

RSC Advances

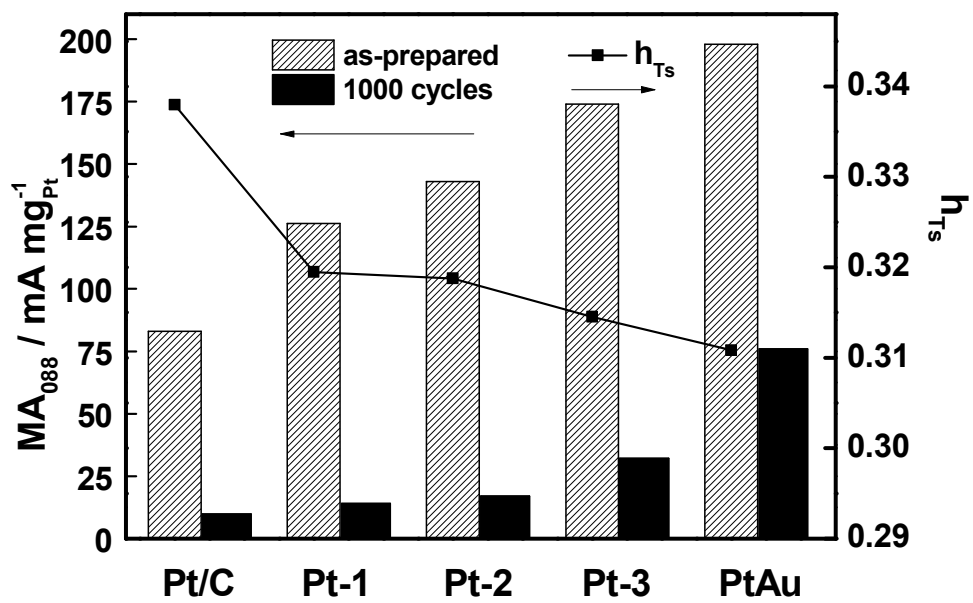


This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



COMMUNICATION

The Enhancement of Oxygen Reduction Reaction Performance of Pt Nanomaterials by 1-Dimensional Structure and Au Alloying

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012Yu-Ting Liang^a, Chen-Wei Liu^b, Hong-Shuo Chen^a, Tz-Jiun Lin^a, Chao-Yu Yang^a, Tian-Lin Chen^a, Chia-Hui Lin^c, Ming-Chin Tu^c, and Kuan-Wen Wang^{a,*}

DOI: 10.1039/x0xx00000x

www.rsc.org/

The effect of aspect ratios and Au alloying on the ORR performance of carbon-supported Pt nanorods (NRs) is investigated. The ORR activity of PtAu NRs after durability test shows excellent stability due to the modification of electronic structure and surface composition.

The strategies for the improvement of the state-of-the-art carbon-supported Pt nanocatalysts (Pt/C) towards oxygen reduction reaction (ORR) include the control of the morphologies, alloying components, core/shell structures, or their combinations.¹ Through novel and complicated processes and modification,² the mass and specific activities (MA and SA) of the Pt-based catalysts can reach the target of Department of Energy (DOE),^{3,4} which are almost unattainable for Pt/C prepared by conventional methods. Generally, the ORR enhancement stem from the ensemble, ligand and geometric effects,^{2,5} and the third one caused by the change in electronic structure is a feasible mechanism applied to improve the ORR performance.^{6,7} However, little attention has been paid to elucidate the intrinsic ORR performance of Pt nanomaterials only resulted from the electronic modification effect, which can be a good indicator for the further improvement of the Pt-based electrocatalysts toward ORR. A term, the number of unoccupied d-state (h_{TS}) extracted from X-ray absorption near edge spectroscopy (XANES) has been used to measure the d-band vacancies of Pt, which is related to their ORR performance strongly.⁸ It has been reported that the d-band vacancy of Pt/C has been modified due to morphological, alloying and support to different extents.⁶

Therefore, in this study, we have demonstrated the effect of electronic structure modification of Pt on its ORR performance. By simply tuning the aspect ratio of Pt nanorods (NRs) through one step chemical reduction process, the d-band states of Pt can be modified, improving the ORR performance accordingly. To the best of our knowledge, this is the first time that the effect of aspect ratios on the ORR durability of Pt/C has been discussed. Besides, Au is alloyed into the Pt NRs to further promote the stability.

