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# Molten salt synthesis of carbon-supported Pt–rare earth metal nanoalloy catalysts for oxygen reduction reaction†

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The synthesis of nano-sized alloys of Pt and rare earth (RE) metal catalysts has been a huge challenge due to a significantly large standard reduction potential difference of Pt and RE metals and the high synthesis temperature. Pt<sub>x</sub>Y/C catalysts with an average particle size of around 21 nm, were synthesized by mixing K<sub>2</sub>PtCl<sub>4</sub> with Y<sub>2</sub>O<sub>3</sub> (a molar ratio of Pt : Y = 1 : 1) with a carbon support in a molten LiCl–CaH<sub>2</sub> system by a one-step molten salt synthesis method at 600 °C. The synthesis processes of the Pt<sub>x</sub>Y/C alloys are proposed as follows: Pt nanoparticles were first obtained by the reaction of K<sub>2</sub>PtCl<sub>4</sub> and CaH<sub>2</sub> at 210 °C, then Y ions were preferentially reduced on the Pt nanoparticle surface by the reduction of CaH<sub>2</sub>, followed by Pt<sub>x</sub>Y alloy formation in the molten LiCl–CaH<sub>2</sub> system at 600 °C. Molten LiCl provides a strong reducing environment and lowers the formation temperature of alloys. Pt<sub>2</sub>Gd/C and Pt<sub>2</sub>La/C were also obtained with Gd<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> as the starting raw materials, respectively by using the same process. When investigated as an electrocatalyst for the oxygen reduction reaction (ORR), the half-wave potentials of Pt<sub>x</sub>RE/Cs are all more positive than that of commercial Pt/C catalyst (e.g., 0.905 V for Pt<sub>x</sub>Y/C while 0.880 V for JM Pt/C), and the nano-sized Pt<sub>x</sub>Y/C alloy shows higher electrocatalytic activity toward the ORR and preferable catalytic durability with respect to JM Pt/C catalysts. This facile synthesis method provides an effective strategy for the preparation of Pt–RE based multicomponent nanoalloys, especially in large-scale production.

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## 1 Introduction

Nowadays proton exchange membrane fuel cells (PEMFCs), directly generating electrical energy through hydrogen oxidation at the anode and oxygen reduction reaction (ORR) at the cathode,<sup>1–3</sup> have received extensive attention in renewable energy fields (e.g. fuel cell electric vehicles), due to their advantages of low pollution and high specific energy.<sup>4–9</sup> Nevertheless, the high cost of PEMFCs still restricts their widespread commercialization in which platinum (Pt) catalysts used at both anode and cathode electrodes account for about 40% of the

cost.<sup>10</sup> In particular, the cathode requires about 9–10 times as much platinum as the anode because of its sluggish oxygen reduction reaction (ORR). Nowadays, many researchers have proposed many strategies to solve this problem, including morphology control, nanoparticles and Pt-based alloys.<sup>11–17</sup>

Pt-based alloys that can adjust the electronic structure of Pt atoms, is one of the effective strategies to enhance the activity and stability with the reduced amount of Pt in many catalysis fields.<sup>18–20</sup>

In the past two decades, the Pt-late transition metals (LTMs, such as Fe, Ni, Co *etc.*) alloys have been widely studied<sup>21</sup> and have remarkably improved the catalytic activities.<sup>22</sup> However, the late transition metals are more likely to dissolve and dealloy in the acidic medium of PEMFCs over time<sup>23</sup> due to the lower alloy formation energy between Pt and LTMs,<sup>24</sup> which results in the decrease of activity and durability of the alloys. Therefore, selection of the Pt alloys with higher alloy formation energy is beneficial to resist dealloying and maintain high stability.<sup>25,26</sup>

More recently, Greeley and his coworkers predicted and demonstrated that the Pt-rare earth metal (RE) alloys showed a significant enhanced activity by using density functional theory (DFT) calculations and experiments.<sup>27</sup> Subsequently, Sung Jong Yoo<sup>25,28</sup> explained that the strong electronic synergistic interaction between Pt and RE atoms results in the d-band center of Pt downshift, which can reduce the adsorption

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strength of oxygenated species (\*O, \*OH, \*OOH) and ultimately improve the activity. In addition, compressive strains in the particle surface will be generated in the alloy because the atomic radius of rare earth metals are larger than that of Pt, which can lower the adsorption of reaction intermediates at the Pt sites, and adjust the binding energy of oxygenated intermediates and boost ORR activity.<sup>25</sup> The application of Pt–RE alloy catalysts can not only improve the catalytic activity of ORR, but also can reduce the loading of Pt.<sup>29</sup>

However, the chemical synthesis of Pt–RE alloys is very challenging because of the vast difference of standard reduction potentials between Pt and RE metals (e.g. +1.19 V for Pt<sup>2+</sup>/Pt, −2.37 V for Y<sup>3+</sup>/Y) and the high oxygen affinity of RE metal atoms.<sup>30</sup> Moreover, synthesis of Pt–RE alloys usually needs high temperatures. For example, Pt<sub>5</sub>Ce alloy phase forms at 1529 °C according to the phase diagram.<sup>31</sup> Hence such high temperature makes it more difficult to synthesize nano-sized Pt–RE alloys. In the past decade, many efforts have been devoted to synthesize Pt–RE alloy catalysts by a variety of methods, however, only a few researches have been proved to obtain Pt–RE alloys in a strict reduction environment.<sup>29,30,32</sup> Schwämmlein *et al.* prepared Pt<sub>x</sub>Y/C alloy *via* thermally reducing YCl<sub>3</sub> with commercial Pt/C catalyst under the atmosphere of highly purified H<sub>2</sub> at 1200 °C.<sup>33</sup> Kanady *et al.* synthesized Pt<sub>3</sub>Y nanoalloy particles by heating the mixture of alkali metal triethylborohydrides (MET<sub>3</sub>BH, M = K, Na), PtCl<sub>4</sub> and YCl<sub>3</sub> to 200 °C in which MET<sub>3</sub>BH was used as the reducing agent.<sup>34</sup> Itahara *et al.* prepared Pt<sub>5</sub>Ce nanoparticles by using sodium vapor as the reducing agent at 600 °C.<sup>32</sup> Recently, Kobayashi *et al.*<sup>35</sup> reported the Pt<sub>2</sub>Y nanopowders with a reckoned particle size of 147.8 nm by molten salt synthesis (MSS), *via* mixing Pt with Y<sub>2</sub>O<sub>3</sub> in a molten LiCl–CaH<sub>2</sub> system under Ar atmosphere at 600 °C, in which CaH<sub>2</sub> was used as the reducing agent.

