Electrochimica Acta 104 (2013) 124–133

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Direct evidence of a triple-path mechanism of formate electrooxidation on Pt black in alkaline media at varying temperature. Part I: The electrochemical studies

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ARTICLE INFO

Article history:
Received 4 March 2013
Received in revised form 13 April 2013
Accepted 15 April 2013
Available online xxx

Keywords:
Formate electrooxidation
Electrocatalysis
Platinum black
Alkaline electrolyte
Fuel cells
Temperature dependence

ABSTRACT

Electrooxidation of formate on high-surface Pt black in alkaline media has been studied at varying temperature by means of cyclic voltammetry and stripping voltammetry. In the positive-going scans from 0.10 to 1.2 V vs RHE, the formate oxidation produces three oxidation current peaks: (i) peak I (at potentials where the coverages of both surface hydrogen and oxygen-species are very low), (ii) peak II (exhibiting obvious potential shift from 0.66 to 0.51 V upon increasing temperature from 20 to 80 °C), and (iii) peak III (at higher potentials where a considerable formation of surface oxygen species commences). Both peaks I and II are closely correlated but they are independent of peak III. Among the three peaks, the temperature dependence of peak II is well in agreement with that of the stripping peak of a CO adlayer. These results suggest a triple-path reaction mechanism. Adsorption of formate onto Pt surfaces may result in formation of precursor adsorbates with different reactivity. Analogous to the reported dual-path mechanism, active precursor adsorbate is responsible for (i) a direct path involving the formate oxidation to CO_2 (leading to peak I), and (ii) an indirect path involving the formation of surface CO and its further oxidation to CO_2 (leading to peak II). An independent third path via oxidation of less-active precursor adsorbate to CO_2 with adsorbed HCOO as the most likely intermediate accounts for peak III. All the oxidation reactions involved in the triple paths are accelerated by increasing reaction temperature with different apparent activation energies. At elevated temperature, diffusion-limited oxidation currents are attained. It is suggested that both the activities of surface OH and precursor adsorbates play a major role in mediating the reaction mechanism as well as participating in the formate oxidation.

1. Introduction

Direct formic acid fuel cells (DFAFCs) have received considerable attention over the past several decades due to facile anode reaction kinetics, high theoretical thermodynamic cell potential and low fuel crossover [1–4]. However, the state-of-the-art DFAFC technology based on proton-conducting membranes faces several challenges. HCOOH is corrosive. It must be handled with care during transportation, storage and uses. It is also expected that sluggish kinetics of the oxygen reduction reaction in acidic media and the precious metal catalysts required at the cathode side will also hinder commercialization of this technology. These challenges could be addressed using the counterpart of HCOOH, formate salt, in an alkaline fuel cell. Formate salts are stable, have low toxicity, and relatively inexpensive to use. They are also easily handled as solids or in solutions. Potassium formate (HCOOK) has been commercially used in oil industry, de-icing and heat transfer [5]. The HCOOK solutions in alkaline media are not volatile at 100 °C, which is also an advantage over HCOOH. These properties indicate that using formate as a fuel would create a potential high-performance, low-cost, and environmentally benign fuel cell technology. Recently, the prospect of direct formate fuel cells (DFFCs) operated with alkaline HCOOK was successfully demonstrated by Jiang and Wieckowski [6], and Bartrom and Haan [7].

Compared to extensive studies of HCOOH oxidation in acidic media [8–11], formate oxidation in alkaline media has received less attention. In alkaline media, formate is relatively stable on Pt and itself cannot be oxidized at mild conditions [12]. Munson reported that the rate of the formate oxidation reaction is very slow and attributed this to poor absorbability of formate on Pt [13]. Facile formate oxidation was achieved on Pd and Pd-based alloy electrodes under similar conditions via a different decomposition

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http://dx.doi.org/10.1016/j.electacta.2013.04.093

mechanism [14]. Recently, Christensen et al. investigated the oxidation of formate anions on a polycrystalline Pt electrode in alkaline media using in situ FTIR technique [15,16]. They detected the formation of linearly adsorbed CO, bridge-bonded CO and carbonate at lower potentials, and the formation of carbonate, bicarbonate and CO_2 at higher potentials. More recently, John et al. performed mechanistic studies of the formate oxidation on polycrystalline Pt in alkaline media employing cyclic voltammetric and differential electrochemical mass spectrometric techniques [17]. They developed a modified dual-path mechanism for the formate oxidation. However, all these studies were conducted at low (room) temperature. The kinetics of formate oxidation in alkaline media at low temperatures is too sluggish to be considered for fuel cell applications. Because increasing reaction temperature has been proven as a simple but very effective approach to promote the electrode kinetics, it is important to study the formate oxidation in alkaline media at elevated temperatures to explore strategies for developing high-performance DFFC technology. Fundamentally, it is also important to study formate oxidation for improving our understanding of small organic molecules in alkaline media since formate is the simplest organic salt. However, there has been little investigation done on formate using these parameters.