Carbon-supported Pt and PtAu NRs with metal loading about 50 wt% were prepared by formic acid method (FAM).^{6,7,9-12} H₂PtCl₆ (Alfa Aesar) was mixed with carbon black (Vulcan XC-72R), and

then reduced by formic acid (98%) at room temperature for 72, 144 and 216 h. The as-deposited samples were then washed and subsequently dried at 340 K for 24 h. The as-prepared Pt NRs with an aspect ratio of 1.84, 2.34, and 3.75 and reacting for 72, 144, and 216 h were named as Pt-1, Pt-2, and Pt-3, respectively. For the preparation of PtAu NRs with a Pt/Au atomic ratio of 3, H₂PtCl₆ mixed with carbon black were reduced by formic acid at room temperature for 216 h and HAuCl₄ (Aldrich) was added and reduced by formic acid for another 48 h. The as-prepared PtAu NRs were named as PtAu. Besides, Pt/C (46 wt%, TKK, Tanaka Kikinokogyo) catalyst was used for comparison.

The X-ray photoelectron spectroscopy (XPS) (Thermo VG Scientific Sigma Probe) using a monochromatic X-ray source (Al K_α) at a voltage of 20 kV and a current of 30 mA was executed to identify the surface chemical states of the catalysts. The morphologies of the catalysts were analyzed by high resolution transmission electron microscopy (HR-TEM) operated at a voltage of 200 kV.

The electrochemical measurements were conducted by a CHI611C potentiostat and a classical electrochemical cell with a three-electrode configuration as reported previously.^{6,7} All potentials in this study was referred to normal hydrogen electrode (NHE). The catalysts were dispersed in 2-propanol, blended with diluted Nafion solution (5 wt %, DuPont), and then deposited onto the glassy carbon rotating disk electrode (RDE, area of 0.196 cm²). The metal loading on a RDE was about 0.04 mg/cm². Oxygen reduction current was gauged by linear sweep voltammetry (LSV) with a scan rate of 5 mV s⁻¹ and a rotational rate of 1600 rpm. The accelerated durability tests (ADT) were obtained in the potential range of 0.6 to 1.2 V with the applied scan rate of 50 mV s⁻¹ under O₂ atmosphere for 1000 cycles. The cyclic voltammograms (CV) were obtained from 0.0 to 1.2 V with scan rate of 20 mV s⁻¹ under N₂ atmosphere. The electrochemical surface area (ECSA) was calculated by measuring the areas of H desorption between 0.05 and 0.4 V after the deduction of the double-layer region. The kinetic current density (I_k) was calculated based on the following equation:

$$I_k = \frac{I_d I}{I_d - I} \quad (1)$$

where I , I_k , and I_d are the experimentally measured, mass transport free kinetic and diffusion-limited current density, respectively. For each electrocatalyst, the mass activity (MA) and specific activity (SA) were obtained when I_k was normalized to the Pt loading and ECSA, respectively.

The X-ray absorption spectroscopy (XAS) of catalysts were obtained in transmission or fluorescence mode at the BL01C1 and 17C beamlines at National Synchrotron Radiation Research Center (NSRRC), Taiwan as reported previously.^{6,7} A Si monochromator was employed to adequately select the energy with a resolution $\Delta E/E$ better than 10^{-4} at Pt L_{II} (13,273 eV) and L_{III} -edges (11,564 eV). Based on the spectra, the fractional change in the number of d-band vacancies relative to the reference material (f_d) can be estimated:

$$f_d = \frac{\Delta A_3 + 1.11\Delta A_2}{(A_3 + 1.11A_2)_r} \quad (2)$$

$$h_{T_s} = (1 + f_d)h_{Tr} \quad (3)$$

where ΔA_2 and ΔA_3 are expressed by:

$$\Delta A_2 = A_{2s} - A_{2r} \text{ and } \Delta A_3 = A_{3s} - A_{3r} \quad (4)$$

The terms A_2 and A_3 , indicating the areas under L_{II} and L_{III} absorption edges of the sample (s) and reference (r) material as well as the calculated h_{T_s} , were evaluated from band structure calculations.

