



Short communication

Eight-electron oxidation of borohydride at potentials negative to reversible hydrogen electrode

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ARTICLE INFO

Article history:

Received 6 July 2008

Received in revised form 26 August 2008

Accepted 26 August 2008

Available online 2 September 2008

Keywords:

Borohydride
Electro-oxidation
Platinum
Titanium oxide
Synergistic effect

ABSTRACT

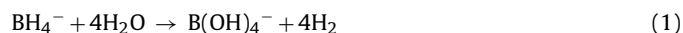
This is the first report of a novel anode catalyst, Pt/Ti₂O, and its use for the complete 8-electron oxidation of borohydride without hydrogen evolution in a potential region negative to reversible hydrogen electrode (RHE). A major obstacle to the development of direct borohydride fuel cells (DBFC) has been the hydrogen evolution at the negative electrode, which causes low coulombic efficiency and safety problems. Attempts to prevent hydrogen evolution during the oxidation of borohydride on a fuel cell anode have always resulted in a shift of the anode potential to values more positive than the RHE potential, thus losing the advantages of DBFC in comparison to conventional hydrogen fuel cells. Pt supported on conductive titanium oxides (Ti₂O) has been found to catalyze the 8-electron oxidation of borohydride without hydrogen evolution in a potential range more negative than RHE, which is desired in order to have a DBFC that is practically applicable. Mechanism of the direct 8-electron oxidation process is discussed on the basis of a synergistic effect at the surface of Pt/Ti₂O catalyst.

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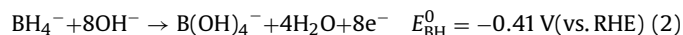
Fuel cells have been widely recognized as a promising energy technology because of their high energy conversion efficiency and environmental friendliness [1,2]. Among the various categories of fuel cells, the proton exchange membrane fuel cell (PEMFC), using hydrogen as fuel, is the most advanced fuel cell today [3,4]. However, the difficulties associated with the mobile storage of hydrogen remain to be a major obstacle to the commercialization of PEMFC [5]. As a result, research and development works are also carried out on fuel cell systems using alternative fuels, such as alcohols (especially methanol) and borohydride [6–9]. In principle, these alternative fuels can be used either directly or indirectly. Direct electro-oxidation of a fuel in a fuel cell gives a more compact device because it does not have a separate fuel reformer. However, before this advantage can be exploited in a fuel cell system, the challenge of finding an anode that can perform a specific and efficient direct oxidation of a fuel must be met.

Borohydride is an attractive alternative fuel for use in fuel cells because of its high energy density and the ease with which it can be stored and transported [10,11]. When borohydride is used as an

indirect fuel, it is first hydrolyzed to produce hydrogen:



The indirect borohydride fuel cell (IDBFC) has two shortcomings compared to a DBFC, namely greater system complexity and 0.41 V lower in theoretical voltage than that of DBFC. This is because the thermodynamic potential of borohydride oxidation is 0.41 V more negative than RHE potential in the same solution:



In order to realize a practical DBFC, two requirements must be met simultaneously. Firstly, the anode must work at potentials more negative than RHE; and secondly, there must be no hydrogen evolution at the anode. However, these two requirements are an apparent paradox. All the presently known highly active catalysts for borohydride oxidation, such as Pt, Ni, and hydrogen-storage alloys, are also highly active toward the hydrogen evolution reactions. Therefore, it seems impossible to fulfill the two basic requirements at the same time. Whenever hydrogen evolution occurs, it consumes a part of the electrons produced by borohydride oxidation, and the apparent number of electrons of borohydride oxidation (n_{app}), defined as the number of electrons generated by each borohydride anion to the external circuit, will be reduced to values more or less below 8. Some researchers were able to prevent hydrogen evolution during 8 e⁻ oxidation of borohydride, but only

