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Article

Interatomic diffusion in Pd-Pt core-shell nanoparticles

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ABSTRACT

Pt monolayer-based core-shell catalysts have garnered significant interest for the application of low temperature fuel cell technology as their use may enable a decreased loading of Pt while still providing sufficient current density to meet volumetric requirements. One promising candidate in this class of materials is a Pd@Pt core-shell catalyst, which shows enhanced activity toward oxygen reduction reaction (ORR). One concern with the use of Pd@Pt, however, is the durability of the core-shell structure as Pd atoms are thermodynamically favored to migrate to the surface. The pathway of the migration has not been systematically studied. The current study explores the stability of this structure to thermal annealing and probes the effect of this heat treatment on the catalyst surface structure and its oxygen reduction activity. It was found that surface alloying between Pd and Pt occurs at temperatures as low as 200 °C, and significantly alters the structure and ORR catalytic activity in the range of 200–300 °C. Our results shed lights on the thermal induced interatomic diffusion in all core-shell and thin film structures.

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1. Introduction

Core-shell nanoparticles consisting of a Pd core and a Pt-based shell with one or a few atomic monolayer thickness have attracted great attention due to their unique properties [1–9]. Most importantly, this Pd@Pt core-shell nanostructure allows efficient utilization of the scarce and expensive Pt by improving its dispersion. Additionally, compressive strain in the Pt surface atoms is induced by the underlying Pd lattice that weakens the interaction of oxygen-containing species with the surface of Pd@Pt in comparison to that with Pt nanoparticles

[1,10]. The weakened oxygen binding energy can promote a more active electrocatalyst toward oxygen reduction reaction (ORR) due to the presence of fewer OH groups blocking the sites [10,11]. The combination of these factors promotes an improvement in Pt mass activity at 0.9 V by up to 5 times in comparison to the commercial Pt/C [12]. Because of these beneficial properties, Pd@Pt core-shell catalysts have garnered significant interest for the application in low temperature fuel cell technology as their use may enable a decreased loading of Pt while still providing sufficient current density to meet volumetric requirements. Despite these attractive properties, one

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concern about their use is the structural stability of the core-shell nanoparticle. Under certain conditions there is a thermodynamic driving force for Pd segregation to the surface and/or mixing of the Pt and Pd near the surface. Due to the relatively low activity and stability of Pd and Pd-Pt alloys [13], this occurrence can significantly decrease the activity and long-term durability of the core-shell catalyst.

The fuel cell performance of Pd@Pt catalysts, however, is still unsatisfactory in consideration of its huge improvement over Pt/C by rotating disk electrode testing in the liquid cell. We even found that the fuel cell performance of Pd@Pt catalysts was even lower than that of Pt/C. We suspect that catalysts might undergo a structure change from core-shell to alloy (at least in the surface and subsurface region) during the ink preparation step. Some dispersion techniques can generate a significant amount of thermal energy causing an increase of the local temperature. The thermal energy/local temperature is high enough to overcome the kinetic barrier of inter-diffusion between Pd and Pt atoms. The migration of the Pd atoms in the core to the surface has not been studied systematically. There is a lack of understanding of the pathways of atomic diffusion in the core-shell structure, the initial and propagation of atomic diffusion as a function of temperature at the atomic scale. More importantly, the threshold temperature at which the structure evolution starts to occur is unknown. In addition, the relationship between the activity and the structure has not been explored. In this work, the thermally induced evolution of Pd@Pt core-shell structures and its impact on the ORR activity are systematically studied by using *in situ* X-ray diffraction (XRD) [14], scanning transmission electron microscopy coupled with electron energy loss spectroscopy (STEM-EELS), and electrochemical techniques. It is confirmed that the obvious surface alloying of Pt and Pd occurs at temperatures as low as 200 °C, which leads to a loss of activity toward ORR.

