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Direct kinetic evidence for the electronic effect of ruthenium in PtRu on the dissociative adsorption of methanol

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ABSTRACT

Dissociative adsorption of methanol on platinum in a PtRu bimetallic electrocatalyst has been studied by an accelerated degradation test and normal pulse voltammetry. PtRu electrodes with a minimum number of potential cycles show the highest electrode rate constant values while the one with platinum-like surface characteristics show the lowest rate constant values, evidencing the promotional effect of Ru.

1. Introduction

Direct methanol fuel cells (DMFC) are appealing as a power source due to the high energy density and easy handling of the liquid methanol fuel [1,2]. Among the various bimetallic combinations that have been studied, PtRu has been accepted as the best electrocatalyst for the methanol oxidation reaction (MOR) in DMFC [3–5]. The two global reactions that comprise the overall MOR are (i) the initial dehydrogenation step culminating in various intermediates like CO that poison the Pt sites,

$$CH_3OH + Pt \rightarrow Pt-CO + 4H^+ + 4e^- \tag{1}$$

and (ii) the slow oxidation of the poisoning intermediates to retrieve the active sites,

$$Pt-CO + H_2O \rightarrow Pt + CO_2 + 2H^+ + 2e^-. \tag{2}$$

In this regard, a bifunctional theory was advanced to account for the promotional effect of the secondary metal. Briefly, the bifunctional model considers Pt sites as adsorption/dehydrogenation centers while Ru acts as the center generating oxygen containing species at lower potentials for the oxidation of the intermediates (Reaction 2) formed at the Pt sites (Reaction 1) [6,7]. Another relevant model considers the electronic effect of Ru on Pt. Accordingly, electron donation by Ru to Pt decreases the Pt-4f binding energy, which in turn reduces the Pt—CO bond strength, enabling a facile removal of the CO intermediate [7]. The electronic effect of Ru has also been suggested to render Pt more susceptible for dissociative adsorption of methanol [8].

The limitations to a systematic analysis of the effect of Ru on the initial dissociative adsorption of methanol are (i) the kinetics of methanol oxidation is complicated involving multi-step electrode reactions and parallel pathways forming poisonous intermediates, (ii) the activity of Pt towards the dissociative adsorption of methanol cannot be compared quantitatively, for example, between Pt and PtRu since the electrochemical active surface area of Pt in PtRu cannot be estimated precisely, and (iii) standard potential (E^0) of dissociative adsorption of methanol on Pt and PtRu is unknown and hence the corresponding standard rate constants cannot be estimated from the voltammetric experiments for evaluating electrocatalysts kinetically. We present here a methodology to circumvent the above limitations as much as possible and observe the electronic effect of Ru on the dissociative adsorption of methanol on Pt in a PtRu electrocatalyst in terms of rate constants. The strategies involved in our study are (i) the two global reactions reactions 1 and 2 can be decoupled with the aid of normal pulse voltammetry (NPV) with short electrolysis time so that the reaction is stopped at the formation of soluble intermediates without progressing to the extent of poisoning the electrocatalyst [9,10], (ii) accelerated degradation cycles (ADC) can be employed to gradually leach out Ru in PtRu to an extent wherein the surface of the PtRu electrocatalyst is devoid of Ru and/or its effect [11,12], and (iii) even without the knowledge of E^0, the rate constants for different electrocatalysts can be compared at convenient reference potentials as suggested by Oldham and Parry [13].

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2. Experimental

NPV studies were carefully designed so as to renew the depletion layer of the reactants for each new pulse without contaminating with the products of the previous pulse. This was achieved by waiting at a base potential for a period of 25 s. Furthermore, a very thin layer of catalyst was applied onto glassy carbon substrate (3 mm diameter) by drop casting 2 μL of the ink prepared typically by sonicating 2 mg of 20 wt.% commercial PtRu on carbon support (1:1 atomic ratio; E-TEK) in 2 mL of water and ethanol mixture (1:1) containing 15 μL of 5% Nafion. A series of ADC-NPV experiments were conducted as follows. The carbon supported PtRu electrode (PtRu/C) was scanned at 0.02–1.2 V for 5, 20, 40, 60, 80, and 100 cycles in 0.5 M H_2SO_4 at a rate of 50 mV s^{-1}, where the initial five cycles can be considered as cleaning cycles. After each specified number of cycles, the electrolyte was replaced with 0.5 M H_2SO_4 and 1 M methanol and the NPV experiments were conducted subsequently. A series of NPV experiments were performed after a specified number of ADCs on the electrodes, which are denoted as PtRu/C-5cy, PtRu/C-20cy, PtRu/C-40cy, PtRu/C-60cy, PtRu/C-80cy, and PtRu/C-100cy. The base potential was deduced from a cyclic voltammogram that was recorded before each NPV experiment [10]. A Hg/HgSO$_4$ electrode served as the reference electrode, and the potentials are referred subsequently with respect to RHE. A Pt wire was used as a counter electrode. The solutions were purged with high purity nitrogen for 10 min before the experiments and blanketed gently over the solution during the experiments. CO stripping voltammetry was carried out by purging high purity CO gas for 30 min at a holding potential of 0.1 V. The purging gas was then switched to nitrogen to remove dissolved CO. CO$_{ad}$ was then stripped by scanning potential between 0.05 and 1.2 V at a rate of 20 mV/s. The amounts of Ru ions in H_2SO_4 solution were measured using inductively coupled plasma–optical emission spectroscopy (ICP-OES, Perkin-Elmer).