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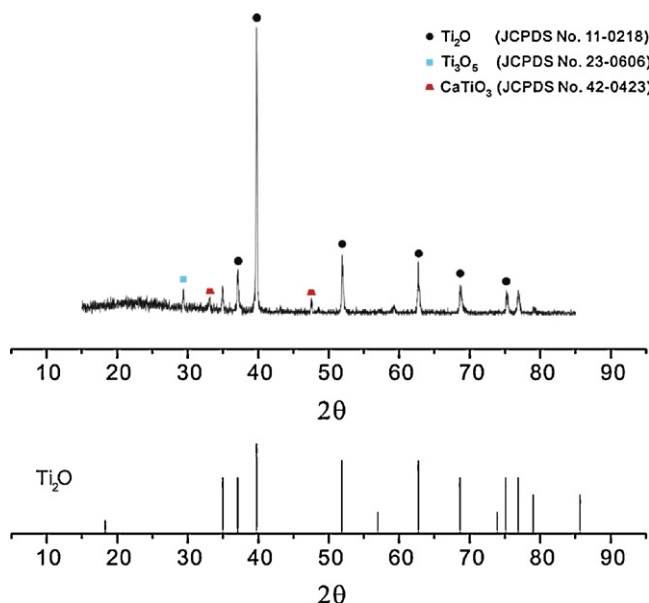


Fig. 1. XRD pattern of Ti₂O used in this work.

at potentials more positive than the RHE, leading to a significant loss in cell voltage. In this paper we report a novel anode catalyst, Pt/Ti₂O, which for the first time allows borohydride to be oxidized without hydrogen evolution and in a potential region negative to RHE.

The catalyst support Ti₂O used here was a conductive titanium suboxide made from solid TiO₂ by electrochemical reduction in molten calcium chloride [12,13]. The X-ray diffraction (XRD) pattern (Fig. 1) indicates that the major component was Ti₂O, with small amounts of Ti₃O₅ and CaTiO₃. The Ti₂O thus obtained was about 40 nm in crystallite size (calculated from XRD peak width) and a few microns in agglomerate size (Fig. 2). The Pt/Ti₂O catalyst was prepared by a simple impregnation-reduction method [14]. The loading level of Pt was 15% by weight and the size of Pt particles was estimated to be 10 nm from XRD peak width. The working electrode was made from the Pt/Ti₂O with acetylene black added for improving conductivity and Teflon as binder. The working electrode size was 2 cm by 2 cm and the total amount of Pt was 10 mg.

The electrochemical tests were carried out using a three-compartment cell. The working electrode was placed in the central

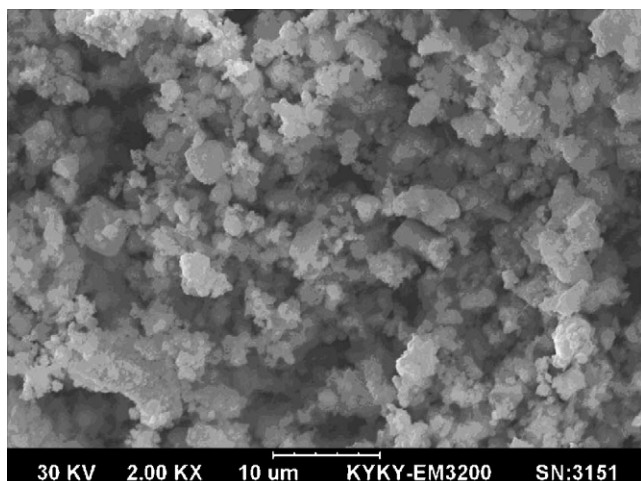


Fig. 2. SEM image of the catalyst support Ti₂O used in this work.

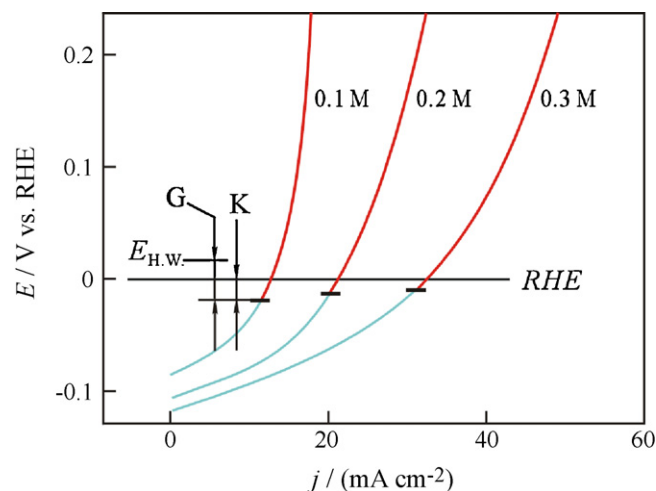


Fig. 3. The potential–current curves of a Pt/Ti₂O electrode in 2 M NaOH containing different concentrations of NaBH₄.