2. Experimental

2.1. Synthesis of core-shell material

A custom reactor was built to synthesize gram-scale batches of core-shell catalysts using commercial Pd nanoparticles supported on Ketjen Black (Pd/C) as the core materials (TKK, 35 wt%). The reactor comprised a graphite sheet as the working electrode, carbon cloth as the counter electrode, and an Ag/AgCl leak-free reference electrode (BASi). The Pd/C nanoparticles were dispersed in a 50 mM H₂SO₄ solution, and then added to the reactor. Pretreatment of the Pd/C was conducted as needed to wet the powder. After pretreatment, a deaerated aqueous CuSO₄ solution in 50 mM H₂SO₄ was added to the reactor to obtain a Cu²⁺ concentration of 50 mM. After addition of the CuSO₄, the potential was held at approximately 0.37 V vs. Ag/AgCl to deposit an atomically thin layer of Cu on the Pd nanoparticles. Immediately upon completion of the Cu UPD (under potential deposition), a deaerated aqueous solution of K₂PtCl₄ was added dropwise to the reactor to perform galvanic replacement of the Cu by the Pt. In addition to the Pt precursor, citric acid was also included in the Pt precursor solution to

minimize the formation of Pt clusters. After the reaction was complete, typically in 30 minutes, catalysts were filtered and rinsed with ultrapure water (Milli-Q UV-plus water). The resulting catalyst powder, denoted as Pd@Pt/C, was dried in a vacuum at 60 °C. Only a trace amount of Cu (less than 0.4%) remained in the final product based on inductively coupled plasma-mass spectrometry (ICP-MS) measurements.

The resulting Pd@Pt/C material was subsequently heat treated in a quartz tube furnace under an inert Ar atmosphere with a flow rate of approximately 100 mL min⁻¹. The atmosphere was first purged for 1 h to remove oxygen prior to elevation of the temperature. The temperature program consisted of a 1 h ramp to and then a 30 min hold at the desired temperature, followed by turning off the heating elements and allowing the material to cool under the flow of Ar. It is assumed that the metal loadings of the annealed materials are the same as the untreated one, a good assumption for the relatively low temperatures used in this study at which carbon combustion is not expected.

2.2. Electrochemical measurements

The ability of these materials to catalyze the electrochemical reduction of oxygen was determined via the rotating disk electrode (RDE) method. Approximately 15 mg of the Pd@Pt/C material was dispersed in a solvent consisting of 7.5 mL of MilliQ UV-plus water, 7.5 mL of isopropanol and 60 μL of 5 wt%, 1100 EW Nafion (Ion Power) via 30 minutes of sonication. Ten μL of the ink was pipetted onto a polished glassy carbon substrate (RDE, 5 mm diameter, Pine Instruments) and allowed to dry. The Pt loading on the electrode was about 1 μg. The resulting electrode was placed in a three electrode electrochemical cell containing 0.1 M aqueous perchloric acid (HClO₄, GFS Chemicals) solution. The working electrode in the setup was the RDE, the counter electrode was a Pt mesh pressed onto a Pt wire, and a reversible hydrogen electrode (RHE) was used to measure the potential. All the potentials were referred to the RHE scale if not otherwise mentioned. Prior to evaluation of the material, ten cyclic voltammetry (CV) cycles between 0.05 and 1.2 V at a scan rate of 100 mV s⁻¹ were performed in N₂-saturated HClO₄ to clean the surface of the catalyst. After cleaning, the electrochemically active surface area (ECA) of the material was determined by performing 2 CV cycles from 0.05 to 1.2 V at 50 mV s⁻¹. For this, the hydrogen adsorption peak was integrated to determine the charge, and this was divided by 210 μC cm⁻², the charge density of an adsorbed monolayer of hydrogen atoms [15]. Finally, the electrode was evaluated for its oxygen reduction reaction (ORR) activity by potential cycling from 1.1 to 0.1 V at 10 mV s⁻¹ while rotating the RDE at 1600 rpm in O₂-saturated 0.1 M HClO₄. The kinetic current, *i_k*, at 0.9 V was calculated from the Koutecky-Levich equation,

$$1/i = 1/i_k + 1/i_L$$

where *i* is the measured current and *i_L* is the diffusion limited current. It is noted that the current was measured during the anodic potential sweep. The specific activity (SA) and mass activity (MA) were then calculated by normalizing the kinetic current by surface area and Pt mass, respectively.

