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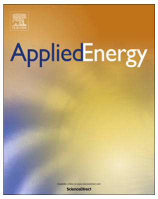

Energy efficiency of platinum-free alkaline direct formate fuel cells

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HIGHLIGHTS

- Alkaline Platinum-free formate fuel cells top 42% efficiency @ 60 °C.
- Palladium efficiently oxidizes formate.
- Power density exceeding 250 mW cm^{-2} @ 60 °C has been achieved.
- Performance exceeds that of Alkaline Direct Alcohol Fuel Cell.

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ABSTRACT

We report the energy performance of a new platinum-free alkaline direct formate fuel cell, equipped with a commercial anion exchange membrane, a nanostructured Pd/C anode and a Fe–Co/C cathode. The cell was investigated both at room temperature and at 60 °C for the determination of the following parameters: (i) maximum power density, (ii) delivered energy, (iii) faradic (fuel conversion) and energy efficiency. These parameters show a dramatic dependence on fuel composition. The highest energy efficiency is obtained using high energy density fuel (4 M KCOOH and 4 M KOH) and with a maximum operating temperature of 60 °C. This represents a key step in the progress of alkaline platinum-free DFFC technology, demonstrating their potential as power sources for portable electronic devices and remote power generation systems. For example, a fuel load of 750 ml in a DFFC device operating at 60 °C would be able to produce 90 W h of energy, that required to fully charge the battery of a laptop computer.

1. Introduction

Direct Liquid Fuel Cells (DLFCs) have multiple advantages over the systems fed with hydrogen. The fuel is easier to handle, store and transport and the volume energy density is much larger. However, most of these advantages are difficult to realize in practice. Indeed the oxidation of liquid fuels shows large anode overpotential that results in poor energy performance [1,2].

To compensate the slow kinetics, DLFC generally employ large amount of noble metals at the anode (anode loadings higher than 2 mg cm^{-2} are common) [3]. Platinum and platinum alloys, particularly platinum–ruthenium, are the most investigated electrocatalysts [4]. It is worth mentioning that the majority of the investigations on systems equipped with platinum based electrocatalyts are in acidic systems [5,6]. Less attention has been devoted to the alkaline environment. Nevertheless, it has been shown that the oxidation of small organic molecules is generally faster than in alkali than acids [3,7].

Amongst the liquid fuels, alcohols are the most widely studied and particularly methanol [8], ethanol [9], and glycerol [10]. Despite the high energy density of alcohols, the energy performance of Direct Alcohol Fuel Cells is still limited low. Maximum power density, energy efficiency and stability are still far from those of Polymer Electrolyte Membrane Fuel Cells fed with hydrogen [2,5].

The use of formic acid as fuel for DLFC has recently attracted much attention and has been proposed to realize power sources for portable electronics [11,12]. Formic acid has numerous advantages over alcohols, such as low fuel crossover, high theoretical cell potential ($E^0 = 1.45$ V), and high power densities and fast oxidation kinetics [13,14].

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Nevertheless, Direct Formic Acid Fuel Cells (DFAFCs) assembled with proton conducting membranes (PEM) have several problems associated with long-term instability of Pd [15] and Pt [16] anode electrocatalysts, corrosion of both the carbon electrocatalyst support and the Nafion membrane, and difficult water–CO_2 management in DFAFC stacks [17–19]. Formic acid is corrosive, dangerous to human health and should be handled with care. Moreover, a critical obstacle that limits the wide application of DFAFCs is the overall system cost, mainly due to the large amount of Pt-based catalysts employed in both anode and cathode electrodes [20,21].

Potentially, most of these challenges can be overcome by using salts of formic acid as fuel under alkaline conditions. Formate salts have low toxicity, are not volatile at temperatures below 100 °C, and can be easily stored and transported. Unlike in acidic media, the kinetics of both the formate oxidation reaction (FOR) and oxygen reduction reaction (ORR) are fast in alkaline media. This has enabled the realization of Direct Formate Fuel Cells (DFFCs) equipped with anion exchange polymeric membranes (AEMs). For example Jiang and Wieckowski have reported a DFFC, using a polybenzimidazole-based membrane, Pd anode and Ag cathode electrocatalysts, fed with 6 M HCOOK and 2 M KOH, capable of producing peak power of 160 mW cm^{-2} at 120 °C [22]. Haan and coworkers have demonstrated a DFFC employing an anion exchange membrane (Tokuyama A201), Pd-black anode and Pt/C cathode, which produces peak power of ca. 270 mW cm^{-2} [23–25]. This has been achieved with a fuel containing 1 M KCOOH. Such low fuel concentrations strongly limit the weight and volumetric energy density of DFFC devices.

There are few reports of DFFCs with completely platinum free electrocatalysts. Amongst noble metals, palladium (Pd) is one of the most effective metals for small organic molecule electrooxidation in alkaline media [26–28]. As cathode catalyst, non-noble metal catalysts such as Fe–Co/C can be readily used as they exhibit remarkable activity towards the ORR under alkaline conditions [29,30].