Molten salts usually composed of inorganic salts, are non-toxic and harmless to the environment,<sup>36</sup> which can well disperse the reactants and products, especially can lower the alloy formation temperature.<sup>37,38</sup> Therefore, MSS can be regarded as a potential candidate for preparation of Pt–RE alloys.

Before MSS of Pt<sub>2</sub>Y nanopowders, Kobayashi *et al.*<sup>35</sup> first prepared the precursor of Pt and Y<sub>2</sub>O<sub>3</sub> mixture by using H<sub>2</sub>PtCl<sub>6</sub> and Y<sub>2</sub>O<sub>3</sub> as raw materials at 500 °C, which not only made the synthesis complicated, but also increased the particle size to more than 100 nm. So, here, we simplified the synthesis procedure in one-step by directly mixing the raw materials including K<sub>2</sub>PtCl<sub>4</sub>, Y<sub>2</sub>O<sub>3</sub>, Vulcan XC-72R, LiCl and CaH<sub>2</sub>, and then directly prepared Pt<sub>2</sub>Y by heating the mixture to 600 °C. The Vulcan XC-72R is used as the carbon support of Pt<sub>2</sub>Y alloy, which can significantly isolate the alloy particles and reduce the particle size to 21 nm. At the same time, we explored the synthesis mechanism of Pt<sub>2</sub>Y nanoalloys in LiCl–CaH<sub>2</sub> molten salts and successfully prepared Pt<sub>2</sub>La and Pt<sub>2</sub>Gd alloys by using the same method. The obtained carbon-supported Pt–RE nanoalloys were used as the ORR catalysts, which showed more positive half-wave potentials than that of commercial Pt/C catalyst, e.g., 0.905 V for Pt<sub>x</sub>Y/C while 0.880 V for JM Pt/C.

## 2 Experimental

### 2.1 Main materials

The materials including lithium chloride (LiCl, ≥99%, AR, anhydrous), calcium hydride (CaH<sub>2</sub>, 95%, AR) and RE metal oxides (Y<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>) were all obtained from Aladdin Company. Potassium tetrachloroplatinate (K<sub>2</sub>PtCl<sub>4</sub>, Pt (wt%) ≥ 46%) was supplied by Tianjin Meisco Chemical, 5 wt% Nafion ionomer solution by Dupont and the carbon support Vulcan XC-72R by Cobalt. The commercial Pt/C catalysts were supplied by Johnson Matthey (20 wt% for Pt content, simplified as JM Pt/C). All the materials were used as received without for further treatment.

### 2.2 Synthesis of carbon-supported Pt–RE nanoalloy particles (Pt<sub>x</sub>RE/C)

Pt<sub>x</sub>Y/C was synthesized in molten LiCl–CaH<sub>2</sub> system by one-step MSS method. First, a precursor was obtained by mixing K<sub>2</sub>PtCl<sub>4</sub> with Y<sub>2</sub>O<sub>3</sub> in a molar ratio of Pt : Y = 1 : 1, in which the Y-rich ratio was used to ensure that all of the Pt salt were completely alloyed with RE. Next, a mixture was prepared by grounding the precursor with carbon support (Vulcan XC-72R), LiCl and CaH<sub>2</sub> in a mortar with a weight ratio of precursor (including Vulcan XC-72R): LiCl : CaH<sub>2</sub> = 1 : 40 : 10. Then the mixture was placed in a furnace to remove air for 1 hour at room temperature by purge with Ar, and heated to 600 °C at a heating rate of 5 °C min<sup>−1</sup>. Through holding 2 hours at 600 °C, the products was taken out by cooling off naturally to room temperature. The products including byproducts and excess reactants, such as Y<sub>2</sub>O<sub>3</sub>, CaH<sub>2</sub>, LiCl and CaO, *etc.* were leached by 1.0 M HNO<sub>3</sub> solution, washed with Milli-Q water and separated by centrifugation (10 000 rpm for 5 minutes) for three times in sequence. Finally, Pt<sub>x</sub>RE/C samples were obtained by freeze drying that contained around 23% Pt content according to ICP analysis.

Pt<sub>2</sub>Gd/C and Pt<sub>2</sub>La/C are also prepared with Gd<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> as raw materials, respectively by using the same process as above.