Fig. 1(a), (b), (c) and (d) shows that the as-prepared Pt-1, Pt-2 Pt-3 and PtAu NRs are well-dispersed on the carbon support with an aspect ratio of 1.84 ± 0.08 , 2.34 ± 0.05 , 3.75 ± 0.11 , and 3.97 ± 0.15 , respectively. The aspect ratio distribution histograms of NRs are displayed in Fig. S1 in supporting information (SI). As Pt NRs are stretching out from the surface of the carbon support, O_2 diffusion toward the Pt surface might be improved.¹² Hence, the ORR performances for NRs with higher aspect ratio may be expected to have enhanced activity.¹² After 1000 cycles of ADT, as shown in Fig. 1(e)-(h), different degrees of Pt aggregation, migration and carbon corrosion occur.¹³ It is worth mentioning that rod-like structure with a diameter of 5 and 4 nm and slight aggregation can be still observed for Pt-3 and PtAu NRs displayed in Fig. 1(g) and (h). It seems that the NRs with a high aspect ratio and/or Au alloying have good stability, suggesting that elongated Pt and/or Au nanostructures may lessen the effect of dissolution, Ostwald ripening, and aggregation in acidic conditions.^{14,15}

Fig. 2(a) represents the LSV of as-prepared Pt, PtAu NRs and Pt/C. The j (experimentally measured current density normalized to the geometric surface area of RDE) of Pt/C, Pt-1, Pt-2, Pt-3 and PtAu are 2.2, 2.6, 2.8, 3.0 and 3.1 mA cm⁻² at 0.88 V, respectively, implying that the ORR performance of Pt nanomaterials is aspect ratio-dependent. It has been reported that the use of Pt nanostructure with high aspect ratio may considerably reduce the voltage loss, without the cathode suffering from slow O_2 diffusion.¹² Moreover, the stability of various catalysts is measured by ADT, which causes surface oxidation/reduction cycles of Pt and the formation of PtOH and PtO originated in the oxidation of water, resulting in the dissolution of Pt through the Pt²⁺ oxidation state.¹⁶ After 1000 cycles of ADT, the LSV results shown in Fig. 2(b) clearly demonstrate that PtAu still maintain high j at 0.88 V of 1.8 mA cm⁻² with a decay of 41 %, while others decrease to about 0.4-1 mA cm⁻² with a decay in j about 67-82 % as listed in Table 1. Au clusters can have a stabilizing effect on Pt, suppress Pt dissolution during applied condition, and further promote the durability of catalysts.^{9,15} The XPS fitting results

summarized in Table 1 elucidate that the surface chemical compositions of various catalysts are covered by Pt and Pt oxide and the Pt/PtO ratio gradually increases while the aspect ratio of NRs increases. The Pt/PtO ratio of PtAu is the highest owing to its high aspect ratio and Au alloying. In order to get insight into the reason of ORR enhancement for NRs, the h_{T_s} values were measured by XANES spectra at Pt L_{III} and L_{II} edges. The Pt electrons transfer from $2p_{3/2}$ to $5d_{5/2}$ at 11564 V and the intensity of white line depends on the degrees of Pt oxidation.⁸ The h_{T_s} values are 0.3380, 0.3195, 0.3188, 0.3145 and 0.3108 for Pt/C, Pt-1, Pt-2, Pt-3 and PtAu, respectively. The h_{T_s} value is decreased obviously due to the formation of Pt NRs, suggesting the morphological change affects the d-band structure of Pt. Moreover, the h_{T_s} value is decreased with the higher aspect ratio of Pt and alloying with Au. In addition, among the various catalysts, the h_{T_s} value for PtAu is the lowest, implying that more electrons transfer to d-state, the Pt-O⁻ binding weaker and the ORR performance is promoted.⁸ Moreover, the CV curve shown in Fig. 2(c) suggests that the oxide formation and reduction peak around 0.75 V¹⁷ of PtAu is also insignificant, implying that PtO⁻ is more difficult to form, consistent with the XPS results.¹⁸ Besides, the calculated ECSA of NRs listed in Table 1 is smaller than that of Pt/C owing to the morphological effect. Fig. 2(d) illustrates the correlation between MA and h_{T_s} of Pt/C and various Pt and PtAu NRs before and after ADT. It shows that PtAu with lower h_{T_s} have lower unoccupied d-states, weaker PtO⁻ bonds, less Pt oxide formation, less pronounced white line, leading to the promotion of ORR kinetics and stability.¹⁰ The relationship of SA and h_{T_s} compared in Fig. S2 in SI emphasizes the effect of morphology and alloying on the ORR stability of Pt. It is worth mentioning that the j of as-prepared PtAu NRs at a voltage < 0.85 is lower than that of Pt-2 and Pt-3 as shown in Fig. 2(a), due to the coverage of some Pt surface atoms by Au cluster. However, surface Au can really promote the stability through the electronic-modification effect. As a result, the enhancement of ORR performance may be due to the morphological effect, the changes in numbers of unoccupied d-states and the surface alloying of Au. It is found that higher aspect ratio and Au alloying modifying the d-band structure can promote the ORR activity and stability of Pt catalysts.

