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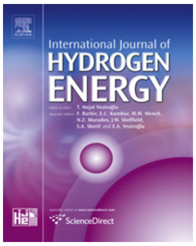

Formic acid–Formate blended solution: A new fuel system with high oxidation activity

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ABSTRACT

Formic acid and formate have been proven to be among the most promising fuels for direct liquid fuel cells. To take advantage of both formic acid and formate, the oxidation activity of a formic acid–formate blended solution was studied using cyclic voltammetry, Tafel polarization measurements, and chromoamperometry. With increased concentration of formate, the oxidation potential of formic acid shifted to the negative direction, and the peak current significantly increased, suggesting a greatly enhanced oxidation activity. The transition of formic acid from an indirect to a direct oxidation route was also observed. The enhanced oxidation activity indicated that a formic acid–formate blended solution is a promising fuel system for direct liquid fuel cells. Hence, a new concept of fuel cell, i.e., direct formic acid–formate blended fuel cell, was proposed.

1. Introduction

Direct liquid fuel cell is a clean, highly efficient, easy-operation energy conversion technology that has attracted much attention during the past decades [1–6]. Numerous organic, inorganic, and bioorganic fuels have been studied for use in these cells. The organic fuels include methanol [3–5], ethanol [7], propanol [8], ethylene glycol [9], glycerol [10], formaldehyde [11], formic acid (HCOOH) [6,12], formate ($HCOO^-$) [13–15], ethyl formate [16], dimethyl ether [17], dimethoxymethane [18], etc. The inorganic fuels include $NaBH_4$ [19], hydrazine [20], etc. The bioorganic fuels include glucose [21], ascorbic acid [22], etc. Among these fuels, HCOOH is the most excellent because of its high theoretical electromotive force, less toxicity to the Pt-based catalysts, and low crossover flux through Nafion® membranes [6,12,23–25]. However, HCOOH has a lower theoretical power density than methanol, smells bad, and is a corrosive liquid. Kita et al. [13] as well as Haan and Masel [26] have reported the increased current density of HCOOH oxidation at high pH. Aoki et al. [27] have compared the current densities generated by $HCOONH_4$, HCOOH, and CH_3OH and found that $HCOO^-$ generated the highest current density. Kjeang et al. [14] have attempted to use $HCOONH_4$ as a fuel in microfluidic direct formate fuel cells (DFFCs). However, because the oxidation of NH_4^+ is quite difficult, it accumulates in the DFFCs' solutions. Therefore, DFFCs cannot continuously work unless the solution is removed and treated. In order to take advantage of the high oxidation activity of $HCOO^-$ and

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enable DFFCs to work continuously, the possibility of using a formic acid– formate blended solution as fuel was investigated in the present study.

2. Materials and methods

2.1. *Preparation and characterization of Pt catalyst*

Vulcan XC-72 activated carbon (0.0062 g) was dispersed in 1 mL of absolute ethanol with aid of an ultrasonic stirrer for 10 min. The activated carbon suspension was dripped on a glassy carbon (GC) electrode (4 mm in diameter). After drying in open air, a drop of Nafion® solution was dripped onto the surface of the activated carbon. The electrode (C/GC) was then dried in air at room temperature for 1 h. A conventional three-electrode cell was used for the electrochemical deposition of Pt nanoparticles on the C/GC electrode. In this three-electrode cell, the C/GC electrode served as the working electrode, an Ag/AgCl/KCl(s) electrode served as the reference electrode, and a 1 cm^2 Pt foil electrode served as the counter electrode. The Pt catalyst was deposited using a cyclic voltammetric method within the potential range of −0.3 V to 0.8 V at a scan rate of 20 mV s^{-1} for three cycles in a 12 mmol L^{-1} H_2PtCl_6 solution. The obtained Pt-C/GC electrode was rinsed with deionized water and directly used for characterization and measurements.

The morphology of the Pt catalyst was characterized using a JEM-2100 high-resolution transmission electron microscope (JEOL, Japan). The diameter of the Pt particle was found to be less than 5 nm. The cyclic voltammetry (CV) of the Pt-C/GC electrode was conducted in 0.5 mol L^{-1} H_2SO_4 solution. The active area of the Pt-C/GC electrode was evaluated based on the CV curves to ensure the reproducibility of the catalyst deposition.