### 2.3 Physical characterizations

The crystal information of the samples was depicted by X-ray diffraction (XRD) method using the Mini Flex 600 X-ray diffractometer (Rigaku) with the radiation source of Cu Kα (λ = 0.15418 nm) with a scan rate of 5.0° min<sup>−1</sup>. The crystal structure and the morphology of the samples were acquired by transmission electron microscope (TEM) method using the F-30 HRTEM (Holland FEI Tecnai) at 300 kV. The elemental mappings were also performed by the F-30 HRTEM (Holland FEI Tecnai) equipped with the energy dispersive X-ray spectroscopy (EDX). The X-ray photoelectron spectroscopy (XPS) was applied to analyze the valence state of the elements in samples on X-ray photoelectron spectrometer (Thermo Fisherto, United State) with an Al Kα X-ray monochromator. The C 1s spectrum (284.6 eV) was used to calibrate the binding energy (BE). Inductively coupled plasma (ICP, NCS Testing Technology, Plasma1000) was carried out to examine the elemental content (Pt). In order to determine the synthesis mechanism, the



reactants were analyzed using simultaneous thermal analysis (STA 449 F3 Jupiter) under an argon atmosphere with a heating rate of 5 °C min<sup>-1</sup>.

## 2.4 Electrochemical measurements

Catalyst inks were prepared according to the follow steps. First, 2 mg of the catalysts or JM Pt/C were added to the solution composing of 990 μL ethanol and 10 μL of the 5 wt% Nafion ionomer solution to form a mixture. Subsequently, the mixture was dispersed by ultrasonic treatment for 3 hours to yield uniform catalyst suspension. Thereafter, aiming to form the catalyst thin film, the catalyst ink (10 μL) was cast to the polished rotating disk electrode (RDE,  $S = 0.196 \text{ cm}^2$ , PINE Instrument) and dried naturally. The loading amounts of Pt on the electrode surface were around 20.41–23.47 μg cm<sub>Pt</sub><sup>-2</sup>.

The electrochemical performance tests were carried out on the CHI730E bipotentiostat (Chenhua Instrument Corporation, Shanghai) at room temperature. The traditional three-electrode system was conducted to measure the ORR electrochemical performance, in which the catalyst ink coated in RDE, KCl-saturated Ag/AgCl electrode and a graphite electrode, were used as the working electrode (WE), reference electrode (RE) and counter electrode (CE), respectively. The electrolyte was 0.1 M HClO<sub>4</sub> solution. All the potentials were normalized to the reversible hydrogen electrode (RHE) after the electrochemical tests according to the following equation:

$$E_{\text{vs. RHE}} = E_{\text{vs. Ag/AgCl}} + 0.197 \text{ V} + 0.059 \times \text{pH}$$

Cyclic voltammogram (CV) was first conducted between 0.00 V to 1.25 V (vs. RHE) with a scanning speed of 500 mV s<sup>-1</sup> in N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>. During CO-stripping cyclic voltammograms, constant potential of -15 mV (vs. RHE) was held for 12 minutes in 0.1 M HClO<sub>4</sub> electrolyte saturated with CO and then cyclic voltammograms were measured in the potential range of 0–1.25 V with 50 mV s<sup>-1</sup> in 0.1 M HClO<sub>4</sub> electrolyte saturated with N<sub>2</sub>. Then linear scanning voltammetry (LSV) was conducted to characterize the ORR catalytic activity of samples under following conditions: sweep rate of 10 mV s<sup>-1</sup>, rotation rate of 1600 rpm and O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution.

The specific activity (SA) and mass activity (MA) of catalysts were figured out from the polarization curve obtained by LSV. The following Koutecký–Levich equation was applied to calculated the kinetic currents ( $i_k$ ), representing the intrinsic ORR activity:

$$i_k = \frac{i \times i_d}{i_d - i}$$

where  $i$  and  $i_d$  were the experimental current and the diffusion limiting current, respectively. For the purpose of measuring the stability of the catalyst, the accelerated durability test (ADT) was implemented by potential sweep cycles in the range of 0.6 to 1.0 V (vs. RHE) for 5000 cycles under the following conditions: scanning speed of 50 mV s<sup>-1</sup> and O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution. To obtain a real comparison of the ORR activity of catalyst, iR compensation was taken into consideration. The

resistance was assumed constant during the ORR activity tests and its value was 32 Ω determined by the electrochemical impedance.

## 3 Results and discussion

### 3.1 Structure characterizations

Fig. 1 displays the XRD spectra of the Pt<sub>x</sub>Y/C catalyst prepared by the MSS method. The main diffraction peaks are completely consistent with the reference pattern Pt<sub>2</sub>Y, in which the obvious peaks at 20°, 39° and 41° are indexed to the (111), (311) and (222) crystal planes of cubic Pt<sub>2</sub>Y, respectively. In addition, the small broaden peak between 20° and 30° is corresponding to the carbon support. It is worth noting that there are some additional peaks in the XRD spectra, which correspond to those of the Pt<sub>3</sub>Y reference pattern. The XRD results demonstrate the formation of Pt<sub>2</sub>Y and Pt<sub>3</sub>Y alloy phases, among which Pt<sub>2</sub>Y is the dominant phase.

To further verify the formation of Pt<sub>x</sub>Y alloys, the high-resolution TEM (HRTEM) and the element mappings of Pt<sub>x</sub>Y have been provided in Fig. 1b–f. The lattice fringe distance of Pt<sub>x</sub>Y particles in Fig. 1b is about 0.229 nm, which corresponds to the interplanar distance of (311) crystal plane of Pt<sub>2</sub>Y. On the other hand, from the element mapping images of Pt<sub>x</sub>Y displayed in Fig. 1c–f, it is obvious that the Pt and Y elements were distributed in the nanoparticles homogeneously, demonstrating that Pt and Y metals are well alloyed. Besides, Pt<sub>x</sub>Y nanoalloy particles are well decorated on the carbon support as shown in Fig. 1g, and most of the particles possess a small particle size. Whereas, there are a few particles with larger particle sizes, which may be caused by the aggregation of the particles. According to the particle size statistics in Fig. 1h, the distribution of particle size is in the range of 9 nm to 90 nm, and most of the particle sizes are around 21 nm. In comparison, as shown in Fig. S1,† the average particle size of Pt in JM Pt/C catalyst is around 2 nm. Obviously, the synthesized Pt<sub>x</sub>Y nanoalloy particles are much larger than the Pt particles of JM Pt/C catalyst due to the high synthesis temperature.