Conclusions

In this study, Pt NRs with different aspect ratios and/or Au alloying have been prepared by FAM. The ADT results of various NRs suggest that the ORR performance of Pt nanomaterials is aspect ratio-dependent since Pt NRs are stretching out from the surface of the carbon support, and O_2 diffusion toward the Pt surface might be improved. After 1000 cycles of ADT, PtAu NRs still remain their original activities about 76 %. The ORR enhancement of PtAu NRs stems from their high aspect ratio and Au alloying, leading to high Pt/PtO surface composition and low Pt unoccupied d-states, further promoting the stability of ORR.

Acknowledgement

This work was supported by the Ministry of Science and Technology of Taiwan (No. 103-2221-E-008-039 and 103-2120-M-007-005) and Ministry of Economics Affairs, Taiwan (104-EC-17-A-22-0775).

Notes and references

^a Institute of Materials Science and Engineering, National Central University Taoyuan 320, Taiwan

^b Green Energy and Environment Research Laboratories, Industrial Technology Research Institute, Hsinchu 310, Taiwan

^c Department of Applied Science, National Hsinchu University of Education, Hsinchu 300, Taiwan

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

- X. Sun, D. Li, Y. Ding, W. Zhu, S. Guo, Z.L. Wang, S. Sun, *J. Am. Chem. Soc.* 2014, **136**, 5745.
- J.A. Wittkopf, J. Zheng, Y. Yan, *ACS Catal.* 2014, **4**, 3145.
- H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, *Appl. Catal. B: Environ.* 2005, **56**, 9.
- H.A. Gasteiger, J.E. Panels, S.G. Yan, *J. Power Sources* 2004, **127**, 162.
- P. Strasser, S. Koh, T. Anniyev, J. Greeley, K. More, C.F. Yu, Z.C. Liu, S. Kaya, D. Nordlund, H. Ogasawara, M.F. Toney, A. Nilsson, *Nature Chem.* 2010, **2**, 454.
- H.S. Chen, Y.T. Liang, T.Y. Chen, Y.C. Tseng, C.W. Liu, S.R. Chung, C.T. Hsieh, C.E. Lee, K.W. Wang, *Chem. Commun.* 2014, **50**, 11165.
- Y.C. Tseng, H.S. Chen, C.W. Liu, T.H. Yeh, K.W. Wang, *J. Mater. Chem. A* 2014, **2**, 4270.
- S. Mukerjee, S. Srinivasan, M.P. Soriaga, J. McBreen, *J. Electrochem. Soc.* 1995, **142**, 1409.
- C.W. Liu, Y.C. Wei, C.C. Liu, K.W. Wang, *J. Mater. Chem.* 2012, **22**, 4641.
- T.H. Yeh, C.W. Liu, H.S. Chen, K.W. Wang, *Electrochem. Commun.* 2013, **31**, 125.
- Y. T. Liang, S. P. Lin, C. W. Liu, S. R. Chung, T. Y. Chen, J. H. Wang, K. W. Wang, *Chem. Commun.* 2015, DOI: 10.1039/C5CC01629K.
- S. Sun, F. Jaouen, J.P. Dodelet, *Adv. Mater.* 2008, **20**, 3900.
- X. Yu, S. Ye, *J. Power Sources* 2007, **172**, 145.

Table 1 The comparisons of j , MA, SA, decay rates at 0.88 V, ECSA, and surface compositions for Pt/C and various NRs.

