

# Electrochemically oxidized carbon anode in direct L-ascorbic acid fuel cells

Sunghyun Uhm<sup>a,b</sup>, Jinsub Choi<sup>c</sup>, Sung Taik Chung<sup>a</sup>, Jaeyoung Lee<sup>b,\*</sup>

<sup>a</sup> Department of Chemical Engineering, Inha University, Incheon 402-751, Republic of Korea

<sup>b</sup> Department of Environmental Science and Engineering, GIST, Gwangju 500-712, Republic of Korea

<sup>c</sup> Nanomaterials Application Division, Korea Institute of Ceramic Engineering and Technology, Seoul 153-801 Republic of Korea

Received 24 June 2007; received in revised form 9 August 2007; accepted 10 August 2007

Available online 22 August 2007

## Abstract

The activity of electrochemically oxidized carbon electrode was investigated in the operation of a direct L-ascorbic acid fuel cell anode. The surface oxygen species placed on electrochemically oxidized carbon electrode were analyzed by X-ray photoelectron spectroscopy and cyclic voltammetry. The electrochemical oxidation process of carbon electrode can facilitate the pore-filling process (i.e., wetting) of the electrolyte into the microstructure of the carbon electrode by increasing the number of more polar functional groups on the electrode surface. The electrochemically oxidized carbon electrode exhibited significantly enhanced electro-catalytic oxidation activity of L-ascorbic acid compared to an unmodified carbon electrode. Moreover, the simplified electrode structure using carbon paper without an additional powder-based precious catalyst layer is very favorable in creating percolation network and generates power density of 18 mW/cm<sup>2</sup> at 60 °C.

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**Keywords:** L-Ascorbic acid; Electro-oxidation treatment; Carbon paper electrode; Fuel cell performance; Percolation network

## 1. Introduction

The practical use of direct liquid fuel cells (DLFCs), given their relatively simple system design and cell operation [1–5], is expected as a promising candidate for portable energy sources. However, many obstacles such as the low-electro-catalytic activity of liquid fuel and low-fuel efficiency due to fuel crossover still prevent their widespread commercial application [2,6]. In addition, the toxicity of the fuel itself and by-products may cause other serious problems.

In order to extend the practical application of DLFCs and facilitate their penetration into the market, it is also desirable to increase the number of liquid fuels that can be employed in these devices. Until now, the most promising one was methanol owing to its high-energy density [1–3,7–9]. Other than methanol, it has also been demonstrated in many studies that several organic fuel options such as ethanol [4,10,11], formic acid [5,12–14], 2-propanol [15], ethylene glycol [16], and dimethyl ether [17] are available for DLFCs. Another alternative is microbial fuel cells, which are devices in which micro-organisms oxidize compounds

such as glucose, acetate or wastewater [18,19]. Such microbial fuel cells are utilized mostly as power generators for implantable devices such as pacemakers, gastrobots and biosensors [20,21].

Of late, in view of its safety and environmentally benign nature, L-ascorbic acid has been investigated for environmentally and biologically friendly fuel cell system [22–25]. L-Ascorbic acid (L-AA), well known as vitamin C, can be easily oxidized and so is used as a reducing agent in various chemical reactions. The electrochemical oxidation of ascorbic acid has been the subject of many studies on various kinds of electrodes. The electrode materials include Pt [22,26,27], Au [28], graphite [29], polypyrrole-coated Pt [30], polyaniline-deposited Ni [23,31], and carbon electrode [24,25,32,33]. Particularly, direct L-ascorbic acid fuel cells (DAFCs) using various forms of carbon black as anode have been extensively developed; it was shown that their performance was dominated by the electrochemically active surface area of the carbon electrode [24].

Carbon is one of the most abundant elements with various forms found on earth. However, despite its widespread use in fuel cell applications (e.g., catalyst support, bipolar plate), carbon is known to undergo electrochemical oxidation easily to surface oxides, and eventually to carbon dioxide [34,35]. Furthermore,

\* Corresponding author.

E-mail address: [jaeyoung@gist.ac.kr](mailto:jaeyoung@gist.ac.kr) (J. Lee).

the wettability of carbon surfaces depends on the extent of surface oxidation [36]. The anode of a direct liquid fuel cell inevitably requires high hydrophilicity to facilitate fuel transport throughout the electrode and enable the efficient removal of product(s) from the electrode [37].

This work attempted to take advantage of commercially available carbon paper as the anode catalyst layer for a versatile and simplified membrane electrode assembly (MEA) design and low-cost anode fabrication. Based on the hypothesis that the binder used in as-received carbon paper electrodes tends to obstruct the micropores, the electro-oxidation treatment of the carbon paper electrodes was therefore examined as a means of increasing the electrochemical active surface and/or double-layer capacitance through the attachment of a variety of functional groups. The surface oxygen species of electrochemically oxidized carbon paper electrodes were analyzed with cyclic voltammetry (CV) [38–42] and X-ray photoelectron spectroscopy (XPS) [40,43,44] to elucidate the nature of different functional groups by way of the deconvolution of the C 1s peaks. The structure of the carbon paper electrode as well as the optimal content of ionomer inside the catalyst layer is also discussed based on the percolation model [45–47].

