



Short communication

Pt hierarchical structure catalysts on BaTiO₃/Ti electrode for methanol and ethanol electrooxidations

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ABSTRACT

Electrooxidations of methanol and ethanol have been investigated on different Pt catalytic titanium-supported electrodes in both acidic and alkaline media using cyclic voltammetry. BaTiO₃ is used for the first time to make a nanoscaled roughness on the surface of Ti foil in order to effectively deposit Pt hierarchical structure and block foulness in solution reactions. The morphology of BaTiO₃ nanocube on Ti foil, Pt catalysts deposited on BaTiO₃/Ti and Ti foil electrodes are characterized by field emission scanning electron microscopy. The results indicate that Pt nanoflowers can be effectively grown on the Ti foil covered with 1 μm layer of BaTiO₃ nanocubes and the catalytic oxidation behaviors to methanol and ethanol are much better than those of the Pt/Ti electrode as Pt nanoparticles can hardly be deposited on the smooth surface of the Ti foil. The Pt/BaTiO₃/Ti electrode could be adopted as excellent catalytic anode in fuel cells.

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1. Introduction

Direct alcohol fuel cells (DAFCs) based on liquid fuels have attracted considerable interest as compact electrochemical power sources for portable electronic devices and fuel cell vehicles owing to their much higher energy density than gaseous fuels such as hydrogen. Among the fuels, methanol is more efficiently oxidized than other alcohols [1]. Ethanol offers another alternative choice because it is safer and can be produced in large quantities [2]. However, the CO poisoning of the anode catalysts is one of the obstacles for the application of direct methanol fuel cell (DMFC) and direct ethanol fuel cell (DEFC) [3]. So it is necessary to prepare some effective catalyst materials and develop new catalyst preparation method for the electrooxidation of methanol and ethanol.

Ti is used as the substrate for its excellent conductivity and chemical stability [4–6]. These Ti-supported catalysts present significant electrocatalytic activity for methanol oxidation [7,8]. And the Ti anodes prepared by deposition of the Pt have shown a higher performance than carbon black supported Pt anodes [9,10]. The catalytic activity of electrooxidation of methanol on PtM_yO_x (M = Sn, Mo, Os or W)/Ti electrodes has been demonstrated that PtSn_yO_x, PtW_yO_x and PtMo_yO_x can promote the oxidation of methanol [11]. Recently, nanostructured materials have become the focus of researches in the areas of catalysis. A large number of Pt, Pd or Au based nanostructures have been used for the catalytic elec-

trooxidation of methanol and ethanol on glassy carbon or metal electrodes, such as Pt nanostructures [12–14], Pd nanowire arrays [15,16] and spherical spongelike particles [17], Au nanostructures [18], and Pt–Ru nanospheres [19]. Shen et al. have systemically investigated the morphology influence of Pd nanostructures on catalysis to direct alcohol oxidation, and they found the Pd spherical flower-like nanostructures possess much better electrocatalytic properties than that of the palladium spherical nanoparticles or multitwinned particles [17]. Therefore, it is a great challenge task to prepare the catalysts into a specific structure that can efficiently perform catalysis.

Herein, a thin layer of BaTiO₃ nanocubes have grown directly on a Ti foil by the composite-hydroxide media (CHM) approach [20]. The BaTiO₃ nanocube layer plays two important roles; one is to produce nanoscale roughness which facilitates the effective deposition of flower-like Pt catalysts, the other is to inhibit foulness of intermediate product, a common problem of a metal electrode. The Pt flower-like structure has higher specific surface area than the Pt particle structure owing to its hierarchical structure. The higher ratio of surface to volume, the better catalysis would be for a catalyst. Besides, compared with the support of the anode catalysts studied present, such as CNTs, BaTiO₃/Ti is low-cost and easy to deposited Pt. The morphology of BaTiO₃ nanocube on Ti foil, Pt catalysts deposited on BaTiO₃/Ti and Ti foil electrodes are characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDS). In addition, the performances of the Pt/BaTiO₃/Ti electrodes for methanol and ethanol electrooxidation are studied via cyclic voltammetry (CV) and linear sweep voltammetry (LSV)

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in both acidic and alkaline media, as well as the comparison with Pt/Ti electrode prepared in the same process.

