar compositions where the resulting materials exhibit different alloying extents (structure). The study investigates how these variations in alloying extent impact the catalytic activity, stability, and selectivity in the oxygen reduction reaction (ORR). One method, based on the slow thermal decomposition of the Cr precursor at a rate that matches the chemical reduction of the Pt precursor, allows fine control of the Pt$_3$Cr$_1$/C alloy’s composition; whereas the second approach, using the ethylene glycol method results in considerable deviation (> 25%) from the projected composition. Consequently these two methods give variations in the alloying extent that has a strong influence on the Pt d-band vacancy and the Pt electroactive surface area (Pt-ESCA). This relationship was systematically evaluated using transmission electron microscopy, X-ray absorption near edge structure spectroscopy, and electrochemical analysis. The ORR activity depends on two effects that nullify each other, namely the number of active Pt-sites and their activity. Here the Pt-site activity is more dominant in governing the ORR activity. The nanocatalyst’s selectivity towards the ORR and the competitive methanol oxidation reaction (MOR) depend on these two effects to act in cooperation to give enhanced ORR activity with suppressed MOR. The number of active Pt-sites is associated with the Pt-ESCA value, while the Pt site activity is associated with the alloying extent and Pt d-band vacancy (electronic) effects. The presence of Cr atoms in Pt$_3$Cr$_1$/C enhances stability during electrochemical treatment. Overall, the Pt$_3$Cr$_1$/C catalyst prepared by the controlled composition synthesis was shown to be superior in ORR activity, selectivity, and stability owing to its favourable alloying extent, Pt d-band vacancy, and Pt-ESCA.

Scheme 1. Illustration of the preparation procedure for the Pt$_3$Cr$_1$/C nanoparticles (NPs) using combined chemical reduction and thermal decomposition of Pt and Cr precursors, denoted as TD method.

Figure 4. (a) Linear scan voltammograms (LSVs) recorded at 1 mV·s$^{-1}$ for the ORR on Pt/C E-etek and Pt$_3$Cr$_1$/C catalysts with rotation rate of 2500 rpm in O$_2$-saturated 0.5 M H$_2$SO$_4$ at 25°C. Inset: Magnified at high positive potential region. (b) Their corresponding mass activities measured at 0.90 V.

Figure 3. Relationship between d-band vacancy and alloying extent for the Pt$_3$Cr$_1$/C NPs prepared by the TD and EG method.

ACKNOWLEDGEMENTS This work was supported by the National Science Council (NSC) Grants No. NSC-97-2120-M-011-001 and NSC-97-2221-E-011-075-MY3, the National Synchrotron Radiation Research Center (NSRRC), the National Center for High-performance Computing (NCHC) and the National Taiwan University of Science and Technology (NTUST) for computer time and facilities.