Sample	$j_{0.88}$ (mA/cm ²)	Decay (%)	ECSA (m ² /g _{Pt})	MA _{0.88} (mA/mg)	SA _{0.88} (mA/cm ²)	Pt/PtO (at %)
Pt/C	2.2	81.8	67.5	83.1	0.12	70/30
Pt-1	2.6	80.0	41.4	126.2	0.30	75/25
Pt-2	2.8	78.6	36.2	143.0	0.40	79/21
Pt-3	3.0	66.7	34.0	174.3	0.51	80/20
PtAu	3.1	41.0	24.7	198.0	0.80	89/11

- S. Guo, D. Li, H. Zhu, S. Zhang, N.M. Markovic, V.R. Stamenkovic, S. Sun, *Angew. Chem., Int. Ed.* 2013, **52**, 3465.
- J. Zhang, K. Sasaki, E. Sutter, R. R. Adzic, *Science* 2007, **315**, 220.
- R. Woods, *Electroanalytical Chemistry*, A. J. Bard, Ed. 9, 1976.
- M. Peuckert, T. Yoneda, R.A. Dalla Betta, M. Boudart, *J. Electrochem. Soc.* 1986, **133**, 944.
- Y. Xu, A.V. Ruban, M. Mavrikakis, *J. Am. Chem. Soc.* 2004, **126**, 4717.

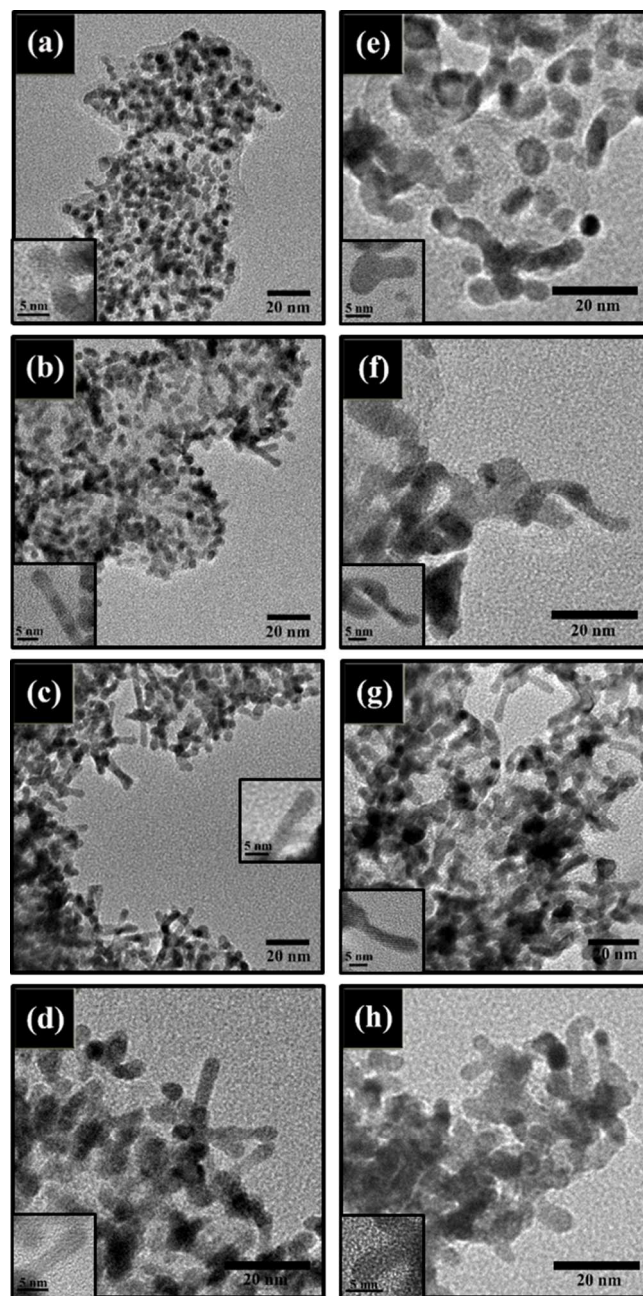


Fig. 1. HRTEM micrographs of catalysts before and after ADT for Pt-1 (a) and (e), Pt-2 (b) and (f), Pt-3 (c) and (g), and PtAu (d) and (h), respectively.