2. Experimental

2.1. Chemicals

Titanium foils (99.94%) of 0.5 mm thickness and silver paste were purchased from Sigma–Aldrich and SPI Supplies, respectively. Methanol, ethanol, H_2PtCl_6 , HCl, HClO_4 , H_2SO_4 , NaOH, KOH and BaCO_3 were from Chongqing Chemical Reagent Company. All chemicals were of analytical grade and were used as received. Deionized water was used throughout.

2.2. The preparation of Pt/BaTiO₃/Ti catalysts

The preparation of BaTiO₃ nanocubes growing directly on Ti foils has been reported previously [20]. In a typical experiment, 9 g mixed NaOH and KOH with Na/K ratio of 51.5:48.5 was first placed in a 25 mL Teflon vessel. Then, BaCO_3 at a concentration of 0.5 mmol, Ti foils, sonicated in deionized water and dried in air, were added into the vessel. And then, the vessel was placed in a furnace preheated to 200 °C for 48 h before being taken out and allowed to cool to room temperature. Finally, the Ti foils covered with BaTiO₃ nanocubes were washed with deionized water and immersed in diluted acid solution for 2 h.

Ohmic contact for the BaTiO₃ nanocube planar film with copper wire was made by silver paste. Then, the BaTiO₃/Ti electrode was

covered with epoxy resin with an area of 5 mm × 4 mm left open. A trace Pt over-layer was electrodeposited by sweeping BaTiO₃/Ti electrode in the deaerated H_2PtCl_6 (1 mM) + HCl (10 mM) + HClO_4 (0.1 mM) solution at scan rate of 10 mV s^{-1} and potential of between –0.4 V and 0.8 V vs. Ag/AgCl for 15 cycles [21]. After Pt deposition, the electrodes were cleaned carefully with deionized water. Pt/Ti electrode was prepared in the same process.

2.3. Instruments and measurements

XRD was taken in a continuous mode over the range of 20–80°. Cu was used as the source of X-ray. The morphology of BaTiO₃ nanocubes on Ti foils was characterized by FESEM (FEI Nova400) and EDS. LK98B(II) electrochemical analyser was employed for the deposition of Pt nanoparticles on the BaTiO₃ nanocubes and the electrochemical measurements. Pt foil and Ag/AgCl (in saturated KCl) was used as the counter electrode and reference electrode, respectively. All the experiments were performed at room temperature (20 °C).

3. Results and discussion

3.1. Characterization of the BaTiO₃ nanocubes and catalysts

The size of BaTiO₃ nanocubes (Fig. 1A) is about 200 nm and thickness of the BaTiO₃ layer is 1 μm . Fig. 1B is the XRD investigations of BaTiO₃ nanocubes prepared directly on Ti foils by the CHM method for 48 h. All peaks are perfectly indexed as the pure cubic phase