High power densities with a completely platinum-free system, fed with 4 M KCOOH and 1 M KOH, have been reported by Zhao and co-workers [31]. Their cell was equipped with a home-made alkaline membrane and produced up to 250 mW cm^{-2} at a cell temperature of 80 °C. However, the stability of commercial state of the art alkaline membranes is at present limited to operating temperatures below 60 °C [32].

For this reason this paper focuses on a novel system equipped with a commercial anion exchange alkaline membrane (Tokuyama) and the optimization of its performance at 60 °C. Furthermore, operations at high formate and alkali concentration have been addressed, in order to explore functioning in conditions that maximize delivered energy density. The paper also reports a comprehensive evaluation of the performance that focuses on the following parameters: (i) maximum power density, (ii) delivered energy per fuel batch and (iii) faradic (fuel conversion) and energy efficiency. The novelty presented in this paper is the presentation of a comprehensive energy assessment of *platinum-free* DFFCs, equipped with an anion exchange membrane, Pd/C (C = Vulcan XC-72) as anode and a proprietary Fe–Co/C (C = Ketjen Black) as cathode [29].

We believe that such an analysis, that was not been addressed up to now, and is essential for the development of DFFCs as practical and commercial devices. Indeed high energy efficiency and energy per single fuel load are essential to weight and volume reduction as well as to limit capital costs [33]. This together with the use of commercial available components such as membranes is the key to drive alkaline direct formate fuel cells toward a practical exploitation to power portable electric systems and for power generation in remote locations.

2. Materials and methods

2.1. Chemicals

All manipulations, except as stated otherwise, were routinely performed under a nitrogen atmosphere using standard airless technique. Carbon black (Vulcan XC-72 pellets) was purchased from Cabot Corp., USA. The Fe–Co/C cathode electrocatalyst was prepared by a method reported elsewhere [29]. All metal salts and reagents were purchased from Aldrich and used as received. All the solutions were freshly prepared with doubly distilled deionized water. All chemicals are analytically pure.

2.2. Synthesis of Pd/C anode electrocatalyst

6.0 g of Vulcan XC-72 was suspended in 250 ml of ethylene glycol and sonicated for 20 min in a 1 l three-neck round-bottomed flask. Then a mixture of H_2O (50 ml) and ethylene glycol (50 ml) and 20 ml HCl (37%) with 2 g of dissolved $PdCl_2$ was added drop by drop under stirring in a N_2 stream. After adequate stirring, an alkaline solution of NaOH (13.2 g) in H_2O (10 ml) and ethylene glycol (35 ml) was introduced in the reactor which then was heated at 140 °C for 3 h again under a N_2 atmosphere. Then the mixture was cooled down to room temperature. The solid product was filtered off and washed with H_2O to neutral pH. The final product was dried in vacuum oven at 40 °C. 7.79 g of catalyst was obtained. Pd content = 20.3 wt.% (ICP-AES).

2.3. Characterization

Field Emission Scanning Electron Microscopy (FMSEM) was performed by using Zeiss Gemini 1530, capable of a spatial resolution 2.1 nm at 1.0 kV.

Transmission electron microscopy (TEM) was performed on a Philips CM12 microscope at an accelerating voltage of 100 kV. The microscope was equipped with an EDAX energy dispersive microanalysis system.

Powder X-ray diffraction spectra was acquired at room temperature with a PANalytical X'PERT PRO diffractometer, employing Cu Ka radiation ($l = 1.54187$) and a PW3088/60-graded multilayer parabolic X-ray mirror for Cu radiation. The spectra was acquired in the 2q range from 5.0 to 120.08, using a continuous scan mode with an acquisition step size of $2q = 0.02638$ and a counting time of 49.5 s.

2.4. Half-cell testing

The anode electrocatalyst ink consisted of Pd/C (22 mg), 2-propanol (2 g) and 0.19 g of Tokuyama™ OH-type anion exchange resin in alcohol solution. Of this ink ca. 4 mg was taken for preparing the electrode for the CV.

The resulting suspension was sonicated for 2 h with a FALC sonic bath and then introduced onto a 5 mm ($A = 0.1963$ cm^2) Teflon potted glassy-carbon rotating disk electrode tip (PINETM). Each electrode was dried for 30 min before it was mounted on the rotating disk electrode shaft and then immersed into the electrolyte.

A typical cyclic voltammogram of Pd/C was measured between the potential range of 0 and 1.4 V in 2 M KOH solution. The activity of formate oxidation was investigated in 2 M HCOOK + 2 M KOH solution by cyclic voltammetry in the range of 0–1.20 V. Reported CVs were acquired at a scan rate of 50 mV s^{-1}.

The reference electrode was a commercial Ag/AgCl/KClsat (Princeton Applied Research). The counter electrode was platinum gauze enclosed in a glass tube with porous bottom. All

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