

Short communication

An evaluation of electrocatalytic activity and stability for air electrodes

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Abstract

The electrocatalytic activity and stability of alkaline air electrodes have been studied. The results show that the stability of the electrodes is determined by a large number of factors. To obtain high reaction rates electrocatalyst with high exchange currents and high surface area is critical. However, it is of equal importance that the pore structure is correct. This determines the transport properties of oxygen, water and electrons to the reaction sites. In the choice of materials care has to be taken also regarding stability to obtain long lifetime at high activity.

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1. Introduction

Porous three-phase carbon electrodes have been studied in a large number of papers dealing with alkaline fuel cells (AFC) and phosphoric acid fuel cells (PAFC) [1–3]. The proposed reaction mechanisms based on potentiodynamic polarisation sweeps are similar in alkaline (*potassium* hydroxide) and acidic (phosphoric acid) media, and is explained by the flooded agglomerate model. Oxygen diffuses through the gas filled hydrophobic pore structure of the active layer. An electrolyte film covers the flooded agglomerates of carbon. Oxygen then diffuses through this film and into the flooded agglomerate where it reacts. A hydrophilic pore structure of liquid filled channels gives ionic transport to and from the reaction site.

At low overpotentials (0–50 mV) the reaction rate is determined by the kinetic of oxygen reduction on the catalyst and carbon support. At intermediate overpotentials (50–300 mV) the ionic and electronic transport limits the reaction rate with increasing overpotentials. At high overpotentials (more than 300 mV) the diffusion of reacting species will have an increasing effect.

For the oxygen reaction the stability and activity of the catalyst is important. In alkaline environments a large number of non-noble catalysts have shown high activity. To be

able to utilise the catalyst a correct pore structure must be obtained for the porous electrode. In this paper the porous structure of the electrodes is discussed with emphasis on activity and stability.

2. Experimental

Porous polytetrafluoroethylene (PTFE) bounded air electrodes were prepared with carbon, PTFE and Pt catalyst on a porous support. Electrodes with a thickness of ~500 μm were obtained by agglomeration and rolling. The preparation method did not involve any high temperature steps or sintering procedures and may easily be up-scaled. To obtain a correct pore structure and good particle to particle contact between the conductive particles several types of carbon were mixed. Carbon 1 with a high BET surface area acts as a pore forming material. To maintain high activity over a long time period (>2000 h) the catalyst support (Carbon 2) should have a lower BET surface area. The carbons were prepared by controlled heat treatment of organic material in a oxygen atmosphere. A full description of the electrode preparation is given in [15]. The amount of PTFE added was varied between 5 and 30 wt.%.

Half-cell measurements were performed using a three-electrode set-up with a nickel counter electrode and a zinc reference electrode ($E^0 = -0.76$ V versus reversible hydrogen electrode, RHE). Circular samples with an exposed area

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of 6.6 cm^2 were used. The samples were exposed in an electrolyte consisting of 6.6 M KOH at 20 and 70°C . The gas chamber was filled with air at 0.05 bar above ambient. The air flows at 2.5 stoichiometry. CO_2 was not removed. This did not cause any reduction in the activity during the first 1400 h in test.

3. Results and discussion

3.1. Degradation mechanisms

By increasing the surface area of the three-phase boundary, porous electrodes with high reaction rates at low overpotentials, have been obtained, see Fig. 1. If the electrodes are used in fuel cells this activity should be maintain over long time periods ($>2000 \text{ h}$). Fig. 1 shows a typical example of an electrode with high initial activity but low lifetime. As can be seen from the figure a reduction in the diffusion limited current initiates the drop in the activity. Inspection of the sample before tests showed a large number of micro-cracks. These cracks probably gave a large three-phase reaction surface, but also a rapid penetration of electrolyte into the structure.

A reduction in the reaction rate with time for porous electrodes can be caused by a large number of factors. Understanding the degradation mechanism is important to be able to increase lifetime. For air electrodes in alkaline media several degradation mechanisms have been proposed.

3.2. Flooding

Reduction of the electrochemical activity is often caused by flooding of the gas transport pores of the electrode structure. The reaction rate is reduced, as less diffusion paths for oxygen to the reaction sites are available. Initially, the flooding of the porous structure is often observed by a reduction in the current density at high reaction rates. After the flood-

ing has started the current drops rapidly. As shown in Fig. 1, the reaction rate is reduced more than 10 times within 60 h due to flooding of the structure. Several mechanisms have been proposed for the flooding phenomena.