compartment which was airtight and connected to a U-shaped volumetric gas meter (see Fig. 1 in Ref. [15]). On immersion of the working electrode into the alkaline borohydride solution, the electrode potential was immediately brought down to substantially below RHE and numerous fine H₂ bubbles were seen to rise from the working electrode. When the potential of the working electrode was shifted stepwise to the positive by means of a potentiostat, anodic current from the working electrode increased and the H₂ bubbling slowed down. It was found that the bubbling ceased at potentials close but still definitely negative to RHE. Fig. 3 shows the potential–current curves obtained with a Pt/Ti₂O electrode in alkaline borohydride solutions. The small bars represent the turning points above which no hydrogen was generated from the working electrode, i.e., 8-electron oxidation was realized. The potential region between the turning point and RHE is marked as K-region within which both $n_{app} = 8$ and $E < RHE$ are realized simultaneously. When a DBFC is working in this region, the energy conversion efficiency would be higher than the theoretical energy conversion efficiency of an IDBFC assuming that there is no excessive crossover of liquid borohydride to the cathode, which would lower the cathode potential and generate hydrogen by borohydride oxidation at the cathode.

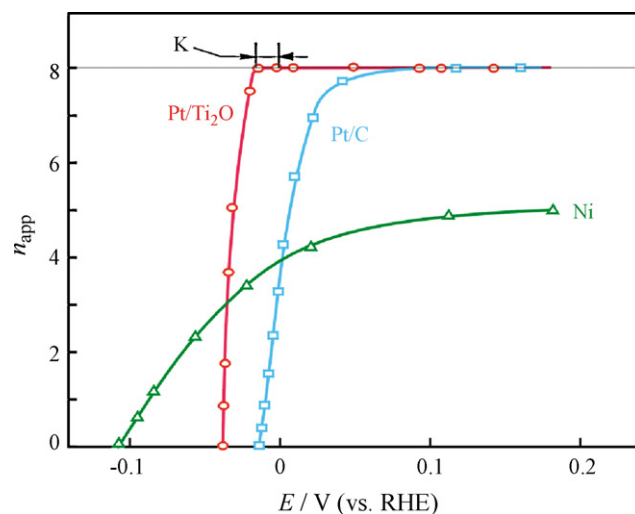


Fig. 4. The changes of the apparent reaction electron number (n_{app}) with the electrode potential for 3 electrodes in 2 M KOH + 0.1 M NaBH₄.

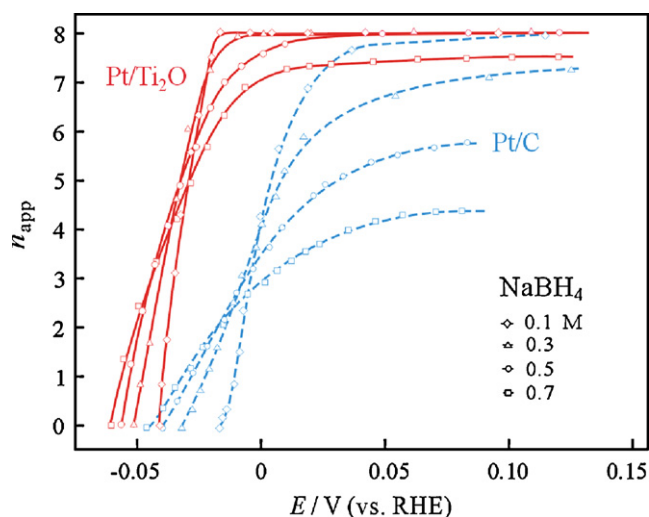


Fig. 5. Borohydride concentration effects on n_{app} . Solid line Pt/Ti₂O; dashed line Pt/C. Supporting electrolyte 2 M NaOH; NaBH₄ concentrations as marked.

