



News & Views

Is platinum a suitable counter electrode material for electrochemical hydrogen evolution reaction?

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To date, due to the excellent electrochemical inertness, superb electrical conductivity and good mechanical stability in both aqueous and nonaqueous solutions, platinum (Pt) has been widely employed as counter electrode material in three-electrode setups to perform electroanalytical chemistry. However, recent reports have revealed that the use of Pt based counter electrodes for hydrogen evolution reaction (HER), without using any ion-exchange membrane to separate the working electrode from the counter electrode, would influence the experimental results substantially owing to the electrochemical dissolution-deposition process of Pt. A controversial issue has therefore arisen regarding whether or not Pt should be continued to be utilized as the counter electrode material for HER.

In fact, before the upsurge of research in electrocatalysis, the dissolution of Pt has been widely investigated in the fuel cell research since the dissolution not only detaches Pt from the electrode surface but also deteriorates significantly the overall cell performance during electrochemical processes. As early in 1988, Ota and his colleagues [1] have systematically studied the weight loss of Pt anode in H₂SO₄ aqueous solution by spectrophotometric method. It was found that there is an accelerated Pt corrosion under cyclic voltammetry scan caused by the reduction of oxide layer, which could facilitate the corrosion of Pt. The electrochemically corroded Pt constituents are then considered to get re-deposited back onto the cathode. For revealing this complete Pt dissolution mechanism, enormous research efforts have been made to evaluate the characteristics of these surface oxides (*i.e.* PtO_x, *x* = 1 or 2), the valence of the dissolved constituents, the influence of potential change, temperature, pH, and the mass-transport on the reactions participated [2–4]. Evidently, Pt is not as stable as it is anticipated.

Even though great achievements have been obtained in the scientific community, very few reports concentrate on the influence of potential Pt contamination on the HER performance when using Pt based counter electrodes during the experiment. In 2015, to the best of our knowledge, we were the first group to propose taking

into consideration of anodic Pt dissolution during electrochemical tests when Pt is used as the counter electrode [5]. As depicted in Fig. 1a, when using Pt wire as the counter electrode, the electrocatalytic activity of graphite rods that has been activated by continuous potential scan of 13,000 cycles is on a par with that of the state-of-the-art HER electrocatalyst–Pt/C, whereas there is not any significant improvement as soon as utilizing graphite rod as the counter electrode (Fig. 1b). Moreover, an emerging Pt peak with a binding energy of *ca.* 76.5 eV in the XPS profile demonstrates clearly the existence of Pt species on the working electrode after the activation of 13,000 CV cycles (Fig. 1c), which further indicates a mass transfer involving the deposition of Pt from the anode to the cathode occurred. A possible schematic illustration was also presented for this transfer process as shown in Fig. 1d. Specifically, the dissolution of Pt is the result of the position exchange between oxygen and Pt atoms that substantially weakens the interaction between the surface Pt atoms and the interior bulk counterparts. All of these results suggest that the improvement of HER performance was mainly caused by the Pt transfer and re-deposition onto the electrocatalysts of cathode, rather than the activation of the carbon materials themselves.

At the same tune, it is a creditable attempt for some researchers to be aware of Pt dissolution effect during the HER process; however, most of them ruled out the possible Pt contamination by comparing the HER performance between two systems, in which one adopted Pt as the counter electrode and another one used graphite rod, only after one or several linear sweep voltammetry (LSV) scan(s) without considering their long-term effects. In order to guarantee the validity as well as to avoid the influence of anodic Pt transfer, we employed Ni plate as the counter electrode in our follow-up work of hierarchical NiMo nanowires for the highly efficient HER electrocatalysts [6]. Similarly, Shi and his co-workers [7] reached the same conclusion when they aimed to ensure the data accuracy with which they contrasted. In their work, when using Pt wire as the counter electrode, there is a remarkable improvement in the HER activity of their catalysts after 3000 cycles; surprisingly, this enhanced activity even exceeds that of commercial Pt/C electrocatalyst. Further XPS investigation also demonstrates and confirms the deposition of Pt onto cathode electrocatalysts. As a result, instead of Pt, they chose graphite rod as the counter