From the theory of electrocapillarity it has been shown that the contact angle between the electrode surface and the electrolyte will be dependent on the electrode potential. A maximum in the contact angle is reached at the pzc (potential of zero charge). At this potential the charge of the double layer is neutralised by the electrochemical potential. Frumkin [4] has measured the pzc to be 1.545 V versus Zn in KOH at $\text{pH } 12$ on a $0.2\% \text{ Pt/g}$ carbon electrode. The contact angle decreases with a decrease in the potential from the pzc. This results in increased wetting of the electrode. A slow flooding of the pore structure will thus take place with time.

The contact angle is also influenced by variations in pH. With increased pH the contact angle decreases. Due to the electrochemical reduction of oxygen and vaporisation of water (especially at temperatures $50\text{--}90^\circ\text{C}$) the OH^- concentration inside the porous layer will increase. This can result in creep of electrolyte and flooding of the electrode structure [14].

If there is a temperature gradient within the porous structure this may also result in flooding. Vapour can then condense and the gas pores will be filled with water. This prevents oxygen diffusion. Especially at high temperatures ($70\text{--}90^\circ\text{C}$) this can influence the lifetime of air electrodes [14].

Radicals (O_2H^-) are formed in the reaction mechanism of oxygen reduction [5]. O_2H^- is aggressive and will attack PTFE and carbon. The consequence is that the hydrophobicity of the porous layer is changed with time. The reduced hydrophobicity can then slowly flood the structure.

Flooding of the porous structure can be prevented or slowed down by optimising the pore structure and hydrophobicity of the electrode. By the use of stable materials and controlled operation conditions long lifetime for the electrodes can be obtained.

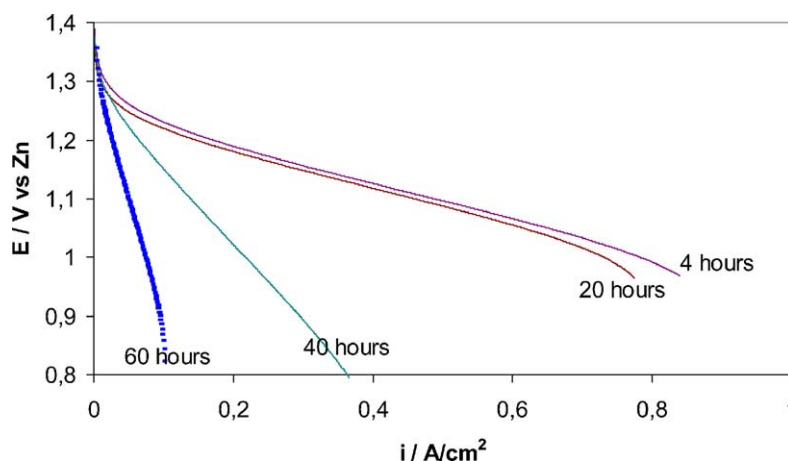


Fig. 1. The reduction of oxygen from air on PTFE bounded high surface area carbon ($>1000 \text{ m}^2/\text{g}$) with catalyst in 6.6 M KOH at 70°C .

