our future through science

Oxygen reduction reaction on a highly-alloyed Pt-Ni supported carbon electrocatalyst in acid solution

H ZHENG, M ROHWER, M MATHE
CSIR Materials Science and Manufacturing, PO Box 395, Pretoria, 0001, South Africa
Email: hzheng@csir.co.za - www.csir.co.za

INTRODUCTION

Alloyed electrocatalysts such as PtNi/C[1-2], PtCo/C[3], PtCr/C[4], PtFe/C [5-6], and non-alloyed Pt-TiO_2/C were reportedly investigated for methanol tolerance during Oxygen reduction reaction (ORR). The high methanol tolerance of these electrocatalysts during the ORR was attributed to a composition effect, disordered stucture and low activity for methanol oxidation reaction. Most Pt alloy electrocatalysts were prepared via a complex procedure or by high temeperature thermal reduction. In this work, Pt_3Ni/C alloy electrocatalysts were synthesised by a simple route at low temperature, resulting in a highly-alloyed product with high ORR activity and excellent methanol tolerance.

EXPERIMENTAL

Twenty percent Pt_3Ni/C alloy electrocatalyst were synthesised by a low temperature method using sodium citrate and PVP as stabilising agents. The mixture of the calculated amount of H_2PtCl_6 , $NiCl_2$ and carbon black (Vulcan XC-72) were pre-reduced by ethylene glycol at 110°C and then further treated with $NaBH_4$ for complete reduction.