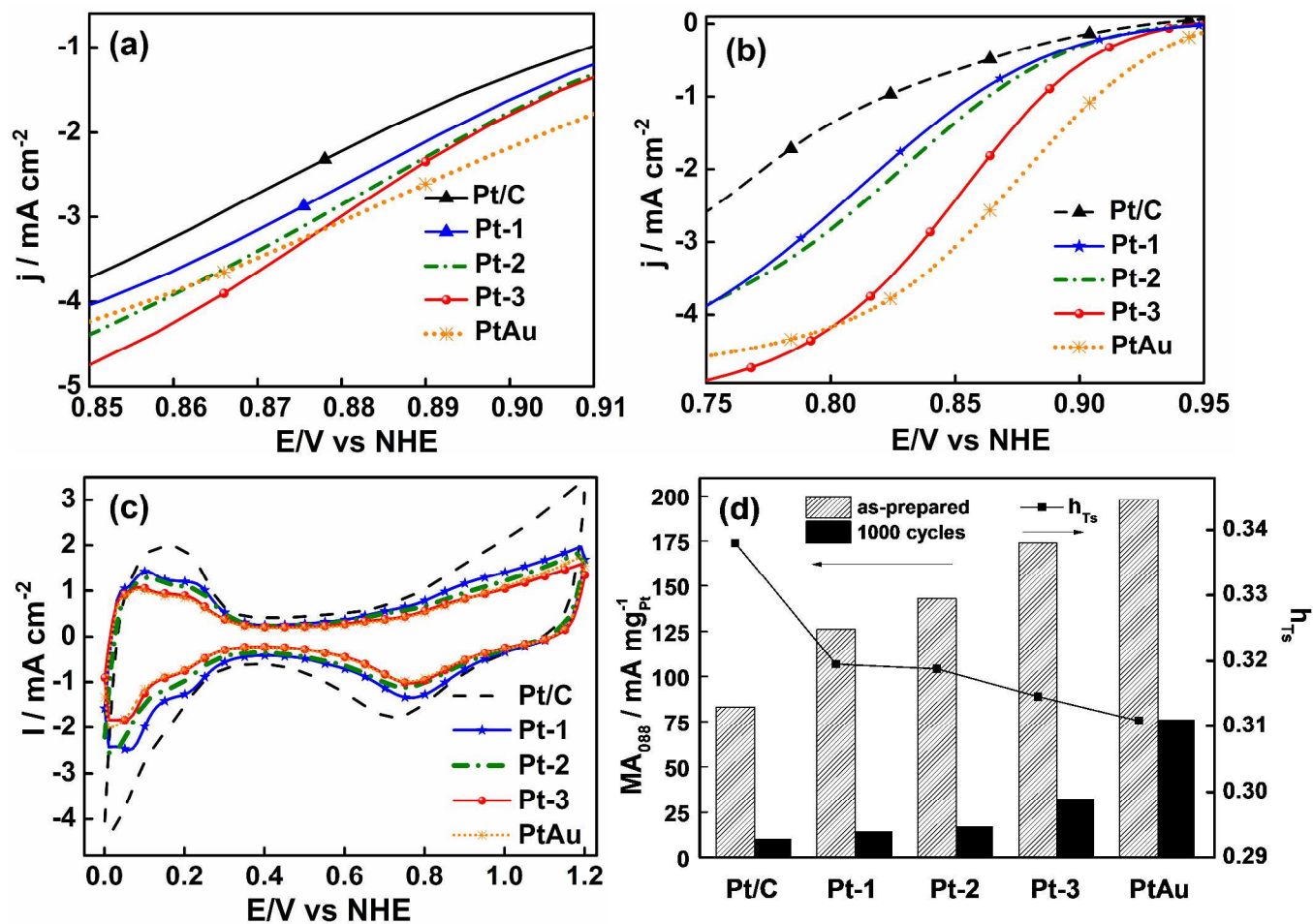


Figure 2 LSV results obtained in O_2 -saturated 0.5 M $HClO_4$ (a) before and (b) after 1000 cycles of ADT, (c) CV scans obtained in 0.5 M $HClO_4$ saturated with N_2 , and (d) the comparisons of h_{Ts} and MA at 0.88 V before and after ADT for Pt/C and various NRs.