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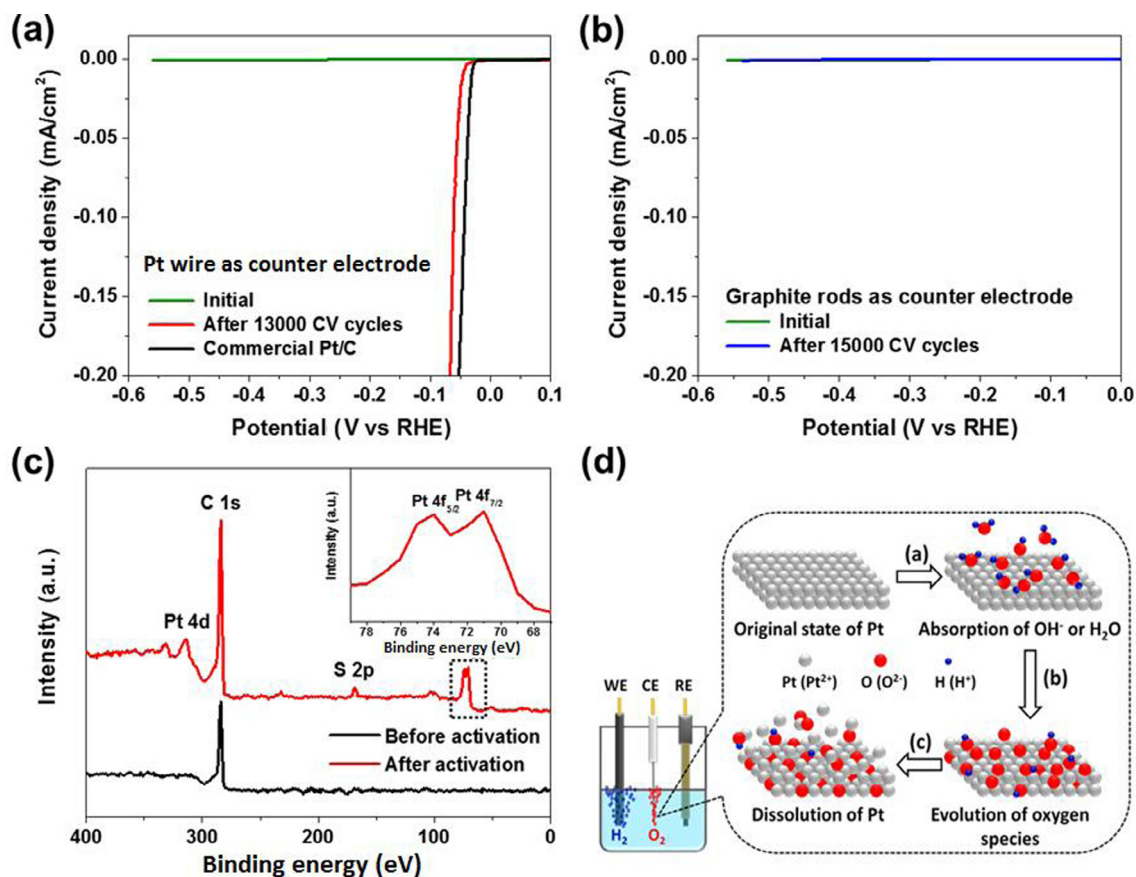


Fig. 1. (Color online) LSV curves on HER of graphite rods activated with (a) Pt wire counter electrode and (b) graphite rod counter electrode, respectively. (c) XPS profile of the graphite rod before and after an activation of 13,000 CV cycles when using a Pt wire as the counter electrode, inset is the enlarged XPS profile for Pt 4f orbitals. (d) The possible schematic illustration for the transfer process of Pt from anode to cathode. Copyright Royal Society of Chemistry 2015 [5].

electrode. Similar opinions have as well been put forward by Wang's group in their recent review article [8].

Apart from replacing the Pt with other inert materials as counter electrodes, such as graphite, carbon cloth, glassy carbon and Ti mesh, another recommended method is to use an ion exchange membrane to separate the working electrode from the Pt counter electrode in order to avoid the aforementioned Pt contamination [9,10]. Chen and his co-workers [10] have studied thoroughly about the anodic dissolution of Pt counter electrode in both acidic and alkaline aqueous solutions, the effect of the area ratio between working and counter electrodes, the effect of CV scan range (especially the upper potential limit) as well as the influence of CV scan rate. It is explicit that many articles published in the recent two years (i.e., 2015 and 2016) about HER studies did not adopt any ion exchange membrane when employing Pt as the counter electrode. However, further experimental results demonstrated that not only in the acidic, but also in the alkaline media, both electrochemical and chemical dissolution of Pt would lead to the deposition of Pt on the working electrode if there is not any ion exchange membrane employed in the electrochemical setup. In consideration of these results obtained, they finally gave several valuable suggestions: (1) purifying the electrolyte before HER process, (2) replacing the Pt with other stable counter electrodes, (3) applying the ion exchange membrane to the setup preventing the Pt transfer across the working and counter electrodes.

In conclusion, Pt is not a suitable counter electrode material for HER testing if there is not any ion exchange membrane exploited in the setup. Careful consideration should be given to the Pt contamination or to the alternative counter electrode choice in every electrochemical system.

Conflict of interest

The authors declare that they have no conflict of interest.

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