RESULTS AND DISCUSSION

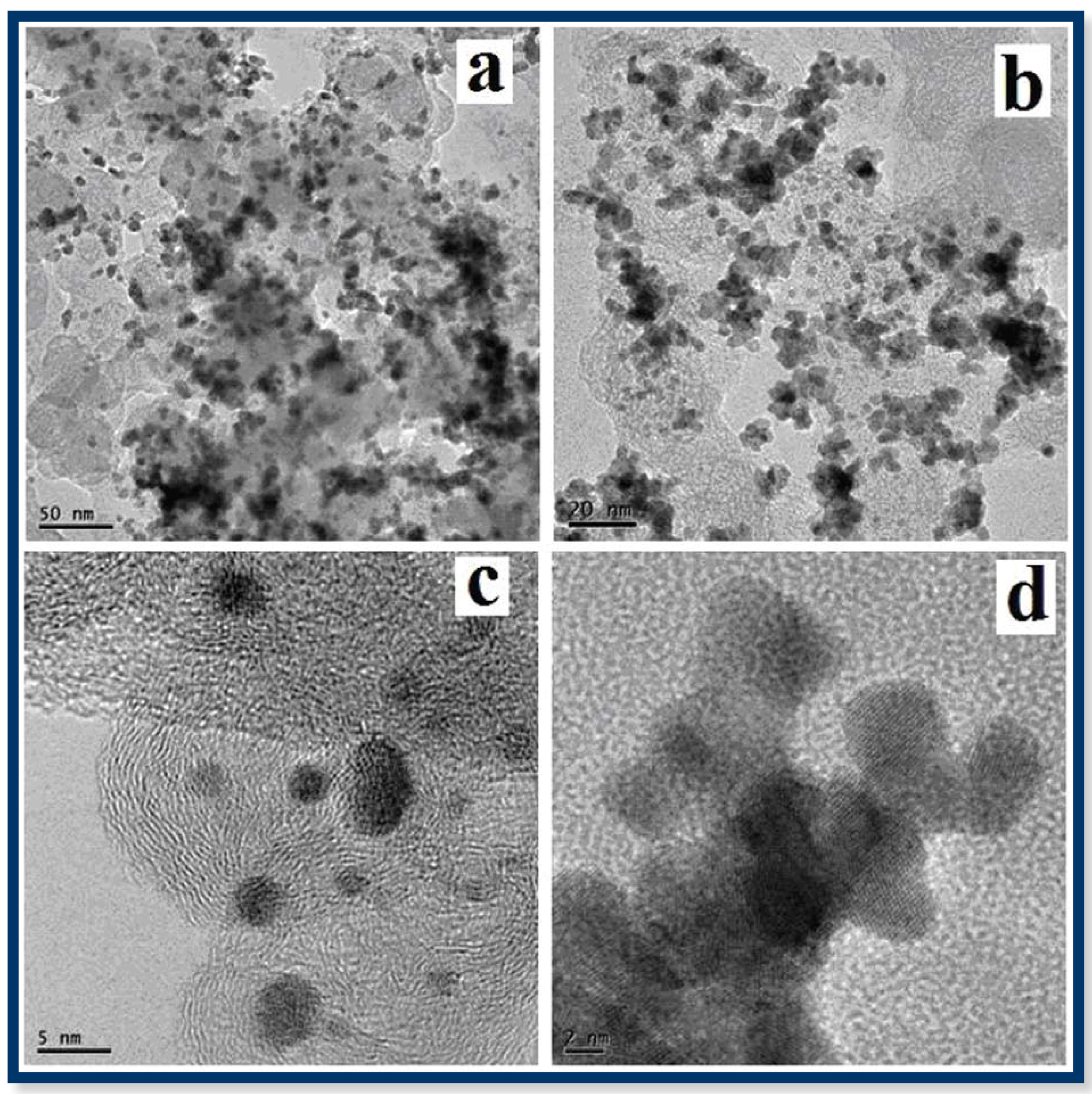

Figure 1: LR-TEM micrographs of Pt_3Ni/C alloy electrocatalyst (a) and Pt/C electrocatalyst (b); HR-TEM micrographs of Pt_3Ni/C alloy electrocatalyst (c) and Pt/C electrocatalyst (d)

Figure 1 shows low-resolution (LR)-TEM and high-resolution (HR)-TEM micrographs of the Pt_3Ni/C alloy electrocatalyst and the Pt/C electrocatalyst. The sizes of particles are 3.7±0.5 nm and 4.0±0.5 nm on Pt_3Ni/C alloy electrocatalyst and Pt/C electrocatalyst, respectively. **Figure 1c** and **Figure 1d** show that the particles of the Pt_3Ni/C alloy and the Pt/C electrocatalysts are crystalline.

