Kinetics of oxygen reduction reaction on nanostructured thin-film platinum alloy catalyst

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HIGHLIGHTS

► Nanostructured thin-film ternary PtCoMn cathode catalyst.
► Pressure and relative humidity dependence of oxygen—reduction reaction kinetics.
► 39.5 kJ mol^{-1} activation energy for ORR kinetics.
► 0.13—0.25 A mg$_{Pt}^{-1}$ mass activity at 0.9 V, 1 atm H$_2$ and O$_2$, 80 °C and 100% RH.
► 1.7—2.0 mA cm$_{Pt}^{-2}$ specific activity at 0.9 V, 1 atm H$_2$ and O$_2$, 80 °C and 100% RH.

ARTICLE INFO

ABSTRACT

The kinetics of the oxygen reduction reaction (ORR) on nanostructured thin-film (NSTF) ternary PtCoMn catalyst was investigated in 50 cm^2 proton-exchange membrane single cell fixtures. The investigation covered a wide range of oxygen partial pressures (0.2—0.5 atm), temperatures (30—90 °C), relative humidities (25—100%), and Pt loadings (0.05—0.2 mg cm^{-2}) in the cathode catalyst. The kinetic data were derived from cell polarization curves measured during Galvanodynamic scans from near open-circuit to a high current density and back to near open-circuit. The kinetic data were correlated with a single Tafel equation and a transfer coefficient that is a function of the relative humidity (RH). The correlation indicates a 0.36 order for the O$_2$ partial pressure, 39.5 kJ mol^{-1} activation energy for the temperature dependence, and an additional 0.9 order for RH dependence. The calculated mass activities and specific activities at 0.9 V Ohmic resistance corrected cell voltage, 1 atm H$_2$ and O$_2$ partial pressures, 80 °C and 100% RH agree well with the measured values of 0.13—0.25 A mg$_{Pt}^{-1}$ and 1.7—2.0 mA cm$_{Pt}^{-2}$ for the cells with different Pt loading.

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1. Introduction

Nanostructured thin film electrocatalysts have shown promise in addressing the performance, cost and durability barriers that must be overcome for mass commercialization of automotive fuel cells. Several studies by Debe and associates [1—3] have demonstrated that the NSTF catalysts can have significantly higher specific activity and durability than the conventional carbon supported highly dispersed Pt catalysts. The NSTF catalysts are formed by vacuum sputter-deposition of catalyst alloys onto a supported monolayer of highly oriented crystalline organic-pigment whiskers [1]. The support whiskers have a high aspect ratio (20—50),

0.6—2 μm length, rectangular lath-like morphology, 55 ± 12 nm width and 27 ± 7 nm thickness, and 3—5 × 10^9 cm^{-2} a real number density [1]. The whiskers have been coated with pure Pt as well as binary and ternary Pt alloys [2,3]. The PtCoMn ternary alloy (nominal 68:29—30:2—3 atomic ratio) is of particular interest as it has been evaluated extensively for performance and durability under potential cycling conditions (cyclic voltammetry with H$_2$/N$_2$), long holds at 1.5 V and higher potentials (support stability), and startups and shutdowns in H$_2$/air [4,5].

The purpose of this work is to characterize the activity of the ternary Pt$_{0.68}$Co$_{0.3}$Mn$_{0.02}$ NSTF catalyst for the oxygen reduction reaction (ORR) in H$_2$/air fuel cells. The intent is to determine the ORR activity as a function of the oxygen partial pressure, temperature, relative humidity and Pt loading. Previous studies on the ORR activities of Pt and PtCoMn catalysts on NSTF whiskers have used the rotating ring-disk electrode (RRDE) method in 0.1 M HClO$_4$ at

room temperature to 60 °C [6]. These studies have shown that the area specific activity of Pt/NSTF is similar to that of bulk Pt and that the activity of the ternary PtCoMn catalyst is about twice the activity of Pt/NSTF. The observed enhancement in the ORR activity in the RRDE measurements is similar to the results obtained in 50 cm^2 H$_2$/air fuel cells [6–10].