XPS analysis was used to determine the electronic structure changes of Pt. Fig. 2a showed the Pt 4f core level peaks of the Pt<sub>x</sub>Y/C and JM Pt/C. The zerovalent metallic Pt (Pt<sup>0</sup>) peaks of JM

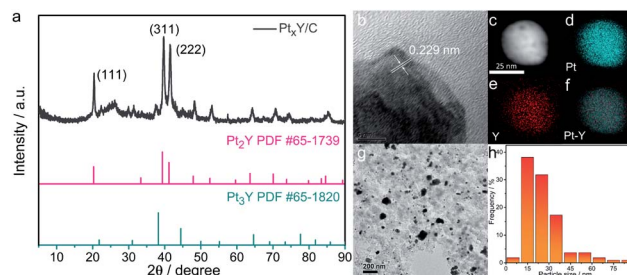


Fig. 1 (a) XRD patterns for the synthesized Pt<sub>x</sub>Y/C catalysts, (b) HRTEM image of a Pt<sub>2</sub>Y nanoparticle and (c) HRTEM image of a Pt<sub>2</sub>Y nanoparticle and its corresponding EDS elemental maps of Pt in blue (e), Y in red (f) and (g) the overlap of Pt and Y, (g) TEM image of Pt<sub>x</sub>Y/C and its corresponding particle size distribution histogram (h).





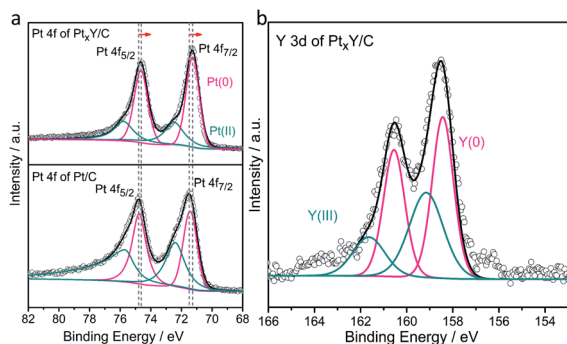


Fig. 2 XPS spectra of (a) Pt 4f core levels for the Pt<sub>x</sub>Y/C prepared and the JM Pt/C catalysts and (b) Y 3d core levels for the Pt<sub>x</sub>Y/C prepared.

Pt/C catalyst emerge at 74.8 and 71.4 eV correlating with the Bes of Pt 4f<sub>5/2</sub> and Pt 4f<sub>7/2</sub>, respectively. Furthermore, the peaks at about 75.6 (Pt 4f<sub>5/2</sub>) and 72.3 eV (Pt 4f<sub>7/2</sub>) are on behalf of the Pt<sup>2+</sup> species. For the Pt<sub>x</sub>Y/C sample, the Bes of 74.7 and 71.3 eV are assigned to Pt 4f<sub>5/2</sub> and Pt 4f<sub>7/2</sub>, separately, corresponding to Pt<sup>0</sup>. Meanwhile, the peaks at the Bes of 75.8 eV (Pt 4f<sub>5/2</sub>) and 72.5 eV (Pt 4f<sub>7/2</sub>) stand for Pt<sup>2+</sup> species. The Bes of Pt<sup>0</sup> doublet of Pt<sub>x</sub>Y/C show a negative shift (about 0.1 eV) relative to JM Pt/C catalyst. This negative shift is ascribable to the change in surroundings around the Pt atoms produced by alloying Pt and Y,<sup>39,40</sup> which changes the electronic structure of Pt. Partial hybridization of d-d band takes place when Pt is alloyed with lower electronegativity metals, which causes the charge to be transferred from the lower electronegativity metals (Y) to stronger one (Pt) through the metal bond.<sup>40</sup> The d-band center of surface Pt shifts in the same direction as the surface core level,<sup>39,41,42</sup> so when the Bes of surface Pt shift to the negative direction, the d-band center of Pt downshifts.<sup>39</sup> The Pt 4f shift is a sign of Pt<sub>x</sub>Y alloy formation,<sup>40</sup> which is in good agreement with the results of XRD and TEM analysis.

The formation of Pt<sub>x</sub>Y alloys is also confirmed from Y 3d high-resolution XPS spectra, as shown in Fig. 2b. By deconvolving the peaks of Y 3d XPS spectra, the peak at Be. 158.4 eV and 160.5 eV close to Y<sup>0</sup>, indicating that the Pt<sub>x</sub>Y alloys are formed.<sup>43,44</sup> Moreover, the other two peaks at 159.2 and 161.7 eV are represented Y<sub>2</sub>O<sub>3</sub>.<sup>34</sup> It can be predicted that a small amount of Y<sub>2</sub>O<sub>3</sub> will appear on the surface due to the high oxygen affinity of Y. This is different from XRD results, mainly because a small amount of Y<sub>2</sub>O<sub>3</sub> on the surface is within the detection limit of XRD measurement, while XPS is surface sensitive.

