Facile preparation of nanoporous platinum and its high electrocatalytic performances

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ABSTRACT

Nanoporous platinum was fabricated by a simple dealloying method. Electron microscope characterizations show that selectively etching Al from PtAl alloy precursors in alkali or acid solution can both easily prepare three-dimensional bicontinuous network nanostructures of Pt. The resulted nanostructure exhibited much enhanced catalytic performance towards methanol electrooxidation compared with commercial Pt/C catalyst. More importantly, CO stripping and potentiostatic tests demonstrated that nanoporous Pt has much higher long-term catalytic stability and CO resistance than the Pt/C catalyst. Copyright © 2011 VBRI press.

Keywords: Dealloying; nanoporous; platinum; methanol; electrooxidation.

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Introduction

Direct methanol fuel cells (DMFCs) represent a particular class of alternative source to the combustion engine in transportation applications and electrical power generation because of their high efficiency and low emission of pollutants [1]. Among various anodic catalysts in DMFCs, platinum shows the highest electrocatalytic activity for methanol electrooxidation. Especially, highly dispersive Pt nanoparticles supported on carbon powder have been employed as commercialized catalysts. In order to further enhance the catalytic efficiency, a variety of Pt nanostructures have been prepared such as nanoparticles [2], nanorods [3], nanowires [4], nanotubes [5], etc, which all exhibit much enhanced electrocatalytic activity compared with particle-type Pt/C catalyst. It is known that the preparation method of Pt catalysts is essential to their practical application considering the simple operation, high yielding, high reproducibility of catalyst, and large synthesis scale etc. However, these Pt nanostructures stated above are commonly fabricated through reducing the Pt precursor salts with the excessive use of organic reducing agents and surfactants at relatively high temperatures [2-6], which usually involve multistep operation, and are consequently difficult to simultaneously achieve a good control to the morphology and structure uniformity of the resulted Pt nanostructures. Consequently, a simple and effective method to highly active Pt nanocatalysts is desired to promote the practical application of Pt catalysts and the development of fuel cell techniques.

Recently, an extremely simple dealloying method (selective dissolution of one or more components from alloys) is demonstrated to be an effective strategy to produce a novel class of open bicontinuous network nanostructure with the advantages of simplicity, perfect yielding, and no usage of organic regents [7-9]. At present, by means of dealloying method many nanoporous metallic materials [10,11] have been successfully fabricated, such as nanoporous gold [12], silver [13], copper [14], PtAu alloy [15], and PtRu alloy [16] etc. More importantly, these nanoporous metallic materials prepared by dealloying have exhibited great application potentials in a variety of fields such as electrocatalysis, sensing, and optics due to their special nanoarchitecture characterized by bicontinuous nanoscale skeletons and interconnected hollow channels, which are favorable for easy mass transport and high electron conductivity. In particular, nanoporous gold (NPG) made by dealloying AuAg alloys shows interesting catalytic and electrocatalytic [17], optical [18] and surface-enhanced Raman scattering [19] performances. Despite the considerable investigations on NPG, there is still little attention paid to the fabrication of nanoporous platinum (np-Pt) by dealloying method. Here, we fabricate np-Pt sample by selectively dealloying of PtAl alloy, and investigated its catalytic performance towards methanol electrooxidation.

Experimental

High purity (>99.99%) Pt and Al were purchased from Shanghai Huachen Noble Metal Company. Analytical reagent (AR) grade H_2SO_4, CH_3OH and NaOH were obtained from Sinopharm Chemical Reagent Co. Ltd and were used as received without further purification. The E-TEK Pt/C catalyst (20 wt. % on carbon) was purchased from Aldrich. High purity N_2 and CO (>99.99%) gas was purchased from Jinan Deyang Special Gas Co. Ltd.

PtAl alloy foils with Al atomic content at ~80% were made by refining high purity Pt and Al under the protection of high purity argon in an arc furnace, and followed by melt-spinning. The typical np-Pt sample was prepared by dealloying PtAl alloy in 0.5 M NaOH solution for 48 h at room temperature.