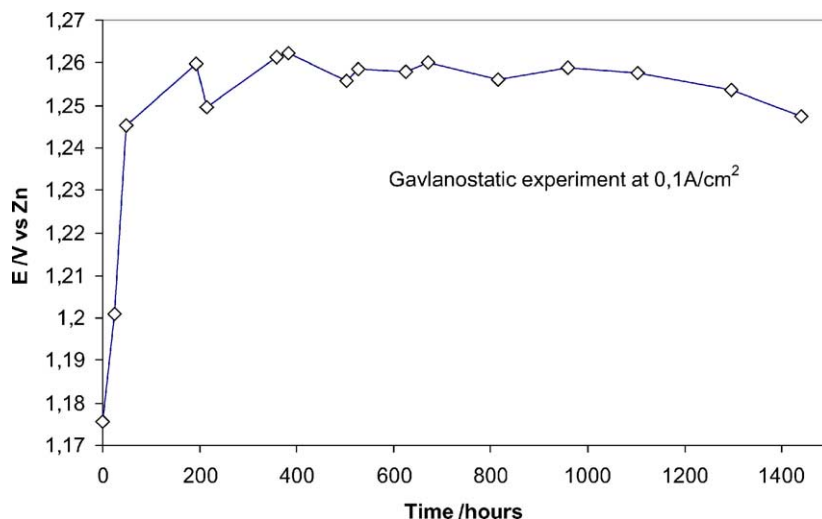


Fig. 2. Stability experiment of air electrode in 6.6M KOH at 70°C. The potential is logged at a constant cathodic current density of 0.1 A/cm².

3.3. The effect of CO₂

The alkaline fuel cell has by many been rejected due to the fact that it has been shown that the activity decreases when exposed to CO₂. However, the consequence of CO₂ is to a large extent determined by the operation conditions. To completely prevent CO₂ deactivation the air can be scrubbed to a concentration of CO₂ < 50 ppm. This can be done by the use of soda-lime or activated carbon filtration of air. For activated carbon the adsorbed CO₂ can be desorbed by heat treatment. The reversibility makes it a well-suited method for fuel cells.

The dissolution of CO₂ from air in the electrolyte will cause a slow replacement of OH⁻ with CO₃²⁻. The conductivity of CO₃²⁻ is lower than OH⁻ and this will result in increased ionic resistance of the electrolyte. A slow reduction in the efficiency has been observed only after >1000 h in test. By exchanging the electrolyte the effect is easily reversed.

A non-reversible CO₂ problem is related to the solubility of KCO₃(s). The solubility of KCO₃(s) is low for a CO₃²⁻ saturated electrolyte. If KCO₃(s) particles are formed inside the pore structure this can prevent liquid transport within the pores and result in a loss in catalytic activity.

3.4. Corrosion and poisoning of the catalyst

Several papers have shown deactivation due to corrosion or poisoning of the catalyst [6–9]. With the use of non-noble catalysts, deactivation has often been observed with dissolution of the catalyst due to attack by radicals (OH₂⁻) formed as intermediates in the oxygen reduction [6,7]. Agglomeration of the catalyst and oxide formation have also been found to reduce the activity [8,9].

4. Activity and stability studies

Fig. 2 shows an electrode with high stability. The experiment has been run galvanostatically at 0.1 A/cm² for more than 1400 h without any significant degradation. This shows that stable air electrodes can be obtained. The electrode was stabilised by reducing the amount of liquid filled pores and making the catalytic support less hydrophilic. The consequence of stabilising the electrode is that the initial activity is lower than for the electrode shown in Fig. 1.

Fig. 3 shows the potentiodynamic polarisation curves of oxygen reduction on 10 wt.% PTFE bounded carbon electrodes. The electrodes are made with a carbon-supported catalyst and a pore forming carbon. As can be seen in the figure the reaction rate varies between the samples. The variation shown in the figure is a result of variations in the amount of pore former and catalyst support. All polarisation curves

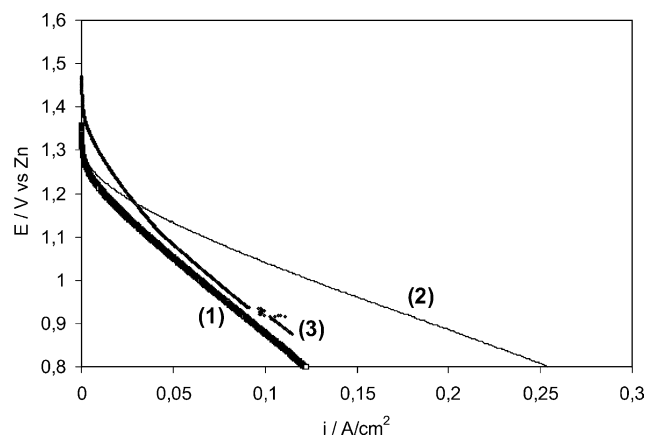


Fig. 3. Oxygen reduction in 6.6M KOH at 20°C on electrodes (1) with 90 wt.% Carbon 1 and 10 wt.% PTFE, (2) with 1 wt.% Pt, 67.5 wt.% Carbon 1, 22.5 wt.% Carbon 2 and 10 wt.% PTFE, (3) with 2 wt.% Pt, 45 wt.% Carbon 1, 45 wt.% Carbon 2 and 10 wt.% PTFE.

have been taken after a steady state polarisation for *approximately* 100 h. This was done to assure that the electrolyte has had sufficient time to penetrate into the structure.

