



Catalytic polymeric electrodes for direct borohydride fuel cells



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HIGHLIGHTS

- Polymeric electrocatalytic electrodes based on PEDOT are introduced to DBFC.
- PEDOT electrodes have efficiently catalyzed redox reaction of DBFC.
- DBFCs based on polymeric electrodes exhibited stable and high power output.
- PEDOT shows very good prospective usages in DBFC.

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ABSTRACT

The direct borohydride fuel cell (DBFC) is a new class of fuel cells that produces non-toxic by-products and has a potential for a high voltage and high energy density. A major challenge in developing efficient DBFCs is the development of an efficient, stable, and economic catalyst for the oxidation of borohydride. In this paper, we report the use of conducting polymer Poly(3,4-ethylenedioxythiophene) (PEDOT) as electrocatalysts in DBFC. PEDOT electrodes prepared by vacuum phase polymerization exhibited electrocatalytic behavior towards oxidation of borohydride and reduction of hydrogen peroxide. Spectroscopic analysis of samples showed that PEDOT can act as an interface for electron transfer from borohydride ions. Comparing the polarization curves of DBFCs with PEDOT coated on graphite electrodes and cells with bare graphite electrodes, demonstrated higher voltage, maximum power density, and stability.

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1. Introduction

There is an increasing demand for clean and sustainable sources of energy other than fossil fuels [1,2]. This is because the heavily relied upon fossil fuels are a limited resource and their use as an energy source releases pollution into the environment [1,3]. The direct borohydride fuel cell (DBFC) is a new energy storage and conversion system that produces non-toxic by-products and has a potential for a high voltage and energy density [1,4]. In terms of energy density, DBFC has a theoretical energy density of 9300 Wh/kg, that places them right below hydrogen-air fuel cells and Li-air batteries [5]. Considering the high cost and limited resources of lithium and the difficulty of storing hydrogen, DBFC seems to have a high potential for the future of energy storage. A major challenge in developing efficient DBFCs is the development of an efficient, stable, and economic catalyst for the oxidation of borohydride. So far

scientists have developed several electrocatalytic anodes for DBFC. However most of these materials are based on precious metals such as silver [6], palladium [7], platinum [7,8] and gold [9,10]. Despite attempts at using non-noble metals [4,6,11–15] or metal oxides [16,17], the efficiency and the output of such system is not enough for making DBFC commercially viable.

Conductive polymers are a class of polymers that contain a conjugated system of double bonds in their backbone. Polyaniline, polypyrrole, polythiophene and Poly(3,4-ethylenedioxythiophene) (PEDOT) are the most common conducting polymers. Among these polymers, PEDOT is shown to be the most conductive [18] and stable polymer. Besides its application as a transparent [19] or flexible [20] electrode, PEDOT has been shown to be able of catalyzing the cathodic reaction such as oxygen reduction reaction [21–23] or hydrogen evolution reaction [24]. However, there has not been any report on its capability for catalyzing anodic reactions. It is previously shown that some conducting polymers can be reduced using borohydride [25], thus it can be expected that these polymers can behave as an interface for electron transfer and oxidation of borohydride.

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In this paper, we report our work on using vapor phase polymerized PEDOT as an electrocatalysts for borohydride oxidation reaction and incorporation of these electrodes in functioning fuel cells. Our results show that PEDOT is capable of catalyzing the oxidation of borohydride ions and reduction of hydrogen peroxide. The fuel cells based on these electrodes exhibited good energy conversion performance and provided a relatively high voltage and current over a long period of time.

2. Experimental

2.1. Preparation of PEDOT samples

Graphite papers (Fuel Cell Earth) were coated with PEDOT using Vacuum Vapor Phase Polymerization (VPP) method at 40 °C, following the previously reported method [19,22,23]. The oxidant consisted of a mixture of 2.0 g of Bytrone CB-40 (Heraeus), 3.0 g of ethanol and 1.5 g of PEG-PPG-PEG mw:5800 Da (Sigma-Aldrich). The oxidant coating was applied to the surface of the graphite paper. The VPP process was conducted at 45 mbar for 1 h. The PEDOT sample was then washed with ethanol to remove any remaining oxidant. This process was repeated 5 times to deposit 5 layers of PEDOT on graphite. By weighting electrodes after deposition of each layer, the mass of each layer of PEDOT was measured to be $0.40 \pm 0.08 \text{ mg/cm}^2$.

2.2. Characterization of electrodes

Upon deposition of PEDOT on graphite substrates, the blue deposited film was visible to the naked eyes. The morphology of electrodes was characterized by scanning electron microscopy using Quanta 450 FEG-SEM. UV-Vis-NIR spectroscopy in transmission mode was employed to study the interaction of PEDOT films with borohydride solution. Using VPP process, PEDOT was deposited on quartz slides followed by soaking in the sodium borohydride solution for 4 min and then studied using an Agilent Technologies, Cary series, UV-Vis-NIR spectrometer.