CO stripping was performed to help elucidate the surface structural changes during thermal treatment. These experiments were performed with the RDE setup described above. After cleaning the surface of the catalyst via potential cycling, the potential was held at 100 mV vs RHE in CO-saturated 0.1 M HClO₄. After holding the potential for 15 min, the cell was then purged with N₂ for 30 min while continuing to hold the potential at 100 mV. Finally, cyclic voltammetry was performed with a scan rate of 20 mV s⁻¹ to electrochemically desorb the CO and to observe the hydrogen adsorption-desorption peaks on the catalyst surface.

2.3. Materials characterizations

In situ XRD experiments were performed at Beamline X18A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) in Upton, NY. Briefly, helium (99.999%, Praxair) and hydrogen (99.999%, Praxair) were metered through a home-made sample cell by two mass flow controllers (Brooks 5850) at a flow rate of ~20 mL min⁻¹. The atmosphere was first purged with He to prevent burning the catalyst powders via the combustion of H₂. The XRD spectra were recorded with a 2D detector (Perkin Elmer XRD 1621 N ES) at 20 keV (calibrated by the Mo K absorption ($\lambda = 0.7107 \text{ \AA}$)) and subsequently processed by standard software. The dark current was collected over 40 s (10 exposures at 4 s per exposure) and the diffraction pattern was recorded over 400 s (100 exposures at 4 s per exposure). After recording the XRD pattern under an inert atmosphere, the cell was purged with H₂ for 10 min and the XRD spectra were then recorded under this atmosphere. Further purging with H₂ did not affect the structure of the material. Finally, the cell was purged with He for 10 minutes and a post-H₂ exposure XRD spectrum was recorded. The sample to detector distance was approximately 400 mm and was calibrated by the use of titanium dioxide (rutile) powder loaded into the sample holder of the cell in an identical fashion as done for catalyst characterization. Performing a calculation of error propagation suggests that an error in sample position of $\pm 1 \text{ mm}$ will result in an error in the lattice constant of $\pm 0.001 \text{ nm}$. Further, there is an internal calibration

standard for each sample corresponding to amorphous carbon peak, which is present in all of the XRD spectra collected in this work, and which always lies at the same value of 2θ . All data was processed by standard data processing software, and the data was transformed to enable direct comparison to data collected with Cu K α incident X-ray irradiation.

High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and electron energy loss spectroscopy (EELS) data were collected using a Hitachi aberration-corrected scanning transmission electron microscope (HD-2700C). An electron probe diameter of 1.3 Å with a convergence angle of 28 mrad was used. At these experimental conditions, the contrast present in the HAADF images is directly related to the atomic number and thickness of the materials. The EELS line scans were collected with a pixel time of 0.02 and 1 s, respectively, using a Gatan Enfina-ER detector.

3. Results and discussion

To experimentally probe the stability of the Pd@Pt core-shell structure to thermal energy, a combination of bulk analysis techniques were performed. *In situ* STEM-EELS provides evidence of an as synthesized core-shell structure and demonstrates mixing of Pd and Pt during annealing. Before treatment (Fig. 1(a)), two sharp Pt peaks at the each end of the EELS spatial scan demonstrated the existence of a thin Pt shell (1–2 atomic layers) on Pd. After thermal annealing in the TEM chamber for 30 min at 250 °C, these features in the same particle disappeared as shown in Fig. 1(b). This result implies that the uniform Pt shell was damaged during heat treatment at 250 °C due to the mixing of Pd-Pt atoms on the surface.

In situ XRD in a H₂ atmosphere enables real-time evaluation of Pd-Pt alloying upon exposure to elevated temperatures. This technique is rooted in the unique ability of Pd to absorb hydrogen to form Pd hydrides (PdH_x), which causes expansion in its lattice parameter from 3.89 to ~4.05 Å for PdH_{0.7} [16,17]. This shift enables the deconvolution of the Pd spectrum from Pt, which has a lattice parameter of 3.92 Å, and cannot be resolved from Pd in standard XRD measurements (in a He atmosphere in this study). For a Pd@Pt core-shell structure, it is

Fig. 1. STEM images of a Pd@Pt particle and corresponding EELS intensities for Pt and Pd of as synthesized Pd@Pt (a), and that is annealed at 250 °C for 30 min (b).