Fig. 3 shows that varying the composition of the electrode results in differences in the rate of oxygen reduction. As should be expected the electrode (3) with the highest exchange current is the sample with highest catalyst loading (2 wt.% Pt). However, at a cathodic potential of 1 V versus Zn the reaction rate is only slightly above the electrode (1) without noble metal catalyst. The electrode (2) with 1 wt.% Pt has the highest reaction rate at 1 V versus Zn. This shows that for porous electrodes it is important to optimise the catalyst loading and the pore forming materials. As the catalyst is supported on a material with low surface area and low porosity the availability of the catalyst is poorly utilised. The large pores prevent liquid penetration into the electrode and the surface available for the reaction is low. The catalytic activity of the carbon support (Carbon 1) is given from electrode (1). It should be noted that the activity of the carbon is high. For systems where the demand for peak power is not too high, electrodes without catalyst should be considered. The problem with such electrodes is that the lifetime of the electrodes is low due to a degradation mechanism with HO_2^- attack of the carbon. This decreases the hydrophobicity of the pores and the structure is flooded. To solve this problem high surface area carbon, with high stability, is required. An alternative is that the electrode is run at a lower temperature where the degradation mechanism is slower. The support used in these investigations has shown high stability for more than 2000 h.

Fig. 4 shows the polarisation curves for electrodes in the potential range where activation control dominates. The kinetic rate of oxygen reduction decreases with *decreased* Pt catalyst loading. By curve fitting the experimental values to the Butler–Volmer equation the kinetic parameters for the reactions can be predicted. Table 1 shows the reversible potential and the Tafel gradient found for the electrodes, also shown in the table are the area specific resistance (ASR).

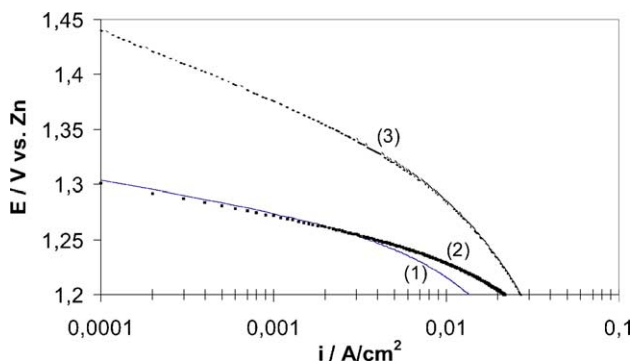


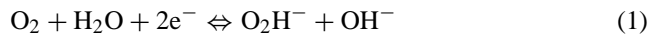
Fig. 4. Oxygen reduction in 6.6 M KOH at 20 °C on electrodes (1) with 90 wt.% Carbon 1 and 10 wt.% PTFE, (2) with 1 wt.% Pt, 67.5 wt.% Carbon 1, 22.5 wt.% Carbon 2 and 10 wt.% PTFE, (3) with 2 wt.% Pt, 45 wt.% Carbon 1, 45 wt.% Carbon 2 and 10 wt.% PTFE.

Table 1

Kinetic parameters for the oxygen reaction in 6.6 M KOH at 20 °C on samples (1) with 90 wt.% Carbon 1 and 10 wt.% PTFE, (2) with 1 wt.% Pt, 67.5 wt.% Carbon 1, 22.5 wt.% Carbon 2 and 10 wt.% PTFE, (3) with 2 wt.% Pt, 45 wt.% Carbon 1, 45 wt.% Carbon 2 and 10 wt.% PTFE, as shown in Fig. 4

| Sample | E_{oc} (V) vs. Zn | Tafel slope (mV per decade) | Area specific resistance, ARS ($\Omega \text{ cm}^2$) |
|--------|---------------------|-----------------------------|---|
| (1) | 1.35 | -27 | 3.4 |
| (2) | 1.36 | -28 | 1.5 |
| (3) | 1.47 | -61 | 3.4 |