3. Results and discussion

Xu et al. [10] showed that by applying potential pulses of short-time (<30 ms) and waiting for large periods between successive pulses, the total electrooxidation of methanol on a polycrystalline Pt can be confined to the formation of soluble species like formic acid and/or formaldehyde:

$$CH_3OH + H_2O \rightarrow HCOOH + 4H^+ + 4e^- \tag{3}$$

The above reaction has a rate determining step of initial dissociative adsorption of methanol, viz.

$$CH_3OH_{sol} \rightarrow CH_2OH_{ad} + H^+ + e^- \tag{4}$$

Making use of reaction 3, the electronic effect of Ru on the dissociative adsorption of methanol on Pt was studied by NPV. A gradual dissolution of Ru from PtRu/C surface was realized by potential cycling between 0.02 and 1.2 V in 0.5 M H_2SO_4. Fig. 1a shows the changes in the voltammograms of PtRu/C to that of Pt through 100 cycles. The changes include fully developed hydrogen adsorption/desorption peaks, decrease in the double layer current, and shifting of Pt oxide reduction peak to anodic potentials. Fig. 1b shows CO stripping voltammograms measured after various potential cycles. Initially the peak potential is 0.57 V, typical of PtRu, which after 100 cycles increases to 0.77 V indicating Pt like surface. A shoulder at higher potential appears after 60 cycles and becomes dominant after 100 cycles. Fig. 1c shows concentrations of dissolved Ru and Pt after various potential cycles measured by ICP-OES. NPV studies were conducted on the electrodes obtained after a specified number of ADCs. Typical S-shaped voltammograms at different sampling times (τ) are shown in Fig. 2. The anodic limiting currents (i_d) vary inversely with τ, and the half wave potentials ($E_{1/2}$) shift anodically with decreasing τ. Fig. 3 shows the variation of anodic limiting current with the inverse square root of τ for various PtRu/C electrodes. The linear variation indicates, as per Cottrell equation (Eq. (5)), that i_d is diffusion-controlled and semi-infinite [14].

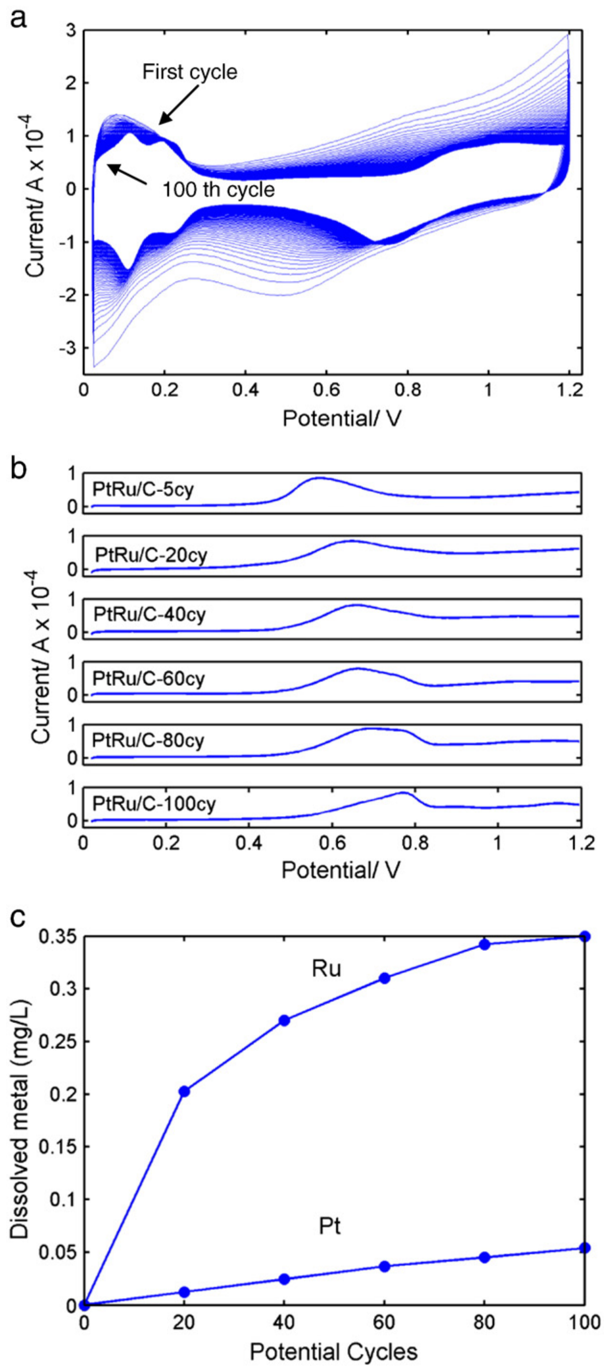

Fig. 1. (a) Cyclic voltammograms of 100 cycles of PtRu/C in 0.5 M H_2SO_4, (b) CO stripping voltammograms of PtRu/C at various potential cycles, and (c) variation of dissolved Ru and Pt concentrations with potential cycles.

$$i_d(\tau) = \frac{nFAC\sqrt{D_{app}}}{\sqrt{\pi\tau}} \tag{5}$$

where D_{app} denotes apparent diffusion coefficient of methanol and other symbols have the usual electrochemical significance [14]. The D_{app} values obtained from the slope of the plots in Fig. 3 vary closely in the order of 10^{-11} cm^2 s^{-1} and are in agreement with the