2.3. Electrochemical analysis

A stock solution of 1 M NaBH_4 + 4 M KOH was prepared and used in all experiments. On the cathode side, a 5 M solution of hydrogen peroxide in 0.75 M sulfuric acid was used. PEDOT coated on graphite paper and bare graphite paper were used as anodic and cathodic electrodes, respectively. All of the electrochemical tests were conducted at ambient temperature (23 °C) using a NuVant bipotentiostat system. Cyclic voltammetry was carried out using a three-electrode cell. A graphite paper was used as the counter electrode and an Ag/AgCl electrode in 4 M KCl was used as the reference. The fuel cells were assembled using parallel flat cathodes and anodes with a cationic membrane (Fumsep FKB) separating two half cells. The electrodes and the membrane were separated using a 5 mm thick polycarbonate spacer. The volume around electrodes were filled with the anolyte and the catholyte solutions. In the continuously fed systems the fresh catholyte and anolyte solutions were pumped into the half cells using a peristaltic pump at the rate of 2 ml min^{-1} . The polarization curves were measured by applying a current that increased in a step fashion to the cell and measuring the resulting voltage. Chronopotentiometry under constant current was used to test the stability of the PEDOT catalyst in a fuel cell. The RDE experiments were performed using PEDOT films deposited on glassy carbon electrodes (RDE, 0.196 cm^2 , Pine Research Instrumentation) with a scan rate of 5 mV s^{-1} . These samples were prepared by initially depositing the films over a glass substrate and then floating the film in ethanol [26] and placing it on

a glassy carbon electrode. The polarization curves for borohydride oxidation collected at six rotation rates and compared to those obtained from glassy carbon electrode.

3. Results and discussion

SEM image (Fig. 1) of the coated electrodes confirms deposition of PEDOT in the form of a continuous thin layer over the porous graphite substrate. It is also noticeable that the porous/rough surface morphology of the substrate is replicated in the deposited polymer films. In order to study the interaction of borohydride ions and PEDOT, UV-Vis-NIR absorption spectroscopy was employed. UV-Vis-NIR spectroscopy is commonly used to investigate the oxidation state and the composition of charge carriers in PEDOT [27–29]. The spectral data presented in Fig. 2a shows that after exposure of PEDOT films to borohydride solution, the IR background ($>1000 \text{ nm}$) decreases which is an indication of the loss of bipolaronic charge carriers in the system [27–29]. At the same time, a pronounced absorption at 600 and 900 nm are observed, which are related to neutral species and polaronic charge carriers within PEDOT, respectively. Such spectral changes suggest that borohydride solution is capable of transferring electrons and reducing PEDOT in absence of any external voltage. Thus, it can be concluded that PEDOT can act as an intermediate to accept electrons from borohydride ions and catalyze their oxidation.

The ability of PEDOT to electrocatalyze the oxidation of borohydride was first evaluated by cyclic voltammetry (CV). As shown in Fig. 2b, oxidation of borohydride occurs at a relatively low voltage in PEDOT coated on graphite paper electrode compared to the bare graphite counterpart. The reaction conversion current is also significantly higher than that of the graphite electrode. Considering that PEDOT is an electroactive polymer that goes through oxidation and reduction, CV results of a similar electrode in KOH solution in absence of borohydride is shown in Fig. 2b in order to cancel out the effect of redox reaction of PEDOT. It can be seen that the current in this sample remained very low which confirms that the PEDOT electrode catalyzed the borohydride oxidation reaction in high current and only a small amount of side reactions such as oxidation of PEDOT or oxygen evolution reaction is occurring on the electrodes. These results demonstrate that PEDOT can effectively catalyze the oxidation of sodium borohydride and, therefore, it is a promising potential catalytic anode in a DBFC.

A series of linear sweep voltammetry (LSVs) have been

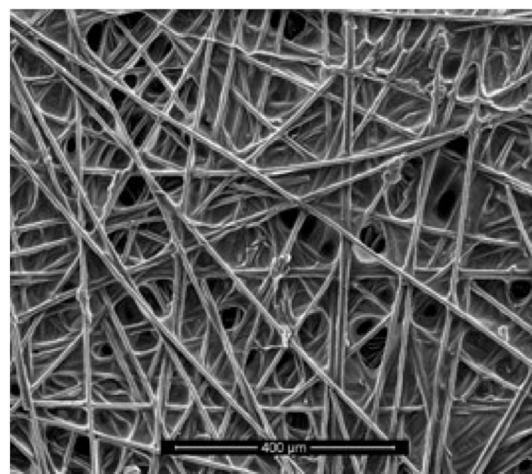


Fig. 1. SEM image of a graphite paper coated with PEDOT using vacuum vapor phase polymerization.

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