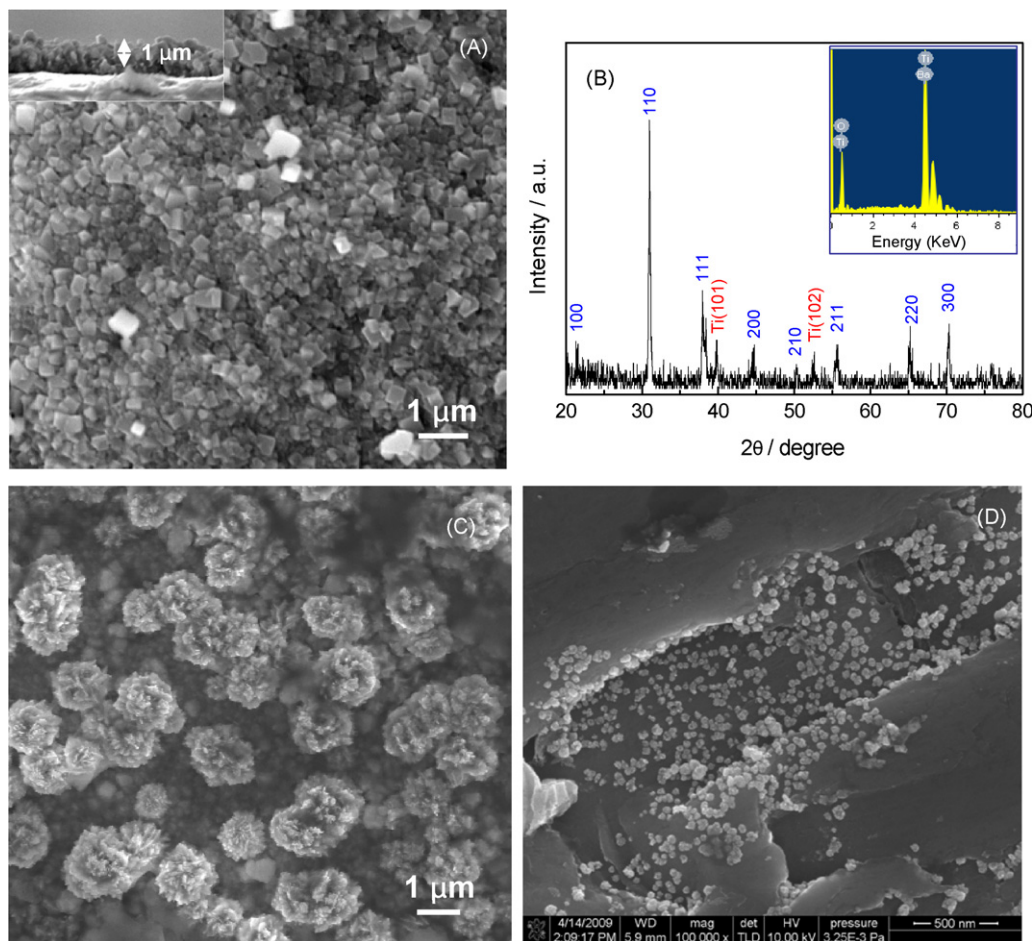


Fig. 1. FESEM image (A) and XRD patterns (B) of BaTiO₃ particles on the Ti foil, and its EDS spectrum (the inset of B). FESEM images of Pt/BaTiO₃/Ti catalyst (C) and the Pt/Ti catalyst (D).

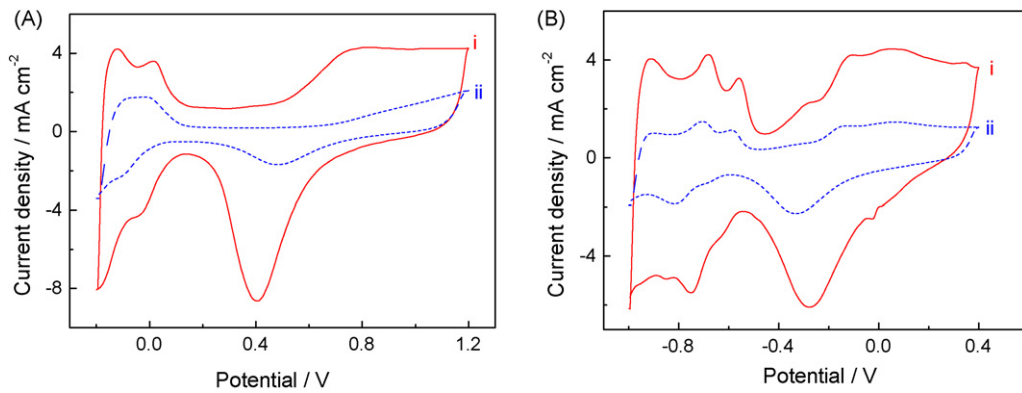


Fig. 2. CVs of the Pt/BaTiO₃/Ti (i) and Pt/Ti (ii) catalysts in 0.5 M H₂SO₄ (A) and 1.0 M KOH (B).

of BaTiO₃ (JCPDS-89-2475, *Pm3m* (2 2 1)). Besides, the sample has two peaks of Ti (101) and (102), but no TiO₂, BaCO₃ and other phases are detected. EDS measurement on the sample shows that the elements are of Ba, Ti, O (Fig. 1B, inset).

After being deposited by Pt, the BaTiO₃/Ti electrodes are covered by Pt nanoflowers. From Fig. 1C, numerous Pt nanoflowers about 1 μm in diameter are deposited on the top of BaTiO₃ nanocubes. Fig. 1D is the morphology of Pt/Ti electrode. Pt nanoparticles about 30–90 nm selectively locate on the accidented surface of Ti foil, while few Pt nanoparticles are found on the smooth surface of Ti foil. Though we prolong the deposition time, more Pt particles accumulate on the accidented sites, but still they hardly deposit on the smooth surface of Ti foil. From the analysis above, we can conclude that roughness of the surface of the electrode is important for the effective deposition of Pt catalysts.