All electrochemical measurements were carried out by CHI760D potentiostat in a standard three-electrode cell with a Pt plate working as the counter electrode and a reversible hydrogen electrode (RHE) as the reference electrode. The catalyst ink was prepared by mechanically mixing 2.0 mg np-Pt sample, 1.0 mg carbon powder, 300 μL isopropanol, and 100 μL Nafion solution (0.5 wt%), and the mixture were sonicated for 30 min to form a uniform suspension. The catalyst suspension was placed on a polished glassy carbon working electrode with 4 mm diameter. Pt/C catalyst was prepared by the same way except the addition of carbon powder. Prior to activity measurements, all electrodes are made pretreatment by cyclic voltammetry scan in the 0.5 M H_2SO_4 solution deoxygenated by bubbling with high-purity N_2 for 30 min. CO stripping experiments were carried out by first holding the thus-made electrodes at 0.15 V (vs RHE) in a 0.5 M H_2SO_4 solution with continuous CO bubbling for 20 min.

The electrode was then transferred into a 0.5 M N_2-purged H_2SO_4 solution to record the profiles. X-ray diffraction data (XRD) were collected on a Bruker D8 advanced X-ray diffractometer using Cu KR radiation (λ=1.5418 A°) at a scan rate of 0.04 s⁻¹. The microstructures of all samples were characterized on a JEOL JSM-6700F field emission scanning electron microscope (SEM).

Results and discussion

In the previous studies, dealloying of Al-based alloys has been found to be an effective method to fabricate nanoporous materials, such as Raney Ni made by dealloying of NiAl alloy in NaOH solution [20]. Recently, the dealloying method has been proved to be very successful to generate other nanoporous metal materials [21, 22]. In current work, we adopted Pt/Al as the precursor alloy to prepare np-Pt because Al metal has more reactive chemical property, rich source, and low cost. To explore the preparation of np-Pt in more detail, both NaOH and HCl electrolyte were selected to dissolve Al atoms. As shown in **Fig.1a**, after selectively etching Al in 0.5 M NaOH solution at room temperature, the remained Pt atoms self-assembled to form an open bicontinuous spongy morphology. It is clearly found that the resulted structure has the narrow size distribution with the typical dimension at ~4 nm. From the cross-section SEM image (**Fig. 1b**); it is evident that the bicontinuous nanoporosity extended along the whole three-dimensional structure, which favors good electronic conductivity and mass transport along the networks during catalysis process [15]. **Fig. 1c&d** illustrated the resulted nanoporous structure after dealloying PtAl alloy in HCl solution, which is similar to that obtained in alkali solution with the typical size less than 10 nm. It is concluded that np-Pt can be easily prepared by dealloying either in alkali or in acid solutions.
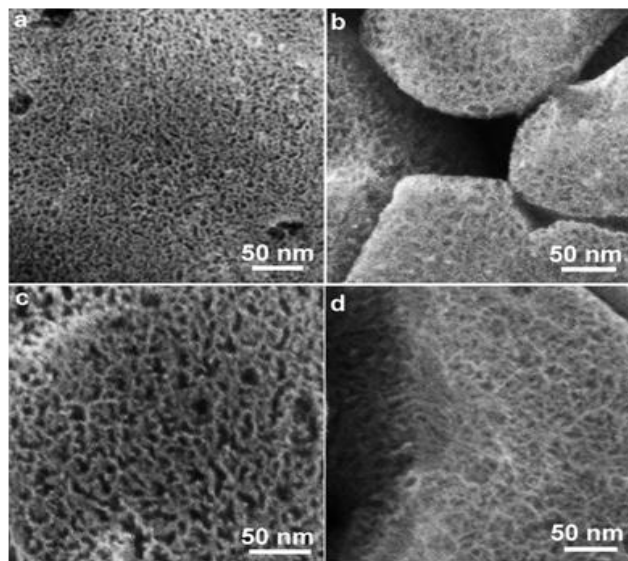
Fig. 1. SEM images of np-Pt samples by dealloying PtAl alloy in 0.5 M NaOH solution for 48 h (a, b), and in 1 M HCl solution for 24 h (c, d), respectively.