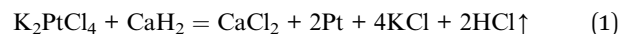
### 3.2 Synthesis mechanism

According to the differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) curves of K<sub>2</sub>PtCl<sub>4</sub> in Fig. 3a, the pure K<sub>2</sub>PtCl<sub>4</sub> begins to melt at 370 °C and decomposes accompanied by decalescence and mass loss after heating to 600 °C. As excess CaH<sub>2</sub> is mixed with K<sub>2</sub>PtCl<sub>4</sub>, the DSC and TG curves in Fig. 3b showed that Pt ions were reduced to metallic Pt at 210 °C in terms of the reaction (1), which also indicates a thermodynamical feasibility based on a negative Gibbs free energy of the reaction. In the temperature range from 210 °C to 600 °C, about

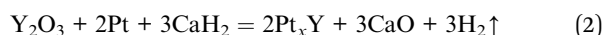
6% of the mass loss of the mixture is observed, which corresponds HCl volatilization and is close to the theoretical value of 8%.

In addition, the TG curve shows an obviously downward trend at 600 °C, which corresponds to the decomposition of excess CaH<sub>2</sub>. Therefore, Pt was first formed by the reaction of K<sub>2</sub>PtCl<sub>4</sub> and CaH<sub>2</sub> at 210 °C during the synthesis progress of Pt-Y alloy. Afterwards Y ions were preferentially reduced on the Pt surface followed by Pt<sub>x</sub>Y alloys formation in the molten LiCl-CaH<sub>2</sub> system.

As LiCl is absent in the MSS process of the alloys, only Pt metal is formed without any alloy peaks in the XRD patterns presented in Fig. S2.† This can be predicted according to the phase diagrams of Pt-RE alloys (e.g., Pt-Y, Fig. S3†), which shows that the synthesis temperature of Pt-Y alloy is above 1000 °C. Differently, after adding LiCl, Pt-Y alloy was successfully synthesized (Fig. 1a). This is probably due to the fact that molten LiCl-CaH<sub>2</sub> provides a liquid and strong reaction environment for Pt<sub>x</sub>Y alloys formation, and lowers the formation temperature of the alloys. The products obtained by MSS after cooled without any treatments were composed of LiCl, CaCl<sub>2</sub>, CaH<sub>2</sub>, CaO and KCl, respectively, as shown in Fig. 3c. The intensity of these products is much higher than that of the Pt-Y alloy, resulting in the alloy phase not being observed. Through the analysis of these byproducts and the previous DSC results, we have summarized the synthesis mechanism and the typical synthesis scheme is described in Scheme 1. In this regard, the possible reactions are proposed as follows:



$$\Delta G = -133.583 \text{ kcal mol}^{-1} (200^\circ\text{C})$$



Further, Pt<sub>2</sub>Gd and Pt<sub>2</sub>La alloys were synthesized using the same method, according to the XRD results shown in Fig. 4. The HRTEM and the element mappings in Fig. 5 further verified the formation of Pt<sub>2</sub>La and Pt<sub>2</sub>Gd alloys. The lattice fringe distances

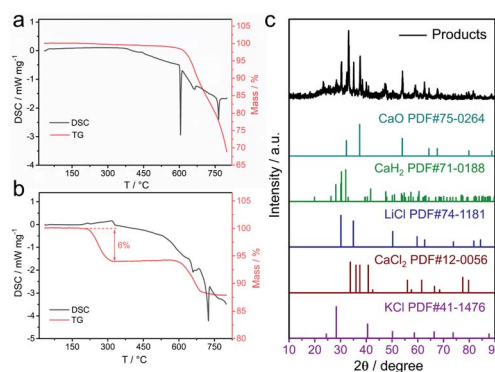
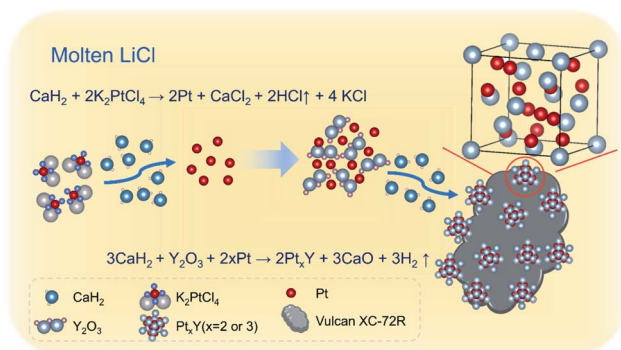
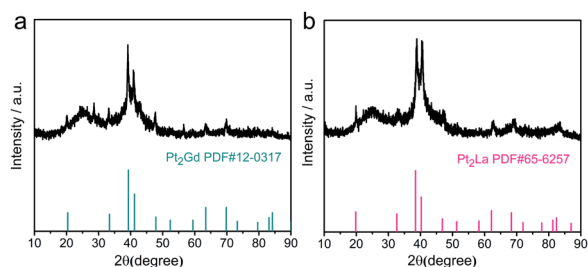


Fig. 3 (a) DSC and TG curves for K<sub>2</sub>PtCl<sub>4</sub>, (b) DSC and TG curves for a mixture of CaH<sub>2</sub> and K<sub>2</sub>PtCl<sub>4</sub>, (c) XRD pattern of the materials synthesized without LiCl.



Scheme 1 Process for the synthesis of  $\text{Pt}_x\text{Y}/\text{C}$  nanoparticles.Fig. 4 XRD patterns of the synthesized  $\text{Pt}_2\text{Gd}/\text{C}$  (a) and  $\text{Pt}_2\text{La}/\text{C}$  (b).