The situation is more favorable when compared to the real energy conversion efficiency of IDBFCs instead of the theoretical one, because there must be some polarization at the hydrogen anode in any real IDBFCs during discharge, i.e., the working potential of the anode in a real IDBFC is always somewhat more positive than RHE, as marked by $E_{H,W}$ level in Fig. 3. Therefore, the real voltage gain would be that marked by G which is larger than K in Fig. 3. Assuming a polarization of 30 mV at the hydrogen anode and the cathode potential to be fixed at 0.9 V (vs. RHE), the voltage output of the IDBFC would be 0.87 V (neglecting ohmic drops for simplicity). In contrast, the working potential of the borohydride anode in the K-region could be 20 mV negative to RHE, corresponding to a cell voltage output 0.92 V and a 5.7% energy gain compared to the real IDBFC.

From the simultaneously measured electric current and the gassing rate, n_{app} could be quantitatively calculated (see Ref. [15] for details). Fig. 4 clearly shows the change of n_{app} with electrode potential. Besides Pt/Ti₂O, two commonly used electrodes, Pt/C and Ni, are also shown for comparison. For Ni electrodes, n_{app} remains far below 8 even at potentials much more positive than RHE. For Pt/C (20 wt%, total Pt loading and electrode size identical to the Pt/TiO₂ electrode), $n_{app} = 8$ can be reached but only at potentials at least 0.1 V more positive than RHE. In contrast to Pt/C and Ni, Pt/Ti₂O reaches $n_{app} = 8$ at potentials notably more negative than RHE, marked as K-region in Fig. 4.

It should be pointed out that the n_{app} values decrease with borohydride concentration for all electrode we tested, including Ni, Ni-based hydrogen-storage alloys, Pt/C and Pt/Ti₂O. The data for Pt/C and Pt/Ti₂O are shown in Fig. 5. The K-region would disappear when borohydride concentration exceeds 0.3 M. However, n_{app} is always much larger with Pt/Ti₂O than with Pt/C.

Although still rather narrow, the K-region is unprecedented and implies a completely new mechanism of the 8-electron oxidation of borohydride. For conventional catalysts, $n_{app} = 8$ can be obtained only at potentials more positive than RHE and, therefore, a mechanism involving molecular hydrogen as an intermediate is possible.

In our case, however, the reaction intermediate is impossible to be molecular hydrogen because the oxidation potential is negative to RHE. In contrast, the intermediates must be more active than molecular hydrogen so that they can be oxidized at potentials negative to RHE. Such an unusual mechanism deserves dedicated investigations. The intermediate might be some special type of adsorbed hydrogen atoms produced during borohydride oxidation. In view of the very strong reducing power of borohydride, such hydrogen ad-atoms might possess a surplus energy (denoted as H_{ads}^*) and therefore oxidizable at potentials negative to RHE. These H_{ads}^* atoms have two fates in principle, either to become hydrogen molecules without generating electricity (for example by $2H_{ads}^* \rightarrow H_2$) or to be electrochemically oxidized to water with electricity generation (such as $H_{ads}^* + OH^- \rightarrow H_2O + e^-$). Note that the latter reaction needs oxygen-containing species. It has been reported that sub-stoichiometric titanium oxides are able to provide active surface OH-containing species [16–20]. Our DFT calculations also indicated that OH[−] adsorption on Ti₂O is favorable.

In summary, by using the new catalyst Pt/Ti₂O, 8-electron oxidation of borohydride was realized in a potential region negative to RHE for the first time. This potential region (K-region) is still small and occurs only for borohydride concentration less than 0.3 M. Using this result to find a DBFC with high energy conversion efficiency is the subject of future studies.

Acknowledgements

This work was supported by the Natural Science Foundation of China (50632050, 20773096, 20433060, 20122101, 20125308), the Program for New Century Excellent Talents in Universities of China (NCET-04-0688), and the National Hi-Tech R&D Program (2007AA05Z142).

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