Table 1 shows that for sample (1) and (2) an activation-controlled gradient of ~ -30 mV per decade was found. The influence of BET surface area on electrochemical activity has been studied by Appleby et al. [10] who tested 47 different types of carbon and graphite. The observed Tafel slopes were ~ -40 mV per decade for materials with high surface area whereas the gradient was larger than -60 mV per decade for materials with low surface area. The reaction order with respect to oxygen was 1. Kukushkina et al., on the other hand, found that for high surface activated carbon Tafel slopes of -55 to -60 mV per decade and -110 to -150 mV per decade occurred [11]. A Tafel slope of -30 mV per decade was discussed by Appleby et al. [10] and explained by the establishment of steady-state diffusion conditions across the diffusion layer, when the surface equilibrium is the two-electron process:



The current–potential relationship then was found to be

$$i = \text{cons.} \times [\text{C}_{\text{OH}^-}]^{-1} \exp \left[\frac{-2(E - E_1^0)F}{RT} \right] \quad (2)$$

where E_1^0 is the standard potential for Eq. (1) and C_{OH^-} the concentration of OH^- ions. This is in conflict with the value found for the coefficient $(\delta E / \delta \text{pH})_i$ that was RT/F instead of $RT/2F$. Maybe the origin of this mistake is that the acid–base properties for H_2O_2 have been neglected. It is given by



Adding this the equilibrium potential for Eq. (1) is given by

$$E = E_1^0 - \frac{RT}{2F} \ln \left[C_t \left(\frac{(\text{C}_{\text{OH}^-})^2}{K + \text{C}_{\text{OH}^-}} \right) \right] \quad (3)$$

with C_t given as the total concentration of peroxide at the surface ($\text{C}_{\text{H}_2\text{O}_2} + \text{C}_{\text{O}_2\text{H}^-}$) and K the equilibrium constant for the reaction. The current is then given by

$$i = \frac{2FD_{\text{O}_2\text{H}^-}}{\delta} (\text{C}_{\text{OH}^-})^{-2} (K + \text{C}_{\text{OH}^-}) \exp \left[\frac{-2(E - E_1^0)F}{RT} \right] \quad (4)$$

As can be seen from Eq. (4) the coefficient $(\delta E / \delta \text{pH})_i$ is $RT/2F$ when $\text{C}_{\text{OH}^-} \gg K$ and RT/F when $\text{C}_{\text{OH}^-} \ll K$.

An extensive study of oxygen reduction on platinum was carried out by Sepa et al. [12,13]. They found two polarisation regions in alkaline media, a -60 mV per decade slope at low currents and a -120 mV per decade slope for high currents. The -60 mV per decade slope was explained with a Temkin adsorption of the reaction intermediates. This provides an explanation for the results shown in Fig. 4. As the platinum content is increased a shift in the Tafel slope from -30 to -60 mV per decade is observed. This is probably due to the fact that the low porosity of the 2 wt.% Pt electrode causes most of the reaction to take place on platinum and on the low surface area carbon support giving a -60 mV per decade slope as shown by Sepa et al. and Appleby [10,12].

As shown in Fig. 3a linear current–potential relationship exists at higher reaction rates. This indicates that ohmic resistance limits the reaction rate. The ohmic losses can be divided into the contribution from ionic resistivity of the electrolyte in the porous structure, the electronic resistivity of the materials in use and the particle to particle resistance within the porous matrix. The various contributions to the voltage losses in alkaline air electrodes will be treated in a separate paper. It has been found that to maintain low ohmic resistance good particle to particle contact between carbons is important. This is controlled by the amount of PTFE added to the agglomerate under electrode production.

5. Studies of hydrophobicity

PTFE fills several necessary functions for the air electrode. First, it gives the electrode mechanical strength. Secondly, the network of PTFE chains in the structure acts as gas transport pores for the diffusion of oxygen to the reaction sites. Thirdly, the high hydrophobicity prevents the pore-structure from being flooded by the electrolyte.

It has been found that variations in the amount of PTFE binder up to 30 wt.% only results in small variations in the conductivity of the electrode. If the amount of PTFE is above 30 wt.% the particle to particle contact between carbon particles is lost and a large increase in the area specific resistance (ASR) is observed. With a PTFE amount lower than 5 wt.% the mechanical strength of the electrode is reduced.