observed that the Pt shell is thin enough and/or has a sufficient number of defects (pinholes) to allow hydrogen to penetrate to the underlying Pd core where it is absorbed to form the Pd hydrides (Fig. S1) [12]. In turn, the Pd XRD peak shifts to a lower angle while the Pt spectrum is not shifted since Pt does not absorb hydrogen (Table S1). While the Pt peak will not shift, it is noted that a Pt monolayer is not detectable in a diffraction measurement since there is not sufficient long range order to create the constructive interference needed to observe a peak. Thus, the appearance of a peak corresponding to Pt in this measurement indicates the formation of Pt clusters, perhaps in the form of islands that are several atoms thick. Another consideration in interpreting this data is that the formation of Pd-Pt bonds could limit the ability of hydrogen to be absorbed by the Pd lattice. This will become more pronounced if there is mixing of the Pt and Pd near the surface. Supporting this notion is the fact that the lattice of a Pd₄Pt alloy only shifts from 3.902 to 3.925 Å upon exposure to hydrogen, an expansion of only 0.6% (Table S1). Clearly, any mixing of Pt and Pd in the structure will cause a decrease in the hydrogen uptake and a concomitant shift of the XRD reflection toward higher 2θ . That said, changes in the peak profile as a response to temperature can unambiguously be attributed to mixing of the Pd and Pt, or perhaps clustering of the Pt. Loss of the peak corresponding to PdH_{0.7}, however, is indicative of Pd-Pt alloying.

Fig. 2 illustrates the results of XRD measured in a H₂ atmosphere for Pd@Pt/C that was annealed up to 300 °C in Ar. The un-annealed Pd@Pt/C exhibited a peak with a maximum at 38.9° assigned to the (111) plane and a slight tail toward high 2θ . The peak location is in good agreement with that of PdH_{0.7}, which is centered at 38.5°. This suggests that hydrogen is able to permeate through the Pt shell, and that the amount of hydrogen absorbed by the Pd is not significantly affected by the presence of a Pt shell. The presence of the tail is indicative of an atomic thin Pt shell as supported by the STEM-EELS result. As the Pd@Pt/C was annealed, its peak shifted toward higher 2θ starting at 200 °C with a shoulder remaining at 38.9°. This suggests that there remains a core of Pd in the center of the nanoparticle, but that the Pt and Pd mix and/or alloy near the surface. With increasing the annealing temperature, the peak further shifted to higher degrees. At 300 °C, the peak increased to 39.3°.

Fig. 2. *In situ* XRD spectra measured in a H₂ atmosphere for Pd@Pt/C that was annealed from room temperature up to 300 °C in Ar.

Further supporting the hypothesis that the Pt and Pd are alloying near the particle surface is the CO stripping data exhibited in Fig. 3. As CO adsorption is not dissociative on these surfaces, the potential at which CO desorbs from the surface of these materials can be used to estimate the surface electronic properties of the catalyst. It is noted that this is a simplistic view of CO stripping since the actual mechanism of desorption involves the interaction of adsorbed hydroxyl species serving to react with CO to remove it from the surface. The CO stripping peak shifted negatively from 0.934 V when a Pt shell was deposited on the Pd/C core. Upon annealing the Pd@Pt/C, the potential of the CO stripping peak increased to 0.904 V for the material annealed at 200 °C and to 0.912 V for that annealed at 300 °C. This is interpreted as being due to alloying of Pt and Pd, with segregation of Pd to the surface being a strong possibility.

The surface alloying between Pd and Pt atoms may have a profound effect on the catalytic activity of Pd@Pt/C toward ORR. As shown in Fig. 4, the Pt mass activity at 0.9 V of the Pd@Pt/C catalysts decreased by 37% when annealed to 200 °C, and decreased by 56% after annealing at 300 °C. The decrease of the activity is due to the fact that the surface Pd-Pt alloys are less active than the core-shell catalysts, which better utilize the available Pt atoms. Besides, previous experimental and theoretical studies indicated that the Pt-O binding strength should be slightly weakened to balance the O-O bond's rupture and O/OH intermediates removal to improve the ORR activity [18]. This can be achieved by adopting the strain and ligand effects to slightly lower the d-band center position of Pt, for instance, the Pt/Pd surface [19]. The interatomic diffusion in Pd-Pt core-shell nanoparticles, however, would expose less-active sites that have a higher d-band center position than Pt/Pd (e.g. Pd, Pd-Pt alloy, Pt cluster and Pd/Pt) [19,20], and lower the catalysts activity. The thermal induced damage in the core-shell structure and accordingly lower activity can also explain the poor performance of Pd@Pt/C in fuel cell when the catalyst ink was prepared by dispersion techniques that can generate a significant amount of thermal energy.