2.2. *Oxidation activity measurements*

A conventional three-electrode cell was used. The Pt-C/GC electrode served as the working electrode, a saturated calomel electrode (SCE) served as the reference electrode, and a 1 cm^2 Pt foil served as the counter electrode. Solutions containing 1 mol L^{-1} HCOOH and different $HCOO^-$ concentrations were used as the electrolytes. All potentials reported in the present study were referred to the SCE. CV, Tafel polarization measurements, and chromoamperometry (CA) were performed using a CHI 604A electrochemical workstation (CH Instrument, China). CV was performed from an open-circuit potential (OCP) to 1.2 V at a scan rate of 20 mV s^{-1}. Tafel linear polarization measurements were conducted from an OCP to 0.6 V at a scan rate of 20 mV s^{-1}. CA measurements were performed by first polarizing the electrode at −0.6 V for 10 s, and then stepping the potential to the predetermined value. The corresponding current transition was recorded for 600 s.

All chemicals used in the experiments were analytical grade reagents. The solutions were deoxygenated by purging with high-purity Ar gas 30 min prior to each measurement and throughout the experiments. All electrochemical measurements were conducted at ambient temperature and pressure.

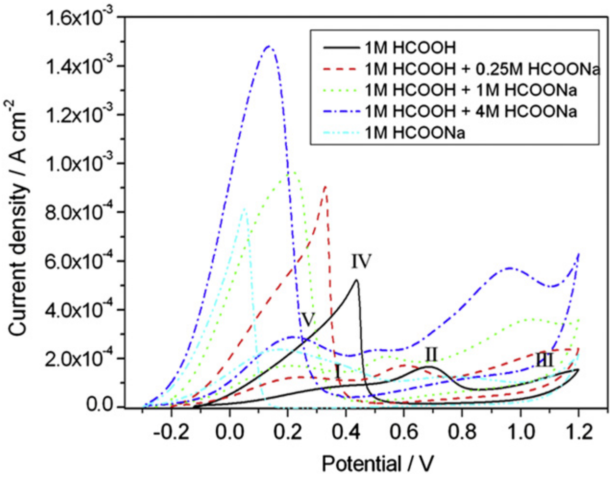

Fig. 1 – CVs of the Pt-C/GC electrode in 1 mol L^{-1} HCOOH solution containing different $HCOO^-$ concentrations. Scan rate: 20 mV s^{-1}.

3. Results and discussion

Fig. 1 shows the CV results of the Pt-C/GC electrode in 1 mol L^{-1} HCOOH solution containing different $HCOO^-$ concentrations. The Tafel plots are shown in Fig. 2. The important electrochemical parameters are summarized in Table 1.

In Fig. 1, there are five oxidation peaks in the entire CV scan, consistent with the report of Okamoto et al. [28]. The peak potential of Peak II which corresponded to the oxidation of adsorbed CO on the Pt surface shifted to the negative direction. Its peak current decreased with increased [$HCOO^-$], suggesting easier oxidation and less amount of adsorbed CO. Hence, after the addition of $HCOO^-$, the indirect oxidation route as shown in Scheme 1 was suppressed.

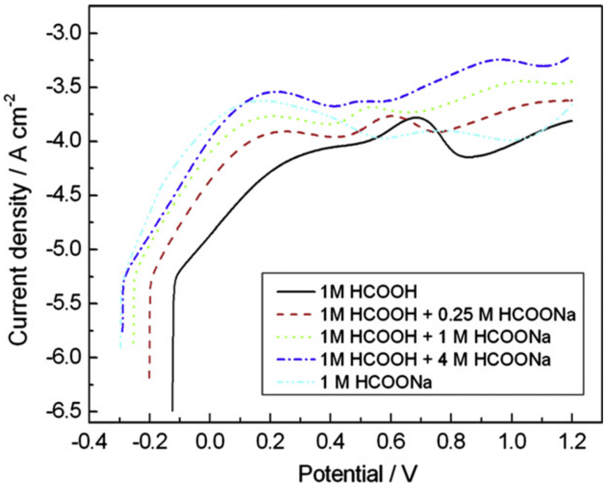

Fig. 2 – Tafel plots of the Pt-C/GC electrode in 1 mol L^{-1} HCOOH solution containing different $HCOO^-$ concentrations. Scan rate: 20 mV s^{-1}.