3.2. Electrooxidation of methanol and ethanol on the Pt/BaTiO₃/Ti and Pt/Ti electrodes

The CVs taken in 0.5 M H₂SO₄ (Fig. 2A) and 1.0 M KOH (Fig. 2B) for the Pt/BaTiO₃/Ti and Pt/Ti electrodes are shown in Fig. 2. In the acid media, there are two hydrogen desorption peaks at –0.12 V and 0.015 V in positive scan and reduction peak at 0.4 V in negative scan for the Pt/BaTiO₃/Ti electrode. Compared with that of the Pt/BaTiO₃/Ti electrode, the reduction peak of Pt/Ti electrode is shifted to 0.48 V. In the alkaline media, there are two peaks at –0.68 V and –0.56 V in positive scan and peak at –0.28 V in negative scan for the Pt/BaTiO₃/Ti electrode. However, the peak in negative scan for the Pt/Ti electrode is shifted to –0.33 V. Further, it is seen from Fig. 2 that the peaks of Pt/BaTiO₃/Ti electrode are stronger than that of Pt/Ti electrode in both acid and alkaline media. This

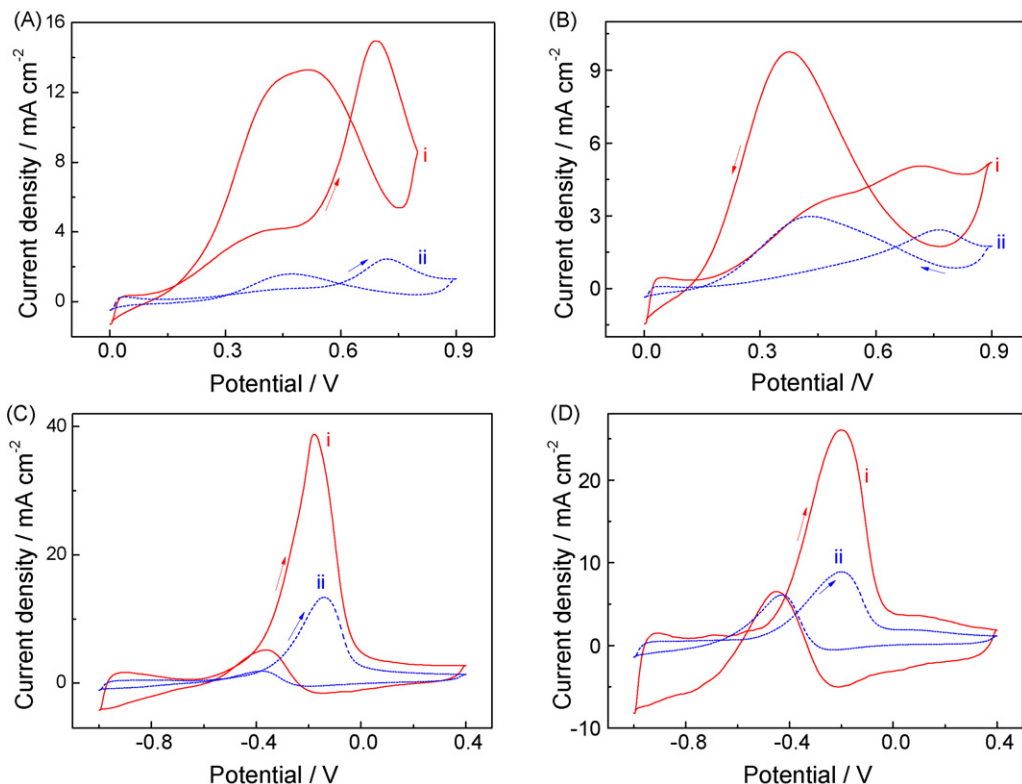


Fig. 3. CVs of the Pt/BaTiO₃/Ti (i) and Pt/Ti (ii) catalysts in 0.5 M H₂SO₄ containing 1.0 M CH₃OH (A), 0.5 M H₂SO₄ containing 1.0 M C₂H₅OH (B), 1.0 M KOH containing 1.0 M CH₃OH (C) and 1.0 M KOH containing 1.0 M C₂H₅OH (D) with a sweep rate of 10 mV s⁻¹.

