

Chemically ordered intermetallic PtFeCo catalyst with improved activity and durability for electroreduction of oxygen

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Polymer electrolyte membrane Fuel Cells (PEMFCs) is one of the key devices to accomplish green energy requirements in near future, due to their zero emission of greenhouse gases.^[1] However commercial viability of device confronted mainly owing to high cost and low durability of Pt based catalyst, which is widely established as cathode catalyst in PEMFCs^[2]. There have been numerous approaches executed to encounter these dual issues. Recently, chemically ordered intermetallic Pt-M alloy has been emerged as an excellent electrocatalyst for oxygen reduction reaction (ORR) and this catalyst has been demonstrated high durability^[3]. High durability might be ascribed due to well defined compositions and an ordered arrangement of Pt and PtM within the alloy.

Herein, we firstly demonstrate that L1₀ or face centered tetragonal (fct), PtFeCo (trimetallic, TM) or fct-TM as an efficient and durable electrocatalyst for ORR. The solid state impregnation method was employed to design the fct-TM and this catalyst has superior activity and durability relative to disordered fcc-TM, state of art Tanaka Kikinzoku Kogyo PtC, TKK-PtC, (45.8 wt%) catalyst.

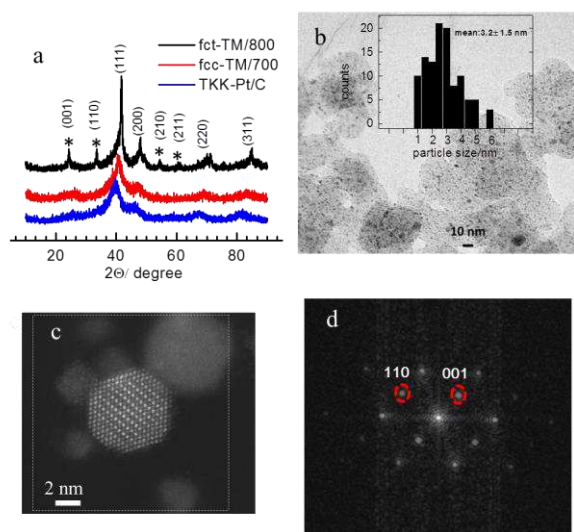


Figure 1. (a) XRD pattern of fct-TM, fcc-TM and TKK-PtC catalyst, (b) TEM image of fct-TM, inset shows particle size distribution, (c) HAADF-STEM atomic resolution of fct-TM catalyst and (d) FFT-STEM image of Figure 1c for fct-TM.

The catalyst was prepared by uniformly mixing respective precursor materials with Ketjen black carbon (KBC) keeping metal loading of 40 wt%. This mixture was then reduced in presence of 20% H₂ with N₂ as carrier gas in a tube furnace for 4 hr at two different temperatures viz., 700°C and 800°C in order to obtain fcc-TM and fct-TM catalyst, respectively. The X-ray diffraction (XRD) was employed to characterize chemically ordered intermetallic at fct-TM, as shown in Figure 1. The appearance of sharp superlattice peaks at 2θ

of 24.35 for (001) and 33.55 for (110) was noticed for fct-TM, in addition to fcc Pt-TM diffraction peaks and these superlattice peaks demonstrate the formation of chemically ordered intermetallic structure and fct-TM average particle sizes are 3.2 ± 1.5 nm (Fig.1b). The chemical ordering and superlattice peak was further confirmed by HAADF-STEM measurement. The presence of alternate bright and darker column confirms chemical ordering. In addition, FFT-STEM (Fig.1d) also yield the presence of (001) and (110) peaks.

The electrochemical properties of these catalysts were verified using rotating disk electrode and cyclic voltammetry (CV) techniques. The 0.1 M HClO₄ electrolyte solution was used to study the electrochemical property of these catalysts. As shown in Figure 2a, the mass activity of fct-TM has 3.5 times higher than TKK-PtC catalyst. The electrochemical active surface area (ECSA) value is same value observed. Durability of these catalysts was examined using square wave potential cycling, i.e., 0.6 V for 3s and 1.0 V for 3s, which is in accordance to Fuel cell commercialization of Japan (FCCJ) protocol. The ECSA at different cycles are shown in Figure 2b. The fct-TM retains high ECSA value while fcc-TM and TKK-PtC substantially loss in ECSA was observed from initial cycle onwards. The fct-TM retains 85 % ECSA value after 5K durable cycle, while both fcc-TM and TKK-PtC losses significant activity. The enhanced activity of fct-TM catalyst could be ascribed due to bi-functional mechanism, electronic factor, Pt-Pt distance, while durability might be expected owing to ordered arrangement of Pt alloy and high enthalpy of formation.

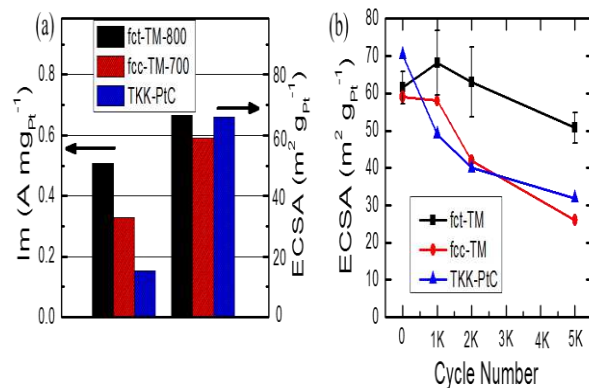


Figure 2. (a) Mass activity and ECSA value, (b) ECSA value at different durable cycle.

In summary, we have succeeded to design highly active and durable Intermetallic and trimetallic PtFeCo electrocatalyst for ORR.

References

1. S.Mukerjee, S.S.Srinivasan, M.P.Soriaga, J.McBreen, *J.Phys.Chem.***1999**, 99, 4577-4589.
2. V.R.Stamenkovic, B.S.Mun, M.Arenz, K.J.J.mayrhofer, C.A.Lucas, G.Wang, P.N.Ross, N.M.Markovic, *Nature Mater.* **2007**, 6, 241-247.
3. D.Wang, H.L.Lin, R.Hovden, H.Wang, Y.Yu, D.A.Muller, F.J.Disalvo, H.D.Abruna, *Nature Mater.***2012**, 12, 81-87.