Our approach to determine the ORR kinetics for PtCoMn/NSTF from the polarization curves for H$_2$/air fuel cells benefits greatly from similar work described in literature on dispersed Pt/C electrodes. The past work has relied on holding the cell at a constant potential for 10 min or longer to ensure that the catalyst reaches the corresponding equilibrium Pt oxide coverage [11]. The advantage of using long hold times is that the data are quite reproducible; the disadvantage is that the data cannot be directly used to analyze the polarization curves that are generally obtained at faster scan rates. We used a slightly different approach of holding for 2 min at each data point and averaging the potentials measured during down-scans from 0.02 to 2 A cm^{-2} and reverse upscans from 2 to 0.02 A cm^{-2} (10 points per decade) to estimate cell voltages at conditions approaching the equilibrium oxide coverages. Future work will explicitly determine the oxide coverage in the ternary catalyst as a function of the cathode potentials, the effect of the oxide coverage on the ORR activity, and the dynamics of Pt oxidation and Pt oxide reduction.

2. Experimental

Eight 50 cm^2 active area single cells were assembled with a 24 μm membrane (850 equivalent weight), the ternary NSTF catalyst, and 3 M gas diffusion layers (GDL) into a Fuel Cell Technologies test cell containing quad serpentine flow fields. The GDL consisted of a backing paper to which was applied a hydrophobic treatment and an MPL (micro-porous layer). All cells had a Pt loading of 0.05 mg cm^{-2} in the anode. Two of the eight cells had a Pt loading of 0.103 mg cm^{-2} in the cathode. The Pt loading in the cathode in the other cells (two each) was 0.054, 0.146 and 0.186 mg cm^{-2}. All cells were first conditioned using a "thermal cycling" process, described in detail in Steinbach et al. [12], which consisted of repeated temperature and voltage cycles over a period of 2–3 days until stable performance was reached. Next, oxygen reduction activity of the cathode catalyst, short resistance and H$_2$ crossover, and electrochemically active surface area (ECSA) of cathode catalyst were measured, after which a series of tests were conducted, as described below.

Table 1 lists the baseline Pt loading in the electrodes and the operating conditions. One of the cells with 0.103 mg cm^{-2} Pt loading in the cathode was considered as the reference. The reference operating conditions were 80 °C cell temperature, 1.5 atm H$_2$ and air inlet pressures, 65 °C inlet dew point temperatures, and H$_2$ and O$_2$ stoichiometries (SR) of 2.

Table 2 summarizes the test matrix with eight series of tests. Series 1 tests varied the cell temperature from 75 °C to 90 °C ($P = 1.5$ atm, SR$_c$ = 2, SR$_a$ = 2) with the inlet dew points predetermined as a function of pressure, temperature and anode/cathode stoichiometry to maintain 100% relative humidity (RH) at cell exit. In all tests, humidification water was injected directly into

the anode and cathode feed streams to reach the set dew points. Also, the outlet RH was not measured but was estimated from the cell operating conditions.

The backpressure regulator was used to vary the cell inlet pressure in Series 2 tests from 1 to 2.5 atm ($T = 80$ °C, SR$_c$ = 2, SR$_a$ = 2). As explained later, the target inlet pressure could not be reached under some conditions even with the backpressure valve completely open to the ambient. As in Series 1 tests, the inlet dew points were also adjusted to maintain 100% RH at cell exit.