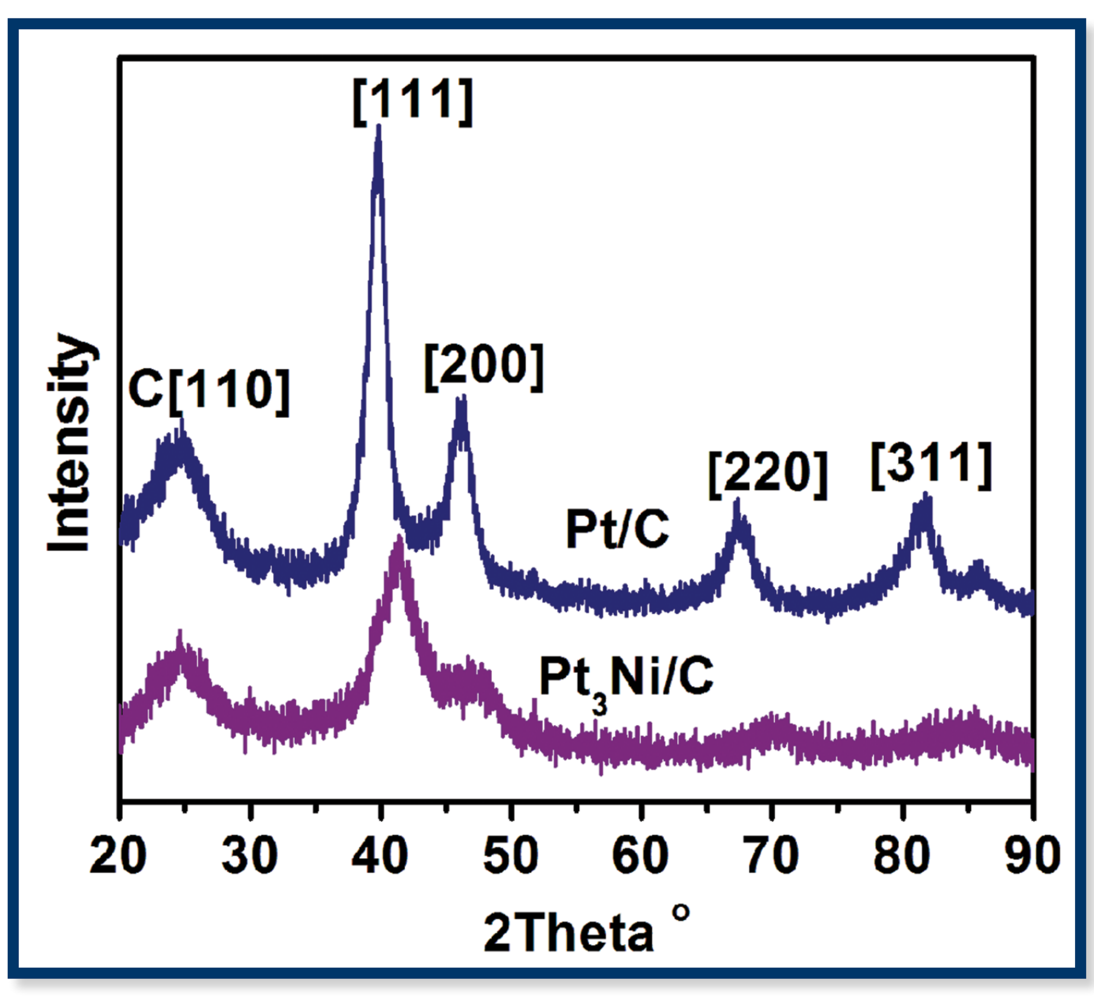

Figure 2: XRD image of Pt3Ni/C alloy electrocatalyst and Pt/C electrocatalyst

Figure 2 shows the XRD diffractograms of prepared carbon-supported Pt_3Ni/C alloy and Pt/C electrocatalysts. The four diffraction peaks in the Pt_3Ni/C alloy electrocatalysts are shifted to higher 2θ values with respect to the corresponding peaks in the Pt/C electrocatalyst, which was caused by the incorporation of Ni in the fcc structure of Pt. These angular shifts reflect lattice contraction due to the replacement of part of Pt with Ni. **Table 1** lists the particle size, lattice parameters and the corresponding Pt-Pt bond distance calculated from Pt (220) using Scherrer formula and Bragg equation, respectively. The reported lattice parameters and Pt-Pt bond distance for the Pt_3Ni/C alloy electrocatalysts are smaller than that of the Pt/C and ETEK- Pt/C, indicating the lattice contraction after alloying. In fact, the decrease of lattice parameters and Pt-Pt bond distance within the alloy electrocatalyst illustrates the conversion of Ni into an alloyed state.

Table 1: Structural parameters of the Pt/C and Pt3Ni/C alloy electrocatalyst

Electrocatalysts	Lattice parameter fcc (nm)	Pt-Pt bond distance (nm)	Particle size from XRD (nm)
ETEK-Pt/C[a]	0.3923	0.2774	3.4
Pt/C	0.3921	0.2773	4.0
Pt_3Ni/C	0.3781	0.2674	3.7

From Ref.[7]

Figure 3 shows a series of steady-state current-potential curves in 0.5 M H_2SO_4 in the absence/presence of methanol, obtained from Pt3Ni/C, Pt/C and ETEK-Pt/C electrodes. **Figure 3a** shows that Pt_3Ni/C electrocatalyst exhibits higher activity for ORR than Pt/C and ETEK-Pt/C. All the electrocatalysts showed an increased ORR over-potential under the same current density in the presence of methanol due to the simultaneous occurrence of oxygen reduction and methanol oxidation reaction, which results in the formation of a mixed potential (**Figure 3b**). In the presence of methanol, the ORR activity of the ETEK-Pt/C electrocatalyst has been observed to decrease more than that of the Pt/C and the Pt_3Ni/C alloy electrocatalyst, indicating that the Pt_3Ni/C alloy electrocatalyst and Pt/C are more methanol-tolerant electrocatalysts during the ORR.