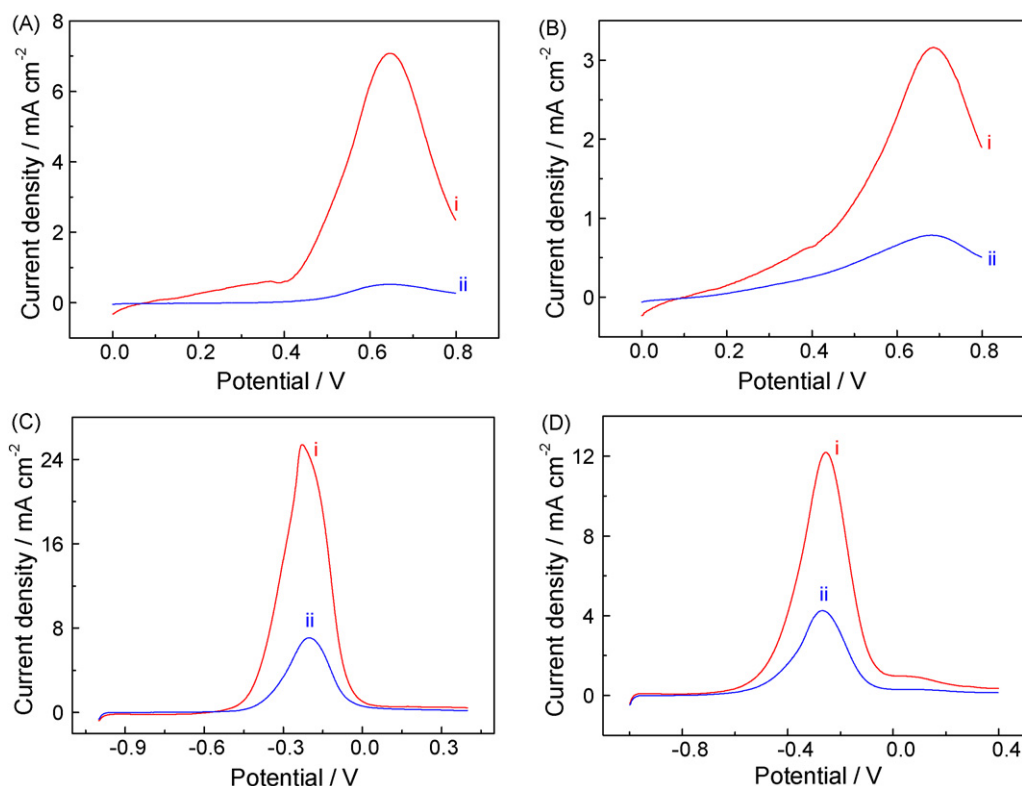


Fig. 4. LSVs of the Pt/BaTiO₃/Ti (i) and Pt/Ti (ii) catalysts in 0.5 M H₂SO₄ containing 1.0 M CH₃OH (A), 0.5 M H₂SO₄ containing 1.0 M C₂H₅OH (B), 1.0 M KOH containing 1.0 M CH₃OH (C) and 1.0 M KOH containing 1.0 M C₂H₅OH (D) with a sweep rate of 5 mV s⁻¹.

suggests that the BaTiO₃ nanoscaled roughness provides an effective site for Pt deposition. The result is consistent with the FESEM characterizations.