XRD was used to examine the crystalline structure of the dealloyed Pt sample in NaOH solution. **Fig. 2** listed the

patterns for PtAl alloy and np-Pt sample along with those of pure Pt and Al for comparison. From the rather complicated diffraction patterns for PtAl alloy, there are no evident diffraction peaks related to individual phases of Pt and Al metals, or there compounds of other type, indicating the formation of uniform PtAl alloy. After dealloying of PtAl alloy in NaOH solution, the resulted structure shows a set of three diffraction peaks, which is corresponding to a single phase face-centered cubic crystal structure of Pt (JCPDS 65-2868).
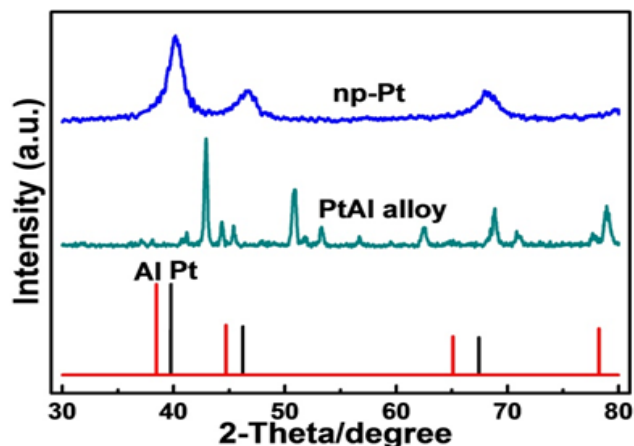

Fig. 2. XRD patterns for PtAl alloy and np-Pt with the standard patterns for pure Pt (JCPDS 65-2868) and Al (JCPDS65-2869) attached for comparison.
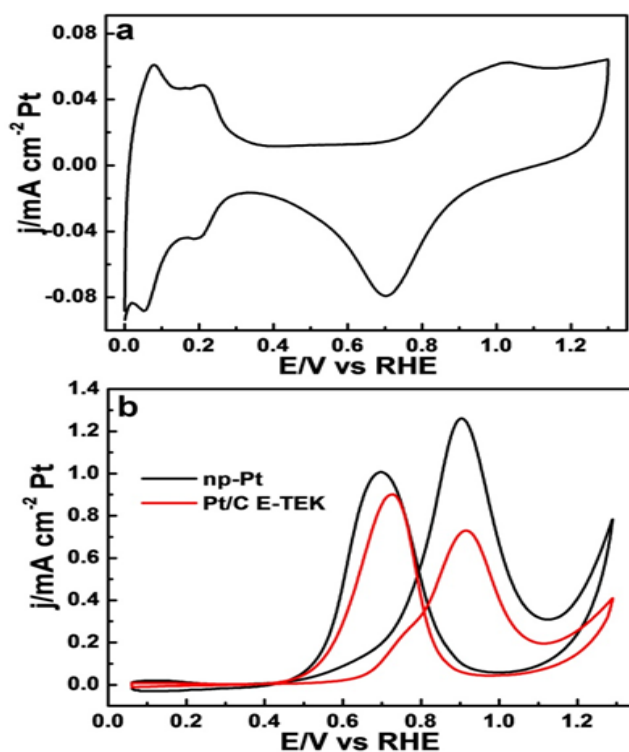

Fig. 3. (a) CV profiles of np-Pt in 0.5 M H_2SO_4 solution. Scan rate: 50 mV/s. (b) CVs of np-Pt and Pt/C catalysts in 0.5 M H_2SO_4 and 1.0 M CH_3OH mixed solution. Scan rate: 20 mV/s.

Np-Pt sample has open interconnected hollow channels and bicontinuous nanoscaled skeleton across the whole structure, which is particularly desirable for electrocatalysis in terms of unlimited mass transport for methanol electrooxidation. **Fig. 3a** gives the CV curve of np-Pt catalyst in 0.5 H_2SO_4 solution, which shows typical electrochemical features including the well-defined hydrogen adsorption/desorption, electrochemical double-layer, and platinum oxides reduction peaks. Two broad peaks in the potential range from 0 to 0.35 V are associated with the adsorption and desorption of hydrogen on Pt surface along with the adsorption/desorption of the SO_4^{2-} anions. During the backward scan the evident cathode peak located at 0.70 V is ascribed to the reduction of Pt oxides. For the aim of exploring the application potential of np-Pt in DMFCs, we tested its catalytic activity toward methanol electrooxidation. As shown in **Fig. 3b**, during the forward scan the current increases rapidly with the increase of electrochemical potential, and reaches a maximum where the kinetic is optimized by a balance between the methanol dehydrogenation and subsequent oxidation of dissociative intermediates [23]. After that, the fast decrease of current density is ascribed to the formation of OH_{ads} on Pt, which occupy the surface active sites for methanol dehydrogenation. In the forward scan the peak located at 0.90 V for np-Pt sample, which is slower than that of Pt/C catalyst (0.915 V) [24]. During the backward sweep, the active metallic Pt surface was regenerated due to the desorption of OH_{ads} or reduction of Pt oxides, which allows further oxidation of methanol molecules. The lower forward peak potential implicated the facile oxidation of methanol molecules on the surface of np-Pt sample compared with Pt/C catalyst. In addition, the specific activity of the np-Pt sample is almost two times of that of Pt/C catalyst. Meanwhile, the onset oxidation potential on np-Pt is around 0.4 V, which is ~20 mV lower than that of Pt/C. The characteristic parameters in terms of onset oxidation potential, peak potential, and specific activity indicate the much higher electrocatalytic activity of np-Pt towards methanol oxidation compared with Pt/C catalyst.

