A non-intermetallic PtPb/C catalyst of hollow structure with high activity and stability for electrooxidation of formic acid

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1. Synthesis of PtPb/C Catalyst

K₂PtCl₆ (7.5 mg), Pb(NO₃)₂ (10.2 mg), and Vulcan XC-72 carbon black (12.5 mg) were added into 10 mL deionized water. Under vigorous sonication, NaBH₄ (60 mg, dissolved in 10 mL water) solution was gradually dropped into the suspension to co-reduce K₂PtCl₆ and Pb(NO₃)₂. (2) After centrifugal separation and re-suspending of pre-formed PtPb/C in water, 5.1 mg K₂PtCl₆ was added, and reduced again by NaBH₄. The resulting PtPb/C catalyst was centrifugally separated and washed by water several times.

The size, morphology, composition and structure of the PtPb/C catalyst were characterized by HRTEM (JEM-2100), EDX (INCA Energy, Oxford Instruments, UK), XRD (P.A. Nalytical X-pert), and XPS (PHI Quantum 2000).

2. XPS analysis of PtPb/C catalyst

Fig. S1 XPS spectra of (a) sputtered PtPb/C and (c) commercial Pt/C catalyst in Pt4f regions, and of PtPb/C in Pb4f regions (b) before and (d) after sputtering.
Surface composition and chemical state of the PtPb/C catalyst were analyzed by XPS. Fig. S1a shows the Pt 4f core region spectra for the sputtered surface of the PtPb/C. The 4f\(_{7/2}\) and 4f\(_{5/2}\) peaks at 70.9, 74.3 eV, can be attributed to metallic Pt, i.e., Pt(0). Several satellite peaks indicate the presence of higher oxidation states of Pt, such as PtO, PtO\(_2\) \(^{s1-s3}\). It is interesting to note that the Pt4f binding energy (BE) of the PtPb/C is negatively shifted by 0.5 eV in comparison with that of the Pt/C (Fig. 2c) \(^{s3}\), suggesting that the electronic environment surrounding the Pt atom is significantly changed due to the doping of Pb. Fig. S2b shows the Pb 4f spectra of the PtPb/C catalyst before sputtering. A couple of weak peaks at 137.0 and 141.5 eV are the 4f\(_{7/2}\) and 4f\(_{5/2}\) of metallic lead Pb(0), and the other couple of strong peaks at 139.2 and 144.1 eV correspond to Pb(II) \(^{s2,s4}\). Clearly, the dominant Pb species is Pb(II) on the pristine surface, which may be attributed to the carbonate and/or hydroxyl species (PbCO\(_3\)/Pb(OH)\(_2\)) \(^{s2}\). After sputtering the surface with Ar\(^+\) ions, the Pb(0) peaks increases significantly (Fig. 2d).

The atomic concentrations were obtained from the XPS core level peak areas of the various components including Pt4f\(_{7/2}\), Pb4f\(_{7/2}\) and their satellite peaks. The relative proportion of surface atoms of Pt, Pb, and the different metal oxidation states, presented in Table S1, were calculated using Eq. (1):

\[
\frac{c_i}{\sum c_i} = \frac{A_i}{S_i} \quad \text{Eq. (1)}
\]

where \(c_i\), \(A_i\), and \(S_i\) are, respectively, the atomic surface concentration, the corresponding core level peak area, and the sensitivity factor of the surface species \(i\).

Based on the XPS spectra shown in Fig. S1, the following composition of PtPb/C catalyst was obtained:

**Table S1.** Relative proportion of surface atoms for pristine and sputtered surface of PtPb/C catalyst

<table>
<thead>
<tr>
<th></th>
<th>Pt</th>
<th>Pb</th>
<th>PtO(_x)</th>
<th>PbCO(_3)/Pb(OH)(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine surface</td>
<td>30.5%</td>
<td>12.5%</td>
<td>19.2%</td>
<td>37.8%</td>
</tr>
<tr>
<td>Sputtered surface</td>
<td>34.4%</td>
<td>38.7%</td>
<td>19.8%</td>
<td>7.2%</td>
</tr>
</tbody>
</table>

### 3. Electrode preparation and electrochemical measurement

**Electrode preparation:** 5 or 25 μL suspension (0.20 mg Pt mL\(^{-1}\)) of PtPb/C catalyst was spreaded on the glassy carbon electrode. As soon as the electrode was dried under infrared lamp, 2 μL Nafion diluents (0.1 wt. % Nafion® solution) was coated onto the surface of catalyst. Suspensions of Pd black catalyst (Alfa Aesar®, Johnson Matthey Company, surface area \(\sim\)20 m\(^2\)g\(^{-1}\)) and 20 wt. % Pd/C catalyst (Alfa Aesar®, Johnson Matthey Company, HiSPECT™ 3000) were also spreaded onto the glassy carbon electrodes using the same method. The precious metal (Pt or Pd) loading on each glassy carbon electrode was 1 μg for cyclic voltammetry test, and 5 μg for chronoamperometry (i.e., current ~ time) test.

**Electrochemical measurements:** The electrochemical measurements were carried
out in a conventional three-electrode cell using EG&G 273A potentiostat/galvanostats. A platinized Pt foil was used as counter electrode, and a reversible hydrogen electrode (RHE) was used as reference electrode. Cyclic voltammetry for oxidation of formic acid was recorded in a solution of 0.5 M HCOOH + 0.1 M H₂SO₄ at a sweep rate of 50 mV s⁻¹. Chronoamperometry was carried out at 0.30 V in the same solution. Formic acid (88%, Analytical reagent) and sulfuric acid (98%, Guaranteed reagent) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All solutions were prepared with 18 MΩ Millipore water and deaerated with high-purity nitrogen (Linde, purity > 99.99%) for at least 20 min before each experiment. All of the electrochemical measurements were carried out in 30±1 °C water bath.

4. Electrochemical in situ FTIR reflection spectroscopy

Electrochemical in situ FTIR reflection spectroscopic studies were carried out on a Nexus 870 FTIR spectrometer (Nicolet) equipped with a liquid-nitrogen-cooled MCT-A detector, an EverGlo IR source, which has been detailed previously. In this configuration, infrared radiation sequentially passed through a CaF₂ window and a thin-layer solution (~ 10 μm), and then it was reflected by the electrode surface. As a result, both dissolved substances in the thin-layer solution and adsorbed species on electrode surface can be detected. The resulting spectra were reported as relative change in reflectivity, that is,

$$\frac{\Delta R}{R} = \frac{R(E_S) - R(E_R)}{R(E_R)}$$

where $R(E_S)$ and $R(E_R)$ are the single-beam spectra collected at sample potential $E_S$ and reference potential $E_R$, respectively. By this definition, the downward bands in the resulting spectra indicate the formation of products, while upward bands denote the consumption of reactants. The spectral resolution was 8 cm⁻¹.