Fig. 3. CO stripping voltammetry on Pd/C (black dashed line), as-synthesized (solid black line), annealed at 200 °C (solid blue line) and 300 °C (solid red line) Pd@Pt/C measured in 0.1 M HClO₄ solution with a scanning rate of 20 mV s⁻¹.

Fig. 4. Comparison of ORR polarization curve (a) and Pt mass activity (b) of as-synthesized and annealed Pd@Pt/C. The activity data was derived at 0.9 V and normalized to the value of the as-synthesized sample.

4. Conclusions

In summary, detailed physical characterizations and electrochemical measurements clearly demonstrated that the core-shell structure of Pd@Pt is not stable to thermal annealing. The mixing of Pd and Pt atoms occurs at temperatures as low as 200 °C, and significantly alters the structure and catalytic activity in the range of 200–300 °C. This could be problematic during the ink preparation process involving dispersion techniques generating a significant amount of heat, and membrane electrode assembly (MEA) fabrication requiring hot press. To realize the full potential of the core-shell structure to reduce the cost of fuel cell electrocatalysts, more work needs to be performed to study these issues before this class of materials will be successfully applied in PEM fuel cells. Our results also shed lights on the thermal induced interatomic diffusion issue in all core-shell and thin film structures.

Acknowledgments

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References

- [1] R. R. Adzic, J. Zhang, K. Sasaki, M. B. Vukmirovic, M. Shao, J. X. Wang, A. U. Nilekar, M. Mavrikakis, J. A. Valerio, F. Uribe, *Top. Catal.*, **2007**, 46, 249–262.
- [2] M. Shao, Q. Chang, J.-P. Dodelet, R. Chenitz, *Chem. Rev.*, **2016**, 116, 3594–3657.
- [3] M. Shao, G. He, A. Peles, J. H. Odell, J. Zeng, D. Su, J. Tao, T. Yu, Y.

Graphical Abstract

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The Pd@Pt core-shell structure can be destroyed by thermal annealing and lowers the activity toward oxygen reduction reaction.