## 2. Experimental

### 2.1. Preparation of electrodes for half-cell test

The <sup>®</sup>SIGRACET GDL 35AA (300  $\mu\text{m}$  in thickness, ca. 50 g/m<sup>2</sup> in a real weight, SGL Carbon Japan Ltd.) was used as received and electrochemically oxidized. The carbon paper contains no hydrophobic agent such as PTFE. For the electrochemically oxidized electrodes, samples were cut to the required size and installed in an acrylic holder and then immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub>. A constant potential of 1.5 V (*vs.* SCE) was applied for 5 min with an EG&G PAR model 273A potentiostat/galvanostat with conventional experimental apparatus consisting of a three-electrode cell setup using a saturated calomel electrode (SCE) reference electrode (+0.24 V *vs.* NHE) and a Pt wire counter electrode. All solutions were prepared with ultrapure water (Millipore Milli-Q water, 18 M $\Omega$  cm) and purged with N<sub>2</sub> gas before and during each experiment. The geometric area of the electrode samples exposed to electrolyte was 0.3 cm<sup>2</sup>.

### 2.2. Characterization of electrodes

Before and after the electrochemical oxidation treatment, cyclic voltammograms (CVs) were recorded at 50 mV/s in 0.5 M H<sub>2</sub>SO<sub>4</sub> at room temperature to analyze capacitive characteristics of carbon paper electrodes. In order to measure electro-catalytic L-AA oxidation activity of carbon electrode, linear sweep voltammetry (LSVs) were performed in 1 M L-ascorbic acid (Kanto) and 0.5 M H<sub>2</sub>SO<sub>4</sub> supporting electrolyte with a scan rate of 10 mV/s. The surface oxygen was analyzed using X-ray photoelectron spectroscopy (XPS) (VG Multilab 2000, ThermoVG Scientific). The individual elements analyzed were, in addition to oxygen, carbon, fluorine, nitrogen and sulfur.

### 2.3. Membrane electrode assembly and performance test

The membrane electrode assemblies (MEAs) with an electrode area of 9.0 cm<sup>2</sup> were prepared as follows: the anode consisted of carbon paper solely as a catalyst layer (SGL 35AA) impregnated with Nafion solution (Aldrich, 5 wt%) by using conventional spraying method. The ionomer content in the catalyst layer was varied to optimize the cell performance. The cathode consisted of a carbon paper as a substrate (SGL 35BC GDL) on which Pt black (Johnson Matthey, 3.0 mg/cm<sup>2</sup>) was loaded with 10 wt% Nafion solution. The electrodes were placed on either side of a Nafion 115 membrane. The assembly was hot-pressed at 100 kgf/cm<sup>2</sup> for 5 min at 140 °C.

The electrochemical oxidation treatment to enlarge the electrochemically active surface area was conducted applying 0.1 M H<sub>2</sub>SO<sub>4</sub> solution with 5 cm<sup>3</sup>/min into the anode compartment. During the oxidation process, humidified hydrogen was fed into the cathode part with a flow rate of 100 sccm. The cell was operated for 5 min at a constant potential of 1.74 V (*vs.* RHE). After the oxidation process, CVs were also recorded to measure the capacitive behavior of the electrode at 50 mV/s. Impedance spectra of the anode were measured in pseudo-galvanostatic mode (constant dc current with superposed ac potential) using a Zahner IM6 potentiostat. The frequency range investigated ranged from 10 kHz to 100 mHz with 15 points per decade and the amplitude of the sinusoidal current was adjusted not to exceed 10 mV of the potential response. Current–potential transients applying 1.0 M L-ascorbic acid aqueous solution and oxygen at flow rates of 5 cm<sup>3</sup>/min and 200 sccm, respectively, were measured using an electronic load.

## 3. Results and discussion

In electrochemical oxidation pretreatment of carbon electrode, the applied potential of 1.5 V (*vs.* SCE) was selected in the experiments because it is sufficiently high to form or change surface functional groups referring to previous study [48]. The representative CV of carbon electrode is shown in Fig. 1 and the current density of the as-received carbon paper electrode (As-

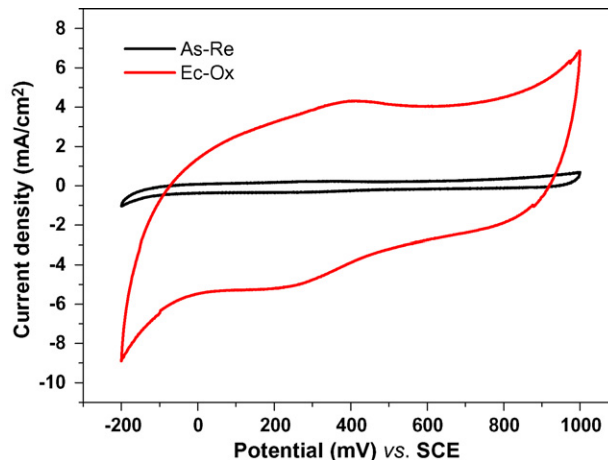


Fig. 1. CVs of As-Re and Ec-Ox carbon electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub>, scan rate = 50 mV/s at room temperature.

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