CO electrooxidation activity on np-Pt sample was also explored to further evaluate its electrocatalytic property. As shown in Fig. 4a, the peak potential for CO oxidation on np-Pt sample is around 0.80 V, which it is ~0.83 V for Pt/C [24]. The more negative CO stripping potential suggests that CO can be more easily removed on np-Pt sample, suggesting a higher CO-tolerance. The activity difference for CO stripping on np-Pt and Pt/C catalysts may be associated with the different nanostructure. It is proposed [25] that CO electrooxidation includes the activation of water to form OH_{ads}, followed by CO_{ads} oxidation by reacting with OH_{ads}. During CO oxidation, CO molecules adjacent to OH active sites are first oxidized, and the residual CO molecules must move to appropriate reaction sites in order to be involved in the reaction. Consequently, CO surface diffusion is considered to be essential for the reaction between CO and OH on Pt, however, which is restricted on smaller Pt nanoparticles [26]. Upon decreasing the particle size, the restricted supply of CO to the active sites may become rate limiting for CO electrooxidation. In addition, many previous reports found a stronger adsorption of CO as well as OH on smaller Pt particles due to the predominant structure effect

[**27**], in which the compression effect can be negligible because of a very small compressive strain compared to bulk Pt [**28**]. The positive shift of the Pt/C nanoparticles compared to bulk Pt foil can be attributed to the interplay between the restricted CO surface diffusion and the strengthened Pt-CO and Pt-OH bonds on smaller platinum particles.
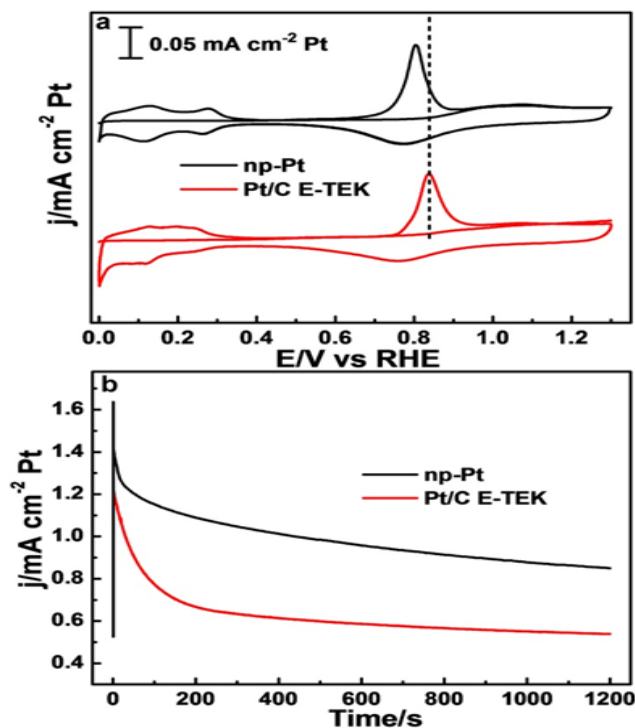
Fig. 4. (a) Electrochemical CO-stripping curves for np-Pt and Pt/C catalysts in N_2-purged 0.5 M H_2SO_4 solution. Scan rate: 20 mV/s. (b) Current-time curves recorded in 0.5 M H_2SO_4 + 1.0 M CH_3OH solution at 0.8 V for 20 min at room temperature.