- Zhu, Y. Xia, *Chem. Commun.*, **2013**, 49, 9030–9032.
- [4] M. Shao, T. Huang, P. Liu, J. Zhang, K. Sasaki, M. B. Vukmirovic, R. R. Adzic, *Langmuir*, **2006**, 22, 10409–10415.
- [5] X. Wang, M. Vara, M. Luo, H. Huang, A. Ruditskiy, J. Park, S. Bao, J. Liu, J. Howe, M. Chi, Z. Xie, Y. Xia, *J. Am. Chem. Soc.*, **2015**, 137, 15036–15042.
- [6] J. Zhang, F. H. B. Lima, M. H. Shao, K. Sasaki, J. X. Wang, J. Hanson, R. R. Adzic, *J. Phys. Chem. B*, **2005**, 109, 22701–22704.
- [7] J. Zhang, Y. Mo, M. B. Vukmirovic, R. Klie, K. Sasaki, R. R. Adzic, *J. Phys. Chem. B*, **2004**, 108, 10955–10964.
- [8] L. Zhang, S. Zhu, Q. Chang, D. Su, J. Yue, Z. Du, M. Shao, *ACS Catal.*, **2016**, 6, 3428–3432.
- [9] M. Zhou, H. Wang, M. Vara, Z. D. Hood, M. Luo, T.-H. Yang, S. Bao, M. Chi, P. Xiao, Y. Zhang, Y. Xia, *J. Am. Chem. Soc.*, **2016**, 138, 12263–12270.
- [10] J. Zhang, M. B. Vukmirovic, Y. Xu, M. Mavrikakis, R. R. Adzic, *Angew. Chem. Int. Ed.*, **2005**, 44, 2132–2135.
- [11] V. Stamenkovic, B. S. Mun, K. J. J. Mayrhofer, P. N. Ross, N. M. Markovic, J. Rossmeisl, J. Greeley, J. K. Nørskov, *Angew. Chem. Int. Ed.*, **2006**, 45, 2897–2901.
- [12] S. Khateeb, S. Guerreo, D. Su, R. M. Darling, L. V. Protsailo, M. Shao, *J. Electrochem. Soc.*, **2016**, 163, F708–F713.
- [13] M. H. Shao, *J. Power Sources*, **2011**, 196, 2433–2444.
- [14] M. P. Humbert, B. H. Smith, Q. Wang, S. N. Ehrlich, M. Shao, *Electrocatalysis*, **2012**, 3, 298–303.
- [15] M. Shao, J. H. Odell, S.-I. Choi, Y. Xia, *Electrochem. Commun.*, **2013**, 31, 46–48.
- [16] G. Alefeld, J. Völkl, in: *Hydrogen in Metals I-Basic Properties*, Berlin and New York, Springer-Verlag (Topics in Applied Physics. Volume 28), 1978. 442 p. (For individual items see A79-16057 to A79-16061), 1978.
- [17] A. Rose, S. Maniguet, R. J. Mathew, C. Slater, J. Yao, A. E. Russell, *Phys. Chem. Chem. Phys.*, **2003**, 5, 3220–3225.
- [18] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jonsson, *J. Phys. Chem. B*, **2004**, 108, 17886–17892.
- [19] M. Shao, P. Liu, J. Zhang, R. Adzic, *J. Phys. Chem. B*, **2007**, 111, 6772–6775.
- [20] S. J. Yoo, H. Y. Park, T. Y. Jeon, I. S. Park, Y. H. Cho, Y. E. Sung, *Angew. Chem. Int. Ed.*, **2008**, 47, 9307–9310.

钯铂核壳纳米催化剂颗粒中的原子扩散

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摘要: 铂原子单层的核壳结构催化剂因其高效的铂原子利用率和优异铂质量活性而广泛应用于燃料电池领域。在该系列材料中, 钯@铂核壳催化剂具有更优于纯铂的氧还原(ORR)催化活性, 因而拥有较好的应用前景。但由于钯原子在热力学上更倾向于富集到材料表面, 钯@铂核壳催化剂的催化稳定性及原子扩散的途径需要更深入的研究。本文探究了热处理条件对钯@铂核壳结构稳定性的破坏, 并确定了原子扩散对催化活性的影响。

原位扫描透射电子显微镜-电子能量损失谱(STEM-EELS)证明了在250 °C的氩气氛围中, 钯@铂纳米颗粒中原本清晰可见的1–2原子铂壳层已经消失, 并伴随着颗粒表面钯铂合金化的形成。因钯金属可以吸收氢气而导致晶格间距的展宽, 钯@铂核壳结构的破坏也可以通过氢气氛围中的原位X射线衍射谱中(111)衍射峰的展宽和位移进行判断。对钯@铂核壳纳米催化剂进行一系列温度的热处理结果显示, 核壳结构的破坏在200 °C左右开始, 并于200–300 °C之间急剧发生。一氧化碳电化学氧化脱附实验表明, 热处理之后的核壳催化剂表面的一氧化碳氧化峰位置发生了明显的正移, 也证明了热处理之后催化剂表面电子结构的变化。核壳结构改变对催化活性的影响也通过旋转圆盘电极进行了测量。相比于未经处理的样品, 200 °C处理之后的钯@铂核壳催化剂在0.9 V电位处的质量活性损失了约37%。进一步提高热处理温度至300 °C之后, 钯@铂核壳催化剂的质量活性只有初始状态的44%。本文揭示核壳结构中因热处理而导致的原子扩散现象, 并为燃料电池中核壳催化剂的应用及膜电极的制备工艺条件提供了参考。

关键词: 核壳催化(单层)剂; 质子交换膜燃料电池; 稳定性; 原子扩散; 电催化剂

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