Fig. 5 shows the polarisation curves at low overpotentials where the reaction rate is dominated by polarisation voltage losses. The amount of PTFE binder was changed from 10 to 25 wt.%. As can be seen from the curve the increased amount of PTFE resulted in a change of the activation controlled region. For both curves an open circuit potential of 1.34 V versus Zn and an initial -30 mV per decade gradient was observed. A rapid decrease of the rate, between 1.3 and 1.17 V, is observed for the sample with 25 wt.% PTFE. This decrease can be explained by the high PTFE content. PTFE increases the hydrophobicity of the electrode and only a small amount of pores are filled with

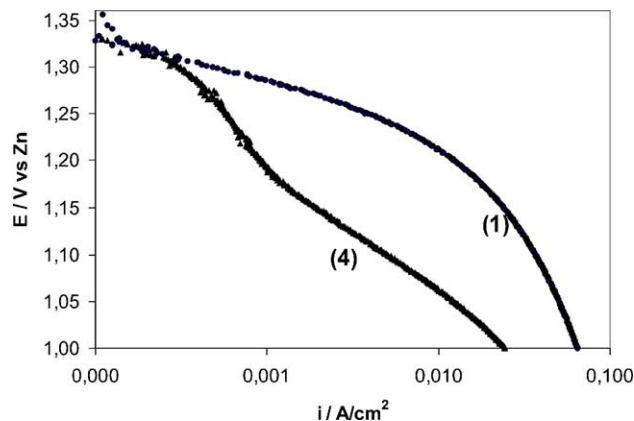


Fig. 5. Oxygen reduction in 6.6 M KOH at 20 °C on electrodes (1) with 90 wt.% Carbon and 10 wt.% PTFE and (4) with 75 wt.% Carbon and 25 wt.% PTFE.

electrolyte. The available surface for the reaction is thus reduced.

At high overpotentials the contact angle will decrease (as explained by the theory of electrocapillarity). This will probably increase the surface area as the electrolyte penetrates deeper into the porous electrode structure. The curve shown in Fig. 5 is then probably a result of variations in the three-phase boundary area for the reaction with increasing overpotentials. Although the 25 wt.% PTFE sample is activated by polarisation, the exposed surface is still much smaller than for the sample with 10 wt.% Pt. This is shown by the much lower reaction rate. Fig. 6 shows the polarisation curves for experiments at high overpotentials. From the linear part of the curve an ohmic resistance can be predicted. The resistance is almost similar for the two samples without Pt (3.25 and 3.4 Ωcm^2). This indicates that with a PTFE content even as high as 25 wt.% the particle to particle contact within the substrate is not broken. The difference in the rate of oxygen reduction is thus most probably due to the wetting properties of the electrode.

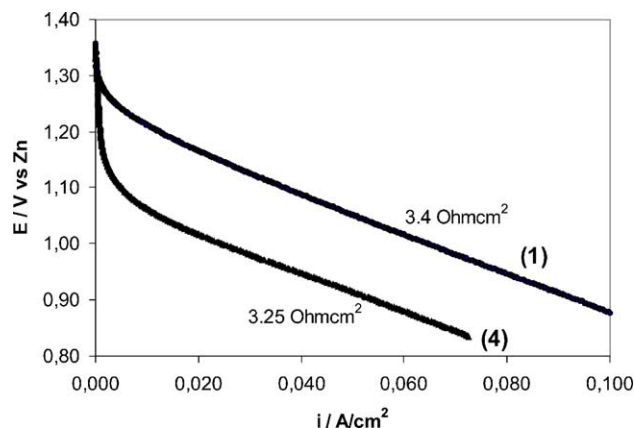


Fig. 6. Oxygen reduction in 6.6 M KOH at 20 °C on electrodes (1) with 90 wt.% Carbon and 10 wt.% PTFE and (4) with 75 wt.% Carbon and 25 wt.% PTFE.

6. Conclusions

Factors influencing the activity and lifetime for alkaline air electrodes have been discussed. It has been shown that stable air electrodes can be produced by careful control of the hydrophobicity and pore structure. The catalytic activity is not only determined by the amount of catalyst present, but also by the electrode preparation. The highest activity for stable electrodes was found with a catalyst loading of 1 wt.% Pt.

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