Journal of Power Sources 272 (2014) 1072–1077

Contents lists available at ScienceDirect

Journal of Power Sources

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

Activity inhibition and its mitigation in high temperature proton exchange membrane fuel cells: The role of phosphoric acid, ammonium trifluoromethanesulfonate, and polyvinylidene difluoride

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HIGHLIGHTS

- Influence of H_3PO_4, ATFMS and PVDF on ORR.
- PVDF promotes ORR.
- H_3PO_4 and ATFMS acts as poison and inhibits ORR.
- ORR enhancement proven in RDE and MEA measurements.

ARTICLE INFO

Article history:
Received 30 July 2014
Received in revised form
1 September 2014
Accepted 7 September 2014
Available online 16 September 2014

Keywords:
ORR
HT-PEMFC
PVDF
ATFMS

ABSTRACT

In the presented work we systematically study the influence of phosphoric acid, ammonium trifluoromethanesulfonate (ATFMS), and polyvinylidene difluoride (PVDF) on the oxygen reduction reaction (ORR) activity of carbon supported, Pt based catalysts. The influence of phosphoric acid is investigated in a mixed solution of perchloric acid with small amounts of phosphoric acid added. Thin-film rotating disk electrode (TF-RDE) measurements show that such a mixed electrolyte is advantageous as the oxygen reduction reaction (ORR) is inhibited without influencing the oxygen solubility in the electrolyte. In contrast to previous reports it is seen when investigating additives that ATFMS acts as a catalyst poison; whereas the results provide evidence of a better performance in case of the PVDF incorporated catalysts as compared to reference samples without PVDF. The technological relevance of the PVDF improvements and its stability over prolonged time was validated by membrane electrode assembly (MEA) tests.

1. Introduction

Phosphoric acid fuel cells were the first commercially successful fuel cells, but are still being improved to reach higher efficiency, longer life-time, and to lower their costs. Modern day phosphoric acid fuel cells operate at temperatures between 150 and 200 °C with the liquid acid electrolyte embedded in a matrix of silica carbide (SiC) [1] or a polybenzimidazole (PBI) [2–5]. The fuel cells using phosphoric acid doped PBI membranes are typically referred to as high temperature proton exchange membrane fuel cells (HT-PEMFCs). The higher operating temperature as compared to low temperature (LT) PEMFCs has several advantages as it (i) provides a higher CO tolerance, (ii) produce water vapour instead of liquid, which simplifies the water management, and (iii) increases the ORR kinetics – at least in theory (see below) [5–8]. Furthermore, the hot water vapour can also be utilized for combined heat and power (CHP) systems, which helps to increase the overall efficiency of HT-PEMFCs. On the downside, the use of phosphoric acid electrolyte contributes to some well-known disadvantages of HT-PEMFCs, including increased corrosion and inhibited ORR kinetics induced by phosphoric acid anion adsorption [9–11]. In addition the high concentration of phosphoric acid in the membrane and the elevated operating temperature lowers the oxygen solubility in the membrane electrolyte and thus limits its mass transport [12]. As a consequence, despite of the higher operating temperature, the ORR kinetics in HT-PEMFCs are in fact lower as in standard PEMFCs.

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http://dx.doi.org/10.1016/j.jpowsour.2014.09.035

Therefore current catalyst research concerning HT-PEMFCs focuses on increasing the ORR kinetics by limiting the inhibiting effect of the phosphoric acid electrolyte [13].

There are two main strategies to overcome the inhibiting effect of the phosphoric acid electrolyte. One is to modify the active phase of the catalyst – the Pt or Pt alloy nanoparticles – in a way that it becomes more selective [13]. That is, the inhibiting phosphoric acid adsorption on the active phase is supressed, while the ORR can proceed unaffected. The other strategy is to improve the (local) solubility of oxygen in the electrolyte, thereby improving the overall kinetics. A successful implementation of the second strategy was recently reported, claiming that the local oxygen concentration near the catalyst can be increased by adding ammonium trifluoromethanesulfonate (ATFMS) into the catalyst layer [14]. In the experimental section of the same work it is described that ATFMS is not used as an additive alone, but always mixed with polyvinylidene difluoride (PVDF) as well. PVDF can be used as binder in HT-PEMFC catalyst layers [15–17]. However, the influence of PVDF on the performance is not described or investigated further in the mentioned publication. By contrast, in a very recent published article by Su et al. [32] it is claimed that PVDF used as binder can increase the performance of membrane electrode assemblies (MEA) in the low current density region. However, the complexity of MEA measurements does not allow interpreting such results. The performance of a MEA not only depends on the catalyst, but also of the structure of the catalyst layer and its hydrophobic/hydrophilic properties. In order to claim a better intrinsic performance of the catalyst further investigations applying rotating disk electrode (RDE) measurements in electrochemical half-cells are required. Therefore the aim of the work presented here is to separately study the influence of phosphoric acid, ATFMS, and PVDF on the catalyst performance towards the oxygen reduction reaction (ORR) activity and to elucidate, which of the two additives can improve the intrinsic ORR kinetics and the overall fuel cell performance. For this purpose we combined thin-film RDE measurements with tests in MEAs. The results provide evidence of a better performance in case of the PVDF incorporated catalysts as compared to reference samples with PTFE instead of PVDF – both in RDE as well as in MEA tests.