Series 3 tests varied the inlet dew points from dry (no water addition) to 80 °C ($P = 1.5$ atm, $T = 80$ °C, SR$_c$ = 2, SR$_a$ = 2). Series 5 tests varied the O$_2$ stoichiometery from 1.5 to 5 with the inlet dew points adjusted to maintain 100% RH at cell exit ($P = 1.5$ atm, $T = 80$ °C, SR$_a$ = 2). Series 6 tests varied the H$_2$ stoichiometry from 1.2 to 5 with the dew points held at the reference value of 65 °C ($P = 1.5$ atm, $T = 80$ °C, SR$_c$ = 2). Series 7 tests were designed to investigate the cell operation during warm-up at 30, 45 and 60 °C with dry feeds ($P = 1.5$ atm, SR$_c$ = 2, SR$_a$ = 2). Similarly, Series 8 tests were designed to investigate cell operation during idling at low pressures and high O$_2$ stoichiometries.

Series 4 tests were conducted on cells with different Pt loadings in the cathode. These cells were only operated at the reference conditions.

To check for cell-to-cell variability, all tests were repeated on the companion cells with identical Pt loadings in the cathode.

Fig. 1a–h present the polarization curves for the eight series of tests. These were obtained during Galvanodynamic scans (GDS) at cell current densities varying from 0.02 to 2 A cm^{-2}. Only the data up to 1 A cm^{-2} are plotted in Fig. 1 since significant mass transfer effects are present at higher current densities. Our procedure was to start the measurements near the open circuit at 0.02 A cm^{-2}, then increase the current density in steps until either 2 A cm^{-2} was reached or the cell voltage decreased to 0.40 V, followed by an upscan back to 0.02 A cm^{-2}. The cell voltages were measured at ten current steps per decade but the maximum step size was limited to 0.1 A cm^{-2}. The cell was held for 120 s at each current step and the cell voltage was recorded every 5 s. Also, the cell resistance was determined every 5 s by on-line AC impedance measurements between 10 and 1 kHz, from which the high frequency resistance (HFR) was estimated by fitting to a Randle's cell model. The cell voltages presented in Fig. 1 are the measured values averaged over the last 30 s at the set current densities.

Prior to the start of the experiments, the electrochemical surface areas were determined by cyclic voltammetry (CV) between 0.085 and 0.65 V (vs. RHE) at 100 mV s^{-1} scan rate, with H$_2$/N$_2$ at 70 °C, 70 °C dew points and ambient pressure. ECSA values were determined by averaging the oxidative and reductive H$_{UPD}$ peak areas from 100 CVs and assuming a 210 μC cm$^{-2}_{Pt}$ charge-to-area conversion factor. The measured ECSA values, listed in Table 3, decrease from 12.4 m^2 g^{-1} at 0.054 mg cm^{-2} Pt loading to ∼7 m^2 g^{-1} at 0.186 mg cm^{-2} Pt loading, and are five to ten times smaller than the ECSA of highly dispersed Pt/C (55–70 m^2 g^{-1} for Pt/C with 0.4 mg cm^{-2} Pt loading).

Table 3 includes the surface enhancement factors (SEF) obtained by multiplying the measured ECSA by the Pt loading. The SEF (cm$^2_{Pt}$.cm^{-2}) grows with increase in Pt loadings at a rate that is less than linear. Also included in Table 3 are the thicknesses of the catalyst layers as measured from SEM cross-sectional images of the NSTF catalyst-coated membranes [10]. These NSTF catalyst layers are only about one-tenth as thick as the conventional Pt/C catalysts with similar Pt loadings.

Hydrogen crossover current density and cell short resistance were determined by measuring the plateau currents between 0.4 and 0.6 V cell potentials with saturated H$_2$/N$_2$ at 1.5 atm total pressure and 80 °C cell temperature. Table 2 shows that the H$_2$

Table 1
Reference Pt loading in electrodes and cell operating conditions. The outlet RH is 100% at all reference operating conditions.

L$_{Pt}$ (c) mg.cm^{-2}	L$_{Pt}$ (a) mg.cm^{-2}	T°C	T$_{DP}$(c)°C	T$_{DP}$ (a)°C	P atm	SR(c)	SR(a)
0.1	0.05	80	65	65	1.5	2	2