The long-term activity of electrocatalysts is also one of the key factors to evaluate their values for practical application. We further explored the steady-state specific activity of np-Pt sample by using potentiostatic method. **Fig. 4b** presents the corresponding current-time curves of np-Pt and Pt/C catalysts. At the beginning the current decreased rapidly for both catalysts due to the formation of double layer capacitance [**29**]. In the following, the current decay is caused by accumulated CO_{ads}, $HCOO^-$, HCO^- intermediates adsorbed on Pt surface during methanol dehydrogenation [**30-32**]. In addition, SO_4^{2-} adsorption [**33**] on the catalyst surface also leads to the current decay by occupying the reaction active sites. It can be found that the current decreases more rapidly on Pt/C catalyst at the earlier stage, indicative of fast poisoning on catalyst surface. With extending the reaction time, the current decay became slow and reached a quasi-equilibrium steady state. In comparison, during the whole reaction process the current density of np-Pt sample declined slowly, and finally maintained much higher steady-state currents than Pt/C. The evidently enhanced catalytic durability of np-Pt sample is considered to result from the special nanoarchitecture. Especially, the bicontinuous hollow channels and skeleton along the three-dimensional structure are beneficial for the

mass transport and electron conductivity. In addition, the much higher CO-tolerance as shown in Fig.4a favors the catalytic durability owing to lessening the poisoning of Pt surface.

Conclusion

In summary, we described a general and simple strategy to fabricate np-Pt with uniform 3D bicontinuous nanoporous network structure, which shows superior catalytic activity, stability, and CO tolerance to methanol electrooxidation than the commercial Pt/C catalyst. Nanoporous Pt shows potential application in heterogeneous catalysis and fuel-cell technologies in terms of simple preparation and high catalytic performance.

Reference

1. Arico, A.S.; Srinivasan, S.; Antonucci, V. *Fuel Cells* **2001**, *1*, 133.
   DOI : 10.1002/1615-6854(200107)
2. Kardash, D.; Korzeniewski, C. *Langmuir* **2000**, *16*, 8419.
   DOI: 10.1021/la000544e
3. Kobayashi, T.; Babu, P.K.; Gancs, L.; Chung, J.H.; Oldfield, E.; Wieckowski, A. *J. Am. Chem. Soc.* **2005**, *127*, 14164.
   DOI: 10.1021/ja0550475
4. Peng, X.; Koczkur, K.; Nigro, S.; Chen, A. *Chem. Commun.* **2004**, 2872.
   DOI: 10.1039/B412677G
5. Yuan, J.; Wang, K.; Xia, X. *Adv. Funct. Mater*. **2005**, *15*, 803.
   DOI: 10.1002/adfm.200400321
6. Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. *Chem. Rev.* **2005**, *105*, 1025.
   DOI: 10.1021/cr030063a
7. Erlebacher, J.; Aziz, M.J.; Karama, A.; Dimitrov, N.; Sieradzki, K. *Nature* **2001**, *410*, 450.
   DOI: 10.1038/35068529
8. Ding, Y.; Chen, M.W. *MRS Bull.* **2009**, *34*, 569.
   DOI: 10.1557/mrs2009.156
9. Rolison, D.R. *Science* **2003**, *299*, 1698.
   DOI: 10.1126/science.1082332
10. Erlebacher, J. *J. Electrochem. Soc.* **2004**, *151*, C614.
    DOI: 10.1149/1.1784820
11. Xu, C.X.; Su, J.X.; Xu, X.H.; Liu, P.P.; Zhao, H.J.; Tian, F.; Ding, Y. *J. Am. Chem. Soc*. **2007**, *129*, 42.
    DOI: 10.1021/ja0675503
12. Ding, Y.; Jonah, E. *J. Am. Chem. Soc.* **2003**, *125*, 7772.
    DOI: 10.1021/ja035318g
13. Xu, C.X.; Li, Y.Y.; Tian, F.; Ding, Y. *ChemPhysChem* **2010**, *11*, 3320.
    DOI: 10.1002/cphc.201000313
14. Qi, Z.; Zhao, C.; Wang, X.G.; Lin, J.K.; Shao, W.; Zhang, Z.H.; Bian, X. F. *J. Phys. Chem. C* **2009**, *113*, 6694.
    DOI: 10.1021/jp808569g
15. Xu, C.X.; Wang, R.Y.; Chen, M.W.; Zhang, Y.; Ding, Y. *Phys. Chem. Chem. Phys.* **2010,** *12*, 239.
    DOI: 10.1039/b917788d
16. Xu, C.X.; Wang, L.; Mu, X.L.; Ding, Y. *Langmuir* **2010**, *26*, 7437.
    DOI: 10.1021/la9041474
17. Zielasek, V.; Jurgens, B.; Schulz, C.; Biener, J.; Biener, M.M.; Hamza, A.V.; Bäumer, M. *Angew. Chem. Int. Ed.* **2006**, *45*, 8241.
    DOI: 10.1002/anie.200602484
18. Ding, Y.; Kim, Y.J.; Erlebacher, J. *Adv. Mater.* **2004**, *16*, 1897.
    DOI: 10.1002/adma.200400792
19. Chen, L.Y.; Zhang, L.; Fujita, T.; Chen, M.W. *J. Phys. Chem. C* **2009**, *113*, 14195.
    DOI: 10.1021/jp035246f