(0.449 nm and 0.229) correspond to the interplanar distance of (111) crystal plane of  $\text{Pt}_2\text{La}$  and (311) of  $\text{Pt}_2\text{Gd}$ , respectively. Meanwhile, the element mapping images in Fig. 5b–e and g–j indicates that Pt, La and Gd are uniformly distributed in the

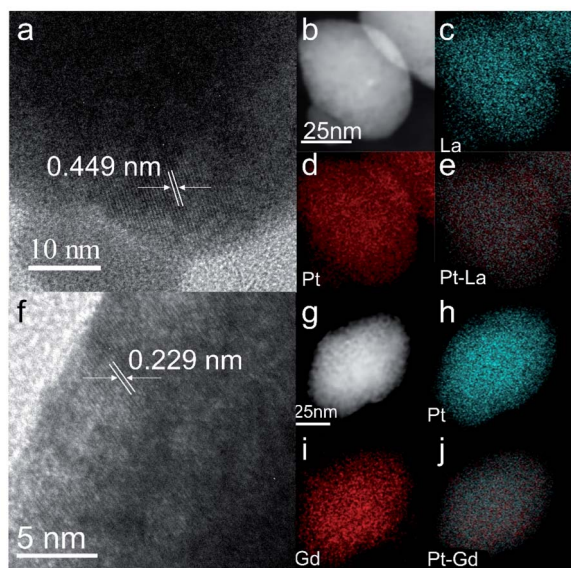


Fig. 5 HRTEM image of a  $\text{Pt}_2\text{La}$  nanoparticle (a) and (b) and its corresponding EDS elemental maps of Pt in red (c), La in blue (d) and (e) the overlap of Pt and La, HRTEM image of a  $\text{Pt}_2\text{Gd}$  nanoparticle (f) and (g) and its corresponding EDS elemental maps of Pt in blue (h), Gd in red (i) and (j) the overlap of Pt and Gd.

particles. The above results prove that  $\text{Pt}_2\text{La}$  and  $\text{Pt}_2\text{Gd}$  alloys have been successfully synthesized.

### 3.3 Electrochemical properties

Aiming to assess the electrocatalytic properties toward ORR of the catalyst, the ORR polarization curves of these three materials synthesized ( $\text{Pt}_x\text{Y}/\text{C}$ ,  $\text{Pt}_2\text{Gd}/\text{C}$ , and  $\text{Pt}_2\text{La}/\text{C}$ ) and JM  $\text{Pt}/\text{C}$  catalysts were measured in oxygen-saturated 0.1 M  $\text{HClO}_4$  electrolyte. The results are shown in Fig. 6a, showing that the half-wave potentials of the synthesized materials are all higher than that of JM  $\text{Pt}/\text{C}$  catalyst. Among them, the  $\text{Pt}_x\text{Y}/\text{C}$  alloy has the highest half-wave potential (0.905 V), which is 25 mV higher than that of the JM  $\text{Pt}/\text{C}$  catalyst (0.88 V), indicating its superior ORR electrocatalytic activity. Furthermore, the half-wave potentials of  $\text{Pt}_2\text{Gd}/\text{C}$  and  $\text{Pt}_2\text{La}/\text{C}$  are 0.901 V and 0.89 V, which are positively shifted 21 mV and 10 mV compared with the JM  $\text{Pt}/\text{C}$  catalyst, respectively. Fig. 6b shows that the mass activities at 0.9 V (vs. RHE) of  $\text{Pt}_x\text{Y}/\text{C}$ ,  $\text{Pt}_2\text{Gd}/\text{C}$  and  $\text{Pt}_2\text{La}/\text{C}$  are 0.3, 0.25, and 0.17  $\text{A mg}_{\text{Pt}}^{-1}$ , which are 2.5 times, 2.08 times and 1.42 times as much as JM  $\text{Pt}/\text{C}$  catalysts (0.12  $\text{A mg}_{\text{Pt}}^{-1}$ ), respectively. This corroborates the ORR activity enhancement of Pt–RE metal alloy catalysts. From the CV curves in Fig. 6c, both  $\text{Pt}_x\text{Y}/\text{C}$  and JM  $\text{Pt}/\text{C}$  show nearly the same trend. On the other hand, as shown by the vertical line in Fig. 6c, the potentials of the oxidation peak and reduction peak of Pt in the  $\text{Pt}_x\text{Y}/\text{C}$  catalyst shift to higher potentials with respect to JM  $\text{Pt}/\text{C}$ , implying the bonding strength between Pt and oxygenated intermediates is weakened<sup>24,45–47</sup> that is associated with the downshift of d-band center of Pt. Under this circumstance, the weakened bonding could be beneficial to the desorption of oxygenated intermediates on the Pt site, thereby promoting the ORR progress and improving the activity.<sup>48,49</sup> Furthermore, the shift of oxidation peak to a higher potential also illustrates that the adsorption strength between Pt and  $\ast\text{O}$  is weakened,<sup>50</sup> which is a sign of enhanced ORR performance.<sup>24</sup> The

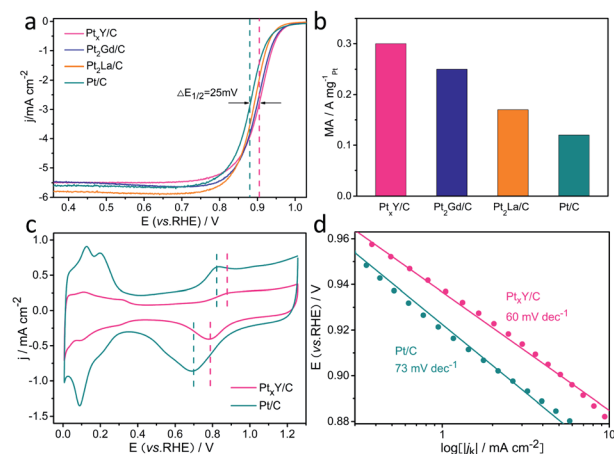


Fig. 6 (a) CVs of  $\text{Pt}_x\text{Y}/\text{C}$  synthesized and JM  $\text{Pt}/\text{C}$  in 0.1 M  $\text{HClO}_4$  solution saturated with nitrogen, (b) the ORR LSV curves of  $\text{Pt}_x\text{Y}/\text{C}$  and JM  $\text{Pt}/\text{C}$  in 0.1 M  $\text{HClO}_4$  solution saturated with oxygen, (c) Tafel plots for  $\text{Pt}_x\text{Y}/\text{C}$  synthesized and JM  $\text{Pt}/\text{C}$ , (d) SA and MA of  $\text{Pt}_x\text{Y}/\text{C}$  synthesized and JM  $\text{Pt}/\text{C}$ .



