

Short Communication

A new method for fabricating flexible polymer electrodes and its application to the oxygen–reduction reaction

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Abstract

The fabrication of flexible polymer electrodes using silver–epoxy-coated poly(vinyl chloride) sheet further coated with a thin layer of conducting poly(phenylene oxide) is described. The electrode displayed improved performance for the oxygen–reduction reaction in alkaline solution compared with a bare silver electrode. This electrode is extremely lightweight and is suitable for application in fuel cells for space craft.

Keywords: Conducting polymers; Silver epoxy polymers; Fuel cells; Space craft; Oxygen–reduction reaction

1. Introduction

In recent years, much attention [1–5] has been focused on the development of oxygen electrodes for fuel cells that are lightweight [6], chemically stable, have high power and energy density, and are inexpensive. Development of a flexible electrode provides a further advantage in that it allows changes in battery shape and size. Lightweight flexible electrodes have special applications in space craft [7] and ion sensors [8].

This short communication describes a method for fabrication of a new type low-cost flexible electrodes that are extremely light in weight. Results are presented of their application of the electrodes to the oxygen–reduction reaction (ORR) in alkaline media.

For ORR in alkaline or acid media usually platinum catalyst in form of platinum deposited on graphite is used as an electrocatalyst [2,4]. Platinum is an expensive material and, therefore, extensive efforts have been made to replace platinum by other low-cost materials. Silver is one of the best performing electrode materials [9,10]; it has a moderate cost, and displays high catalytic activity for ORR in alkaline solution.

Therefore, the specific objective of this research is to fabricate flexible electrodes using silver as a catalyst and to enhance its catalytic activity through surface modification by applying a thin coating of conducting poly(phenylene oxide).

2. Experimental

2.1. Fabrication of electrodes

A poly(vinyl chloride) (PVC) sheet (from Exide Battery, used as separator in lead/acid batteries, thickness 0.5 mm) with a connector strip was covered by a thin layer (~50 μm) of conducting silver–epoxy (Ted Pella, USA). This silver-coated PVC electrode was used as a special type of extremely lightweight electrode with a maximum catalyst (Ag) utilization factor. The front sides are conducting and may be designed to any desired shape and size.

The surface of the silver-coated PVC electrode was modified further by a very thin layer (10 to 50 μm) of conducting poly(phenylene oxide) (PPH) using the ferricyanide ion as dopant. This was achieved by the electropolymerization technique discussed below.

2.2. Electropolymerization

An electrolytic solution was prepared by dissolving an appropriate weight of distilled phenol (SRL, India) in 100 ml of 0.1 M potassium ferricyanide (E. Merck, India) solution in aqueous 3 M KOH (SRL, India) solution so that the resulting solution becomes 50 mM phenol. 30 ml of this solution was taken in a one-compartment cell in which the silver-coated PVC sheet (1 cm²) was used as an anode. The counter electrode was a platinum wire and a saturated calomel electrode (SCE) as used as a reference electrode. Electro-

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Table 1
Electrochemical parameters for oxygen reduction reaction in 3 M KOH at 25 °C

Electrode	Oxygen-reduction peak potential (mV) from CV at scan rate 40 mV s ⁻¹	Oxygen-reduction peak current; i_p (mA cm ⁻²) ^a obtained from CV	Oxygen-reduction current at 1 V; i (mA cm ⁻²) ^a at 1 V from linear polarization
PVC-Ag	761	5.1	0.5
PVC-Ag-PPH (60 s) ^b	761	6.4	0.6
PVC-Ag-PPH (150 s) ^b	761	90.0	1.4
PVC-Ag-PPH (300 s) ^b	761	30.0	0.8
PVC-Ag-PPH (600 s) ^b	961	6.3	0.4
PVC-Ag-Pt	441	85	1.7
	841	54	

^a With an apparent surface area of 1 cm².

^b Time of polymerization.

polymerization was performed potentiostatically at 1.6 V versus SCE for different periods (60, 150, 300 or 600 s) so as to obtain different weights of deposited polymer. After polymerization, the polymer electrodes were washed repeatedly with distilled water and stored in the de-aerated distilled water for a few days.

Since platinum is the best electrocatalyst for the ORR, for the purposes of comparison, a platinum-deposited modified PVC-silver electrode using the usual electroplatinization technique was fabricated [11].

2.3. Electrochemical study

The electrochemical properties of the ORR on the silver-coated PVC electrode, modified PVC-silver electrodes and the platinum-coated electrode was studied by linear polarization and cyclic voltammetry (CV) techniques using 3 M aqueous KOH solution in a three-compartment cell to avoid mixing of hydrogen and oxygen. The solution was pretreated by prolonged electrolysis (12 h) at constant potential to reduce any impurities [12].

For CV studies, a computerized potentiostat galvanostat (Vibrant model VSMCS-30, Lab-India) was coupled with interface and data acquisition software. Different scan rates (40, 20 and 10 mV s⁻¹) were used over the potential range 0 to 1 V. Linear polarization studies were undertaken using the same instrument in the potential range 0 to 1 V with a scan rate of 3.3 mV s⁻¹.

3. Results and discussion

The fabricated electrodes are chemically stable when dipped in distilled water and 3 M KOH solution. The film conductivity is 5 to 18 S cm⁻¹. CV studies at different scan rates (40, 20 and 10 mV s⁻¹) clearly indicate that the ORR on this catalytic electrode surface is quasi-reversible in

nature. Thus, it is not possible to report the reversible electrode potential.

The cathodic peak potential of the ORR on these electrodes at a scan rate of 40 mV s⁻¹ in 3 M KOH solution are given in Table 1. It is interesting to note that two distinct peaks for the ORR (at 441 and 841 mV) are obtained on a platinum-supported electrode. These correspond to a two-electron transfer path involving the formation of hydrogen peroxide as the intermediate and a four-electron transfer direct path for the ORR. By contrast, one distinct peak (at 761 mV) is obtained on the PVC-silver and PVC-silver-conducting polymer electrode modified with a medium deposition of polymer. In the case of a PVC-silver electrode modified by a relatively thick deposited PPH, the ORR occurs at a higher potential (at 961 mV, Table 1). This is an important observation and it suggests that the ORR on PVC-silver and the PVC-silver modified electrode by coating with conducting PPH follows a direct four-electron transfer path.

The apparent cathodic peak current densities obtained from CV studies (without correcting for the roughness factor), and the current densities for the ORR at 1 V obtained from linear polarization (without correcting for the roughness factor) are shown in Table 1. Though it is difficult to compare the catalytic activity of these electrodes in absence of a knowledge of the true surface area, it seems that while platinum exhibits excellent catalytic activity, the catalytic activity of modified PVC-silver PPH with a medium polymer loading is also significantly high. The decrease in apparent catalytic activity as noted from cathodic peak current and the current at 1 V for a relatively high loaded polymer electrode appears to arise from blocking of the porous structure due to the thick deposition. The enhanced catalytic activity of the PVC-silver electrode upon modification by PPH may be due to an increase in the surface roughness factors. The possible application of these thin polymer-supported electrodes in practical systems appears to be promising.

4. Conclusions

The PVC–silver-coated electrode is a new type of electrode where silver utilization is maximum. This electrode when coated with a medium loading of poly(phenylene oxide), displays enhanced electrocatalytic activity. This is attributed to an increase in the activated porous structure. These electrodes may find their potential application in fuel cells for space craft and ion-sensors.

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