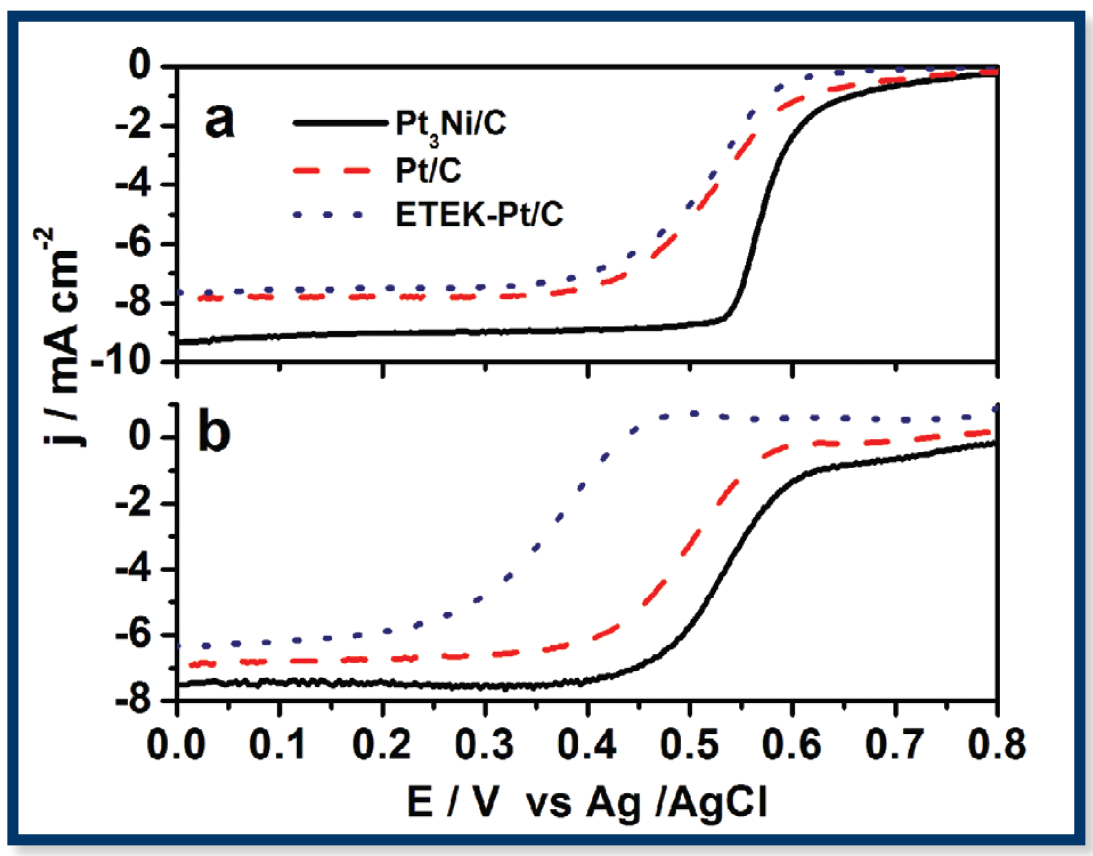

Figure 3: Oxygen reduction curves on Pt_3Ni/C, Pt/C and ETEK-Pt/C electrodes in 0.5 M H_2SO_4 at the scan rate of 5mV/s and a rotating speed of 2500rpm; a: in the absence of CH_3OH b: in the presence of CH_3OH

CONCLUSION

Pt_3Ni/C alloy and Pt/C electrocatalyst were prepared by a low temperature method using sodium acetate and PVP as stabilizing agents. The Pt_3Ni/C alloy electrocatalyst demonstrated a superior activity and high methanol tolerance during ORR compared with commercial ETEK-Pt/C electrocatalyst. The Pt_3Ni/C electrocatalyst is therefore superior in terms of ORR activity and methanol tolerance, making it a good choice for a direct methanol fuel cell cathode electrocatalyst. These results suggest that using sodium acetate and PVP as stabiliser at low temperature is a promising method for the preparation of highly-alloyed electrocatalyst.

REFERENCES

1. Yang, H., Coutanceau, C., Le'ger, J.M., Alonso-Vante, N., Lamy, C. 2005. *J. Electroanal. Chem.*, 576 :305- 310.
2. Antolini, E., Salgado, J.R.C., Gonzalez, E.R. 2006. J. Power Sources, 155:161-170.
3. Lima, F.H.B., Lizcano-Valbuena, W.H., Teixeira-Neto, E., Nart, F.C., Gonzalez, E.R., Ticianelli, E.A. 2006. *Electrochim. Acta* , 52:385-390.
4. Antolini, E., Salgado, J.R.C., Santos, L.G.R.A., Garcia,G., Ticianelli, E.A. , Pastor, E., Gonzales, E.R., 2006. J. Appl. Electrochem., 36: 355-361.
5. Li, W., Zhou,W., Li, H., Zhou, Z., Zhou, B., Sun, G.Q., Xin,Q. 2004. *Electrochim. Acta*, 49 :1045-1051.
6. Shukla, A.K., Raman, R.K., Choudhury, N.A., Priolkar, K.R., Sarode, P.R., Emura, S., Kumashiro, R. 2004. J. *Electroananl. Chem.*, 563:181-186.
7. Yang, H., Vogel, W., Lamy, C., Alonso-Vante, N., 2004. J. *Phys.Chem.* B, 108:11024-11028.
8. Markovic, N.M. , Ross, P.N. 2002. *Surf. Sci. Rep.*, 45: 121-125
9. Lamy,C., Lima, A.,Le-Thun,V., Coutanceau, C., Leger. J.M.2002. J. Power Sources, 105: 283-289
10. Gasteiger, H.A., Markovic, N.M., Ross, P.N., Cairns, E.J. 1994. *Electrochim. Acta*, 39: 1825-1830.

A simple route to prepare nano-cathode catalysts for fuel cells that provides a highly-alloyed product in comparison with commercial catalysts.