2. Experimental

2.1. Catalyst material

As mentioned above, the aim of this work was to separately study the influence of phosphoric acid, ATFMS, and PVDF on the oxygen reduction reaction ORR activity in comparison to PTFE. To investigate the influence of phosphoric acid and ATFMS we used a polycrystalline platinum disk of 5 mm in diameter, which was embedded in Teflon, as working electrode. By this we can exclude any influence of the catalyst layer itself. Prior to each measurement the polycrystalline platinum electrode was polished with alumina powder to a mirror finish.

The influence of PVDF on the electrocatalytic performance was studied on two high surface area carbon (HSAC) supported platinum catalysts with polytetrafluoroethylene (PTFE) or PVDF as a binder, respectively. Both catalysts have been synthesized under similar conditions with slightly different Pt loadings, 28 $\mathrm{wt\%_{Pt}}$ (Pt/C with PTFE) and 38 $\mathrm{wt\%_{Pt}}$ (Pt/C with PVDF), which was due to the preparation procedure. The catalyst with PTFE as binder serves as reference in the measurements.

2.2. Rotating disk electrode measurements

In order to prepare a catalyst ink for the RDE measurements, the catalyst powders were ultrasonically dispersed in ultrapure water to a concentration of 0.196 $\mathrm{mg_{Pt}\ cm^{-3}}$ for at least 15 min. Before each measurement the catalyst suspension was again put into the ultrasonic bath for 5 min. For the ORR measurements, a volume of 20 μl of the suspension was pipetted onto a polished glassy carbon substrate (5 mm diameter, 0.196 $\mathrm{cm^2}$ geometrical surface area) leading to a Pt loading of 20 $\mathrm{\mu g_{Pt}\ cm^{-2}}$ for the catalyst sample. The catalyst suspension was then dried onto the glassy carbon electrode in air.

The RDE investigations were conducted in a three compartment Teflon cell [18] at room temperature using a home build potentiostat [19], a saturated calomel reference electrode (SCE), and a platinum wire counter electrode. Throughout the manuscript, all potentials are referring to the reversible hydrogen electrode (RHE), which was experimentally determined for each set of measurements. The resistance of the electrolyte was determined using an AC signal (5 kHz, 5 mV) and thereafter compensated for using the analogue positive feedback scheme of the potentiostat [20]. The electrolytes were prepared using concentrated H_3PO_4 and $HClO_4$ (suprapur; Merck, Germany) and Milli-Q water (>18.3 MΩ cm, TOC < 5 ppb). The CO-stripping method was used to determine the electrochemical active surface area of Pt (ECSA) [21]. The CO-stripping curves were recorded in CO- free Ar purged solution, after adsorbing CO at a potential of 0.05 V until the saturation coverage was reached. The specific activity (SA) of the ORR is calculated from the positive going polarization curves recorded in oxygen saturated electrolyte (Alphagaz1, N5.0, Air Liquide). The polarization curves were recorded at a scan rate of 50 mV $\mathrm{s^{-1}}$ and were corrected by the capacitive background [20]. The rotation rate was 1600 rpm.

The investigation of the effect of ATFMS on the ORR was conducted in 0.1 M $HClO_4$ electrolyte adding stepwise small amounts of ATFMS (Sigma–Aldrich, 99%). The effect of phosphate ions on the ORR was conducted by stepwise adding small amounts of H_3PO_4 to 0.1 M $HClO_4$ electrolyte.

2.3. Single cell measurements

A single cell setup with an active area of 50 $\mathrm{cm^2}$ and a single serpentine channel flow field structure on anode and cathode was used. Reactant flow rates were measured and controlled using mass flow controllers. The cell temperature was set to 160 °C controlled by electrical heating cartridges and the stoichiometry was kept constant at 1.2 for hydrogen and 2.0 for air.

The Long term operation test was conducted under constant load with a current density of 0.2 A $\mathrm{cm^{-2}}$ at 160 °C with hydrogen on the anode and air on the cathode with a stoichiometry of 1.2 and 2.0 respectively.

The ORR activity of the cathode catalyst was determined in-situ under flow rates of 100 ml $\mathrm{min^{-1}}$ (H_2) and 166 ml $\mathrm{min^{-1}}$ (air) at a cell temperature of 160 °C. With a Zahner IM6 the 1 kHz AC resistance (10 mV amplitude at 5 A) was recorded. Afterwards, the cell was set to OCV and the current was gradually increased, from 0.5 A up to 4 A and the corresponding voltage was recorded and corrected with the inner resistance of the fuel cell. The air flow at the cathode was kept constant at high stoichiometry to prevent mass transport limitations effects, especially at currents near 4 A. The current density is plotted on a logarithmic scale against the cell potential and the slope of the resulting straight line is calculated.

3. Results and discussion

We start our discussion with the influence of phosphate ions on the electrochemical properties of polycrystalline platinum; the results are summarized in Fig. 1. Fig. 1a compares the cyclic voltammograms of polycrystalline platinum recorded in argon