comparative CO-stripping voltammograms of Pt<sub>x</sub>Y/C and JM Pt/C catalyst are represented in Fig. S4.† Apparently, the onset potential and the CO stripping peak of Pt<sub>x</sub>Y/C shifts negatively, illustrating the reduced interaction of Pt–CO and the weakened bonding between Pt and CO.<sup>48</sup> This is also correlated with the downshift of the d-band center of Pt,<sup>48,51</sup> which coincides with the XPS results and the analysis of positive potential shift in Fig. 2a. Additionally, the negative shift of CO stripping peak proves that Pt<sub>x</sub>Y/C has excellent resistance to CO poisoning on the surface.<sup>52,53</sup>

Fig. 6d presents the Tafel curves of Pt<sub>x</sub>Y/C and JM Pt/C catalyst. The Tafel slope of Pt<sub>x</sub>Y/C reveals a smaller value (60 mV dec<sup>−1</sup>) with respect to that of JM Pt/C catalyst (73 mV dec<sup>−1</sup>), demonstrating the minor charge transfer resistance and an improvement in ORR kinetics of Pt<sub>x</sub>Y/C. The improved performance of Pt<sub>x</sub>Y/C alloys can be put down to the electronic structure changes of Pt influenced by alloying Y with Pt. The d-band center downshift of Pt in Pt<sub>x</sub>Y/C can decrease the adsorption strength of reaction intermediates (\*O, \*OH, \*OOH) during the ORR, thus enhance the activity of ORR. In brief, we can conclude that the incorporation of RE metal (*e.g.*, Y) and the formation of the alloy between Pt and RE are conducive to enhance the ORR activity through these electrochemical tests.

The durability of the catalysts significantly influences even dominates the practical applications of the catalysts. Therefore, the ADT was performed to assess the durability of the Pt<sub>x</sub>Y/C and the JM Pt/C catalysts, and the results were shown in Fig. 7a–c. Obviously, the LSV curves of Pt<sub>x</sub>Y/C and JM Pt/C catalysts both shifted toward to negative potential direction after 5000 potential cycles, indicating the catalytic activity of the catalysts displayed a decreased trend. Pt<sub>x</sub>Y/C reveals the negative half-wave potential shift of 10 mV with regard to a more obvious shift of 15 mV for the JM Pt/C catalyst, demonstrating the relatively high stability of Pt<sub>x</sub>Y/C. As shown in Fig. 7c, the initial MA value of Pt<sub>x</sub>Y/C is 0.26 A mg<sub>Pt</sub><sup>−1</sup>, which is 2.2 times

that of JM Pt/C (0.12 A mg<sub>Pt</sub><sup>−1</sup>). After 5000 cycles, the MAs of Pt<sub>x</sub>Y/C catalyst (0.19 A mg<sub>Pt</sub><sup>−1</sup>) is about 3 times that of JM Pt/C (0.064 A mg<sub>Pt</sub><sup>−1</sup>). In addition, the Pt<sub>x</sub>Y/C shows only 27% loss of MA, while the MA of JM Pt/C catalyst decays by 47%. The results reveal that Pt<sub>x</sub>Y/C has significantly higher durability over JM Pt/C catalyst, which is attributed to the negative alloy formation energy of Pt<sub>x</sub>Y alloy, therefore leading to a high kinetic stability to prevent continuous dealloying.<sup>43</sup> The nanoparticles of Pt<sub>x</sub>Y alloys are well-retained after ADT as seen in Fig. S5,† which is conducive to maintaining high performance toward ORR,<sup>54,55</sup> thereby improving its durability. As for the JM Pt/C, the Pt particles have been agglomerated and grown up after durability test in Fig. S6.† Furthermore, the detachment of a few Pt particles from the support leads to the degradation of ORR performance. On the other hand, the XRD spectrum of Pt<sub>x</sub>Y/C after ADT shown in Fig. S7† indicates that the peaks still correspond to Pt<sub>2</sub>Y but the peak shape is not obvious. Compared the Pt 4f XPS spectra before and after ADT in Fig. S8,† the Pt 4f peaks shift to a lower binding energy, indicating an enhanced stress effect, which leads to enhanced adsorption of Pt and O atoms.<sup>55</sup> The above results revealed that after ADT, Pt<sub>x</sub>Y/C shows a trend of lower catalytic performance.