The present work was undertaken to study the formate oxidation on Pt nanoparticles in alkaline media as a function of reaction temperature. We found that formate oxidation can be improved by increasing temperature. It produces three well-defined oxidation current peaks in a potential range of 0.10–1.20 V vs RHE, which are strongly dependent on the surface electrochemistry of Pt. Peak I is seen at potentials where the coverages of both surface hydrogen and oxygen-containing species are very low and a sharp peak II is observed in the double-layer zone followed by a broad peak III at potentials where considerable formation of the surface oxygen-containing species commences. This provides are direct evidence of a triple-path reaction mechanism of formate oxidation. Analogous to the reported dual-path mechanism, a direct path involving the formate oxidation to CO_2 is responsible for peak I. An indirect path involving the formation of CO_{ads} and its further oxidation is responsible for peak II. An independent third path involving the formation and oxidation of adsorbed HCOO accounts for peak III. These facts are useful for understanding oxidation of small organic molecules in alkaline media and the development of DFFC technology.

2. Experimental

All electrochemical measurements were performed using an Autolab general purpose electrochemical system (Ecochemie, Netherland). The working electrode was prepared by attaching high-surface Pt black (HiSPEC® 1000) onto a gold microdisk electrode of 100 μm diameter, following a mechanical rubbing approach [18,19]. The Pt black has a specific surface area of 27 $m^2\,g^{-1}$ and an equivalent particle size of 8 nm. A platinized Pt wire of 0.5 mm diameter and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The electrochemical surface area of the Pt black layer was assessed from the charge associated with hydrogen adsorption/desorption with double layer charge correction. In the following, all potentials were corrected to a RHE scale, and all currents were corrected to the electrochemical surface area of the Pt black electrode, unless stated otherwise. The effective radium of the Pt black electrode calculated from the diffusion-limiting current measured in 0.01 $mol\,dm^{-3}$ $K_3Fe(CN)_6$ + 0.5 $mol\,dm^{-3}$ KCl solution [4], was around 75 μm.

All solutions were prepared from analytical grade reagents with deionized water having a resistivity of 18.2 MΩ cm. All formate oxidation experiments in alkaline media were carried out in 0.5 $mol\,dm^{-3}$ KOH containing HCOOK at different concentrations. Cyclic and steady-state voltammograms were measured at 50 $mV\,s^{-1}$ and 5 $mV\,s^{-1}$, respectively. During the measurements of electrochemical CO stripping, CO was adsorbed onto the electrode surfaces by bubbling high purity CO through 0.5 $mol\,dm^{-3}$ KOH solution for 15 min while the potential was held at 0.05 V. After adsorption, the dissolved CO was removed from the solution by bubbling high purity Ar for 15 min while still holding the potential at 0.05 V. The potential was then scanned in the positive direction from 0.05 to 1.30 V at 50 $mV\,s^{-1}$. The resulting currents were integrated and corrected for the effects of oxide growth and the double layer charging currents by subtracting the charge for the same electrode in the absence of an adsorbed CO monolayer.

To measure electrochemical stripping of adsorbed species formed during the formate oxidation, a combined potential-step and subsequent potential-scan were applied. During the measurements, the electrode potential was initially held at 1.20 V for 1 s to remove all adsorbates. Then the electrode was polarized at 0.10 V for 2 s to reduce adsorbed oxides formed on the electrode surfaces at a previous oxidizing potential. After the polarization of 60 s at 0.25 V, the electrode was floated out from the formate solution while the potential was held at 0.25 V. Subsequently, the electrode was rinsed with deionized water and then transferred into 0.5 $mol\,dm^{-3}$ KOH solution at the controlled temperature. The stripping voltammograms were obtained by scanning the potential from 0.25 to 1.20 V at 50 $mV\,s^{-1}$.

To minimize the influences of solution impurities produced by possible glass corrosion in alkaline electrolyte [20,21], all measurements were performed in a short period of time with fresh solution used for each run. This is ensured by no obvious distortion of our base cyclic voltammograms from normally expected responses at varying temperature.

3. Results and discussion

3.1. Cyclic voltammetric studies

Base cyclic voltammograms for the Pt black electrode in 0.05 $mol\,dm^{-3}$ KOH solution as a function of temperature are shown in Fig. 1. Analogous to literature results [13], three characteristic regions corresponding to hydrogen adsorption (H_{ads}) and desorption (H_{de}), double layer and oxide formation/reduction are observed. The peak potentials associated with H_{ads}/H_{de} over the

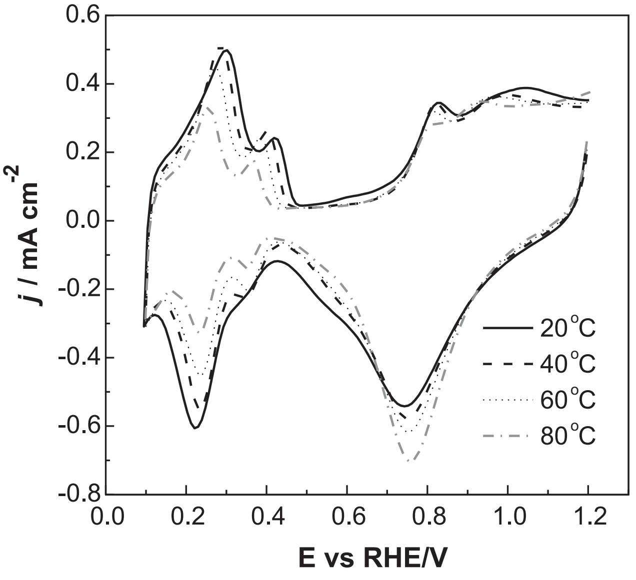

Fig. 1. Base cyclic voltammograms for a Pt black electrode in 0.5 $mol\,dm^{-3}$ KOH at 500 $mV\,s^{-1}$ as a function of reaction temperature.