20. Tappan, B. C.; Steiner, S. A.; Luther, E. P. *Angew. Chem. Int. Ed* **2010,** *49*, 4544.
    DOI: 10.1002/anie.200902994
21. Zhang, Z.H.; Wang, Y.; Qi, Z.; Zhang, W.H.; Qin, J.Y.; Jan, F. *J. Phys. Chem.* **2009**, *113*, 12629.
    DOI: 10.1021/jp811445a
22. Koh, S.; Strasser, P. *J. Am. Chem. Soc.* **2007**, *129*, 12624.
    DOI: 10.1021/ja0742784
23. Tripkovic, A.V.; Popovic, K.D.; Grgur, B.N.; Blizanac, B.; Ross, P.N.; Markovic, N. M. *Electrochim. Acta* **2002**, *47*, 3707.
    DOI: 10.1016/S0013-4686(02)00340-7
24. Xu, C.; Wang, L.; Wang, R.; Wang, K.; Zhang, Y.; Tian, F.; Ding, Y. *Adv. Mater.* **2009**, *21*, 2165.
    DOI: 10.1002/adma.200702700
25. Maillard, F.; Savinova, E.; Stimming, U. *J. Electroanal. Chem.* **2007**, *599*, 221.
    DOI: 10.1016/j.jelechem.2006.02.024
26. Maillard, F.; Eikerling, M.; Cherstiouk, O.V.; Schreier, S.; Savinova, E.; Stimming, U. *Faraday Discuss*. **2004**, *125*, 357.
    DOI: 10.1039/b303911k
27. Arenz, M.; Mayrhofer, K. J. J.; Stamenkovic, V.; Blizanac, B. B.; Tomoyuki, T.; Ross, P. N.; Markovic, N. M. *J. Am. Chem. Soc.* **2005**, *127*, 6819.
    DOI: 10.1021/ja043602h
28. Zhang, J.; Mo, Y.; Vukmirovic, M. B.; Klie, R.; Sasaki, K.; Adzic, R. R. *J. Phys. Chem. B* **2004**, *108*, 10955.
    DOI: 10.1021/ja053695i
29. Li, X.; Qiu, X.; Yuan, H.; Chen, L.; Zhu, W. *J. Power Sources* **2008**, *184*, 353.
    DOI: 10.1016/j.jpowsour.2008.03.058
30. Prabhuram, J.; Zhao, T. S.; Tang, Z. K.; Chen, R.; Liang, Z. X. *J. Phys. Chem. B* **2006**, *110*, 5245.
    DOI: 10.1021/jp0567063
31. Chen, Y. X.; Miki, A.; Ye, S.; Sakai, H.; Osawa, M. *J Am Chem Soc* **2003**, *125*, 3680.
    DOI: 10.1021/ja029044t
32. Lin, W. F.; Wang, J. T.; Savinell, R. F. *Electrochem Soc* **1997**, *144*, 1917.
    DOI: 10.1149/1.1837721
33. Guo, J. W.; Zhao, T. S.; Prabhuram, J.; Chen, R.; Wong, C. W. *Electrochim. Acta* **2005**, *51*, 754.
    DOI: 10.1016/j.electacta.2005.05.056

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