Chronoamperometry (CA) is measured to study the electrochemical stability of the catalysts, and the results are shown in Fig. 7d–e. The Pt<sub>x</sub>Y/C and JM Pt/C have shown a sharp drop of the initial currents during the first 400 s, and then a slow drop of currents until 5000 s. Within the initial 100 s, the currents of the Pt<sub>x</sub>Y/C and JM Pt/C decrease in the same manner. As time goes by, Pt<sub>x</sub>Y/C has exhibited a slower decrease trend in current than JM Pt/C. It demonstrates that Pt<sub>x</sub>Y/C has shown better electrochemical stability than JM Pt/C, in good agreement with the ADT assessments. The improvement of durability may be due to the exceptional negative alloy formation energy in the Pt–Y alloy to some extent,<sup>43</sup> which provides a higher kinetic stability

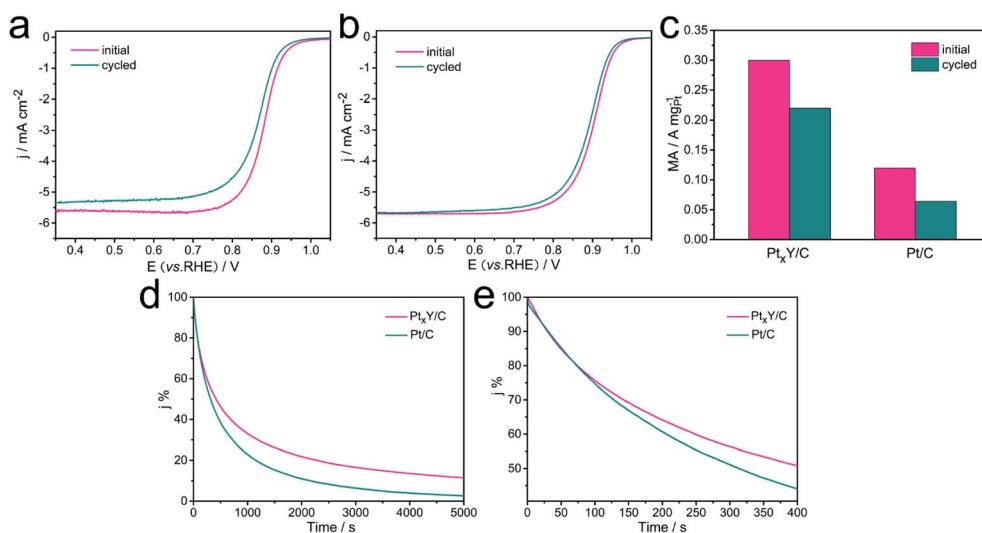


Fig. 7 (a) ORR LSV curves of JM Pt/C before and after 5000 CV cycles, (b) ORR LSV curves of Pt<sub>x</sub>Y/C synthesized before and after 5000 CV cycles, (c) mass activity of Pt<sub>x</sub>Y/C synthesized and JM Pt/C before and after 5000 CV cycles, (d) chronoamperometry curves of Pt<sub>x</sub>Y/C and commercial Pt/C, (e) the first 400 s of chronoamperometry curves of Pt<sub>x</sub>Y/C and commercial Pt/C.





and can resist continuous dealloying under PEMFC reaction conditions.

The electrochemical performance comparison of this material with Pt<sub>2</sub>Y and Pt<sub>3</sub>Y alloys recently reported by other researchers is summarized in Table S1.† In this work, the particle size of the obtained material is much larger than that in these literatures, but it still improves the ORR catalytic activity, indicating that the Pt-RE alloys have great potential in catalyzing ORR. The MA and SA are inferior to some previously reported materials, which may be related to the larger particle size of Pt<sub>x</sub>Y nanoalloy. Indeed, the MA and SA for Pt<sub>x</sub>Y/C are closely connected with the particle size of Pt<sub>x</sub>Y and the optimal particle size is approximately 8–9 nm.<sup>44</sup> Most of the synthesized Pt<sub>x</sub>Y particles have larger particle diameters (>10 nm), which also leads to an insignificant improvement of the half-wave potential. Therefore, it is expected to improve the activity of the material by reducing the particle size.

## 4 Conclusions

In conclusion, it is the first time that the carbon-supported Pt-RE nanoalloys were successfully synthesized in one step by a simple MSS method, and the synthesis mechanism is discussed in this paper.

Pt<sub>x</sub>Y/C catalysts with the average particle sizes of around 21 nm, was synthesized by mixing K<sub>2</sub>PtCl<sub>4</sub> with Y<sub>2</sub>O<sub>3</sub> (in a molar ratio of Pt : Y = 1 : 1) with carbon support in molten LiCl-CaH<sub>2</sub> system by one-step MSS method at 600 °C. Pt<sub>2</sub>Gd/C and Pt<sub>2</sub>La/C are also obtained with Gd<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> as the starting raw materials, respectively by using the same process as above.

In the synthesis processes, Pt nanoparticles were first obtained by the reaction of K<sub>2</sub>PtCl<sub>4</sub> and CaH<sub>2</sub> at 210 °C, then Y ions were preferentially reduced on the Pt nanoparticles surface followed by Pt<sub>x</sub>Y alloys formation in the molten LiCl-CaH<sub>2</sub> system at 600 °C. CaH<sub>2</sub> has the high reduction capacity to extract the oxygen atoms from RE<sub>2</sub>O<sub>3</sub>, which is beneficial to form Pt-RE alloys. Molten LiCl provides a strong reducing environment and lowers the formation temperature of alloys.

The half-wave potentials of Pt<sub>x</sub>RE/Cs are all more positive than that of commercial Pt/C catalyst (e.g., 0.905 V for Pt<sub>x</sub>Y/C while 0.880 V for JM Pt/C). Furthermore, electrochemical characterizations have demonstrated that Pt<sub>x</sub>Y/C samples show higher electrocatalytic activity toward ORR and preferable catalytic durability with respect to JM Pt/C catalysts. This facile synthesis method provides an effective strategy for the preparation of Pt-RE based multicomponent nanoalloys, especially in a large-scale production.

## Conflicts of interest

There are no conflicts to declare.

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