Fig. 3A and B shows the CVs of the methanol (Fig. 3A) and ethanol (Fig. 3B) electrooxidation on Pt/BaTiO₃/Ti and Pt/Ti electrodes in acid media. The peak current density for methanol and ethanol electrooxidation on the Pt/BaTiO₃/Ti electrode is 14.95 mA cm⁻² and 5.05 mA cm⁻², respectively. However, the peak current density of the Pt/Ti electrode is 2.44 mA cm⁻² for the methanol electrooxidation and 0.28 mA cm⁻² for the ethanol electrooxidation. The anodic peak of Pt/BaTiO₃/Ti electrode is 0.69 V and 0.72 V, while that of Pt/Ti electrode shift to 0.72 V and 0.76 V. This is related to the different amount and morphology of Pt deposited on the surface of the electrode under the same condition. Few Pt nanoparticles on the smooth surface of the Ti foil result in no better performance for methanol and ethanol electrooxidation. Compared with Pt/C catalyst and polycrystalline Pt nanocatalyst [14], the Pt/BaTiO₃/Ti electrode reveals not only tremendous current densities of electrooxidation, but also lower onset potentials. The hierarchical structure of Pt flowers growing on the Pt/BaTiO₃/Ti electrode presents a perfect catalysis to electrooxidation of methanol and ethanol.

The CVs of the methanol (Fig. 3C) and ethanol (Fig. 3D) electrooxidation on Pt/BaTiO₃/Ti and Pt/Ti electrodes in alkaline media are shown in Fig. 3C and D. Like that in the acid media, the Pt/BaTiO₃/Ti electrode has the higher peak current density for methanol and ethanol electrooxidation in the alkaline media compared with the Pt/Ti electrode. Clearly, the catalytic activities of the two electrodes are higher in the alkaline media than those in the acid media. As is shown in Fig. 3C and D, the peak current density for methanol and ethanol electrooxidation of the Pt/BaTiO₃/Ti electrode is 38.80 mA cm⁻² and 26.05 mA cm⁻², respectively, which is higher than the Pt/Ti and Pd/Ti electrode (6.4 mA cm⁻²) [22]. The alcohol electrooxidation on Pt/BaTiO₃/Ti electrode is characterized

by two well-defined current peaks on the forward and reverse scans in acid and alkaline media. In the forward scan, the oxidation peak is corresponding to the oxidation freshly chemisorbed species coming from ethanol adsorption. The reverse scan peak is primarily associated with removal of carbonaceous species not completely oxidized in the forward scan than the oxidation of freshly chemisorbed species [23]. The magnitude of the peak current on the forward scan indicates the electrocatalytic activity of the Pt/BaTiO₃/Ti for the oxidation reaction of alcohol [22]. This implies that the Pt/BaTiO₃/Ti electrode can provide a better catalytic activity for methanol and ethanol electrooxidation.

To further study the catalysis, LSVs at very slow potential scan rate of 5 mV s⁻¹ are conducted, in acid and alkaline media, as shown in Fig. 4. The peak currents for methanol and ethanol electrooxidation of the Pt/BaTiO₃/Ti electrode are 7.08 mA cm⁻² at 0.646 V and 3.16 mA cm⁻² at 0.686 V in the acid media. However, the peak currents on the Pt/Ti electrode are 0.52 mA cm⁻² at 0.641 V and 0.78 mA cm⁻² at 0.681 V, respectively. In alkaline media, the peak currents for methanol and ethanol electrooxidation are observed 25.41 mA cm⁻² at -0.229 V and 12.18 mA cm⁻² at -0.256 V for the Pt/BaTiO₃/Ti electrodes, respectively. The methanol and ethanol electrooxidation potentials of Pt/Ti electrode are moved to -0.203 V and -0.270 V, respectively. Obviously, the Pt/BaTiO₃/Ti electrode exhibits extremely high oxidation current densities in both acid and alkaline media from these quasi-steady-state polarization curves. This suggests that the hierarchical structure of Pt flowers growing on the Pt/BaTiO₃/Ti electrode enhances greatly electrocatalytic activity towards methanol and ethanol oxidation. The results observed here are in agreement with the CV studies.

4. Conclusions

BaTiO₃ can be used to make a nanoscaled roughness on the surface of Ti foil in order to effectively deposit Pt hierarchical structure

and block foulness in solution reactions. The Pt hierarchical structure of flowers can effectively grow on the Ti foil covered with 1 μm layer of BaTiO_3 nanocubes and the catalytic oxidation behaviors to methanol and ethanol are much better than those of the Pt/Ti electrode in both acid and alkali solution as Pt nanoparticles can hardly be deposited on the smooth surface of the Ti foil. In addition, the electrooxidation of methanol and ethanol is better in the alkali solution than that in the acid solution. The Pt/ BaTiO_3 /Ti electrode could be adopted as excellent catalytic anode in fuel cells.

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