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Surfactant modified platinum based fuel cell cathode studied by X-ray absorption spectroscopy

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ABSTRACT

A carbon supported Pt catalyst with tetradecyltrimethylammonium bromide (TTAB) adsorbed to the nanoparticle surface was operated and tested as a cathode in a polymer electrolyte membrane fuel cell. The fuel cell with the TTAB@Pt/C catalyst showed a higher current relative to the amount of Pt used than the fuel cell with a commercial Pt/C catalyst. Besides, CO stripping evidenced that for the TTAB@Pt/C electrode large parts of the Pt surface were covered by TTAB. Hence, the fuel cell with the TTAB@Pt/C cathode showed a larger current related to the electrochemical active surface area as compared to the fuel cell with the commercial Pt/C cathode. This improvement in the ORR kinetics was further investigated by X-ray photoelectron and in-situ X-ray absorption spectroscopy, and was found to have been caused by two effects: (1) the presence of a metal-ligand charge transfer in the TTAB@Pt/C electrode and (2) the prevention of oxygen containing adsorbates which were being formed in large amounts on the Pt/C electrode. Furthermore, the latter effect also explains the higher stability observed for the TTAB@Pt/C compared to the Pt/C electrode.

1. Introduction

The oxygen reduction reaction (ORR) is one of the most important reactions in electrochemistry [1]. In fuel cells, the ORR at the cathode side limits the fuel cell performance due to its relatively slow reaction kinetics [2]. State-of-the-art catalysts for the ORR are Pt nanoparticles (NPs) supported on conductive carbon materials [3] such as Vulcan XC72. The ORR on Pt proceeds as a multistep reaction with two parallel pathways [1], where either oxygen becomes adsorbed dissociatively or non-dissociatively [4], as given by the following equations: $O_2 + 2^* \rightarrow 2O^*$ or $O_2 + (H^+ + e^-) + 2^* \rightarrow O^* + OH^*$ (dissociative) or $O_2 + (H^+ + e^-)^* \rightarrow OOH^*$, $OOH^* + (H^+ + e^-) \rightarrow HOOH^*$ (non-dissociative). In the dissociative pathway, O- or OH-adsorbates are further reduced to form H_2O as the final product:

$O^* + (H^+ + e^-) \rightarrow OH^*$ and $OH^* + (H^+ + e^-) \rightarrow H_2O + ^*$. By the non-dissociative pathway, the formation of H_2O_2 and H_2O is possible by either desorbing the adsorbed peroxide intermediate, or by splitting the adsorbed peroxide intermediate to form adsorbed OH which is than further reduced to H_2O.

The ORR kinetics strongly depend on the reaction conditions [5,6,7]. By combining rotating disk electrode (RDE) measurements with reaction modeling studies, it was shown that the rate determining step changes with potential, where the H_2O_2 mediated pathway becomes dominant below 0.8 V vs. reference hydrogen electrode (RHE) [5,7]. In-operando X-ray absorption spectroscopy in a fuel cell showed that the kind of adsorbate on the Pt nanoparticle surface changes with increasing current (decreasing potential) from O to OH to OOH [6]. In addition, electrochemical investigations demonstrated that oxide coverage influences the ORR kinetics [8].

The ORR activity and also the selectivity for the dissociative pathway of Pt can be altered by modifying the electronic structure (d-band center) [9] and thus the binding energy (BE) of the

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adsorbed reaction intermediates [10,11]. Jia et al. showed that compressive strain due to substitution of Co into the Pt lattice correlates with an increase in ORR activity [12,13]. Thus, certain alloy catalysts such as PtCo and PtNi [14] show an improvement in ORR kinetics. Additionally, specific facets are known to have different ORR activities [15], and increased ORR activity is observed for larger Pt NP sizes which were found to correlate with an increased proportion of terrace sites [16]. The proportion of certain NP facets, and thus the ORR activity, can also be increased by using shape-selected nanoparticles [17]. Another possibility to alter the ORR activity of Pt NP catalysts is the use of capping agents [18,19] which are usually employed to synthesize shape-selected NPs by inducing the crystal growth in certain directions [20]. The capping agents are commonly removed from the catalyst surface before the catalyst is used; however, if small portions remain on the nanoparticle surface, these can also impact reactions [21,22,23]. Using polydiallyldimethylammonium (PDDA) chloride in NP synthesis, Pt NPs with certain shapes depending on the PDDA concentration were obtained. These showed a higher stability and an improved ORR activity as found by Koutecky-Levich analysis of RDE measurements [18]. Both effects were assigned to an electronic structure modification of the platinum, as an increasing PDDA concentration correlates with a shift of the Pt 4f XPS lines towards more positive BEs. Likewise, the cuboctahedral Pt NPs synthesized in the presence of tetradecyltrimethylammonium bromide (TTAB) demonstrated a power density four times higher relative to the amount of Pt [24]. However, the reason for the increased power density was not discussed in the respective paper and could be due to different effects. On the one hand, the presence of larger amounts of Pt {1 1 0} and Pt {1 0 0} facets, as they have been found to exist for unsupported cuboctahedral NPs [24], could have affected the ORR positively. On the other hand, from FTIR spectroscopy, it is also known that an electronic interaction between TTAB and the Pt NP surface exists [25]. Additionally, an electronic interaction with Pt was also observed to exist for N-containing polymers, such as polyaniline (PANI) [26,27]. By C and N K-edge near edge X-ray absorption fine structure spectroscopy it was demonstrated that Pt interacts with the amine groups in the PANI, shifting electrons from Pt NPs into the π-conjugated system of the aromatic ring, thereby increasing its electron density [27]. Accordingly, an improved fuel cell performance of PANI/Pt/C composite electrodes was found [26,28]. However, the interaction between Pt and PANI might be of a different nature compared to the interactions observed for TTAB or PDDA with Pt due to ammonium ions being tetrahedrally coordinated. Nevertheless, it has been shown by FTIR and Raman spectroscopy that an interaction between Pt and TTAB exists which has been attributed to electron-molecular vibration coupling [25]. Altogether, the use of capping agents seems to be a very promising way to improve the activity of the ORR and thus the fuel cell performance and the electrode stability.

In this work, the effect of an adsorbed surfactant, TTAB, on the ORR in an operating fuel cell is further investigated. Therefore, two catalyst coated membranes (CCM) identically prepared with the exception of different cathode materials, a carbon supported Pt NPs catalyst with adsorbed TTAB, and a conventional Pt/C have been prepared. Both CCMs are electrochemically characterized by cyclic voltammetry and CO stripping in order to determine their electrochemical active surface area and thus their current density related to the amount of active Pt. Additionally the stability of the cathode materials was studied using an accelerated stress test (AST) protocol. Finally, the observed effects of improved ORR activity and stability were further investigated by in-operando X-ray absorption spectroscopy (XAS) and by ex-situ characterization of the material using X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Synthesis and ex-situ characterization of catalysts

The Pt nanoparticles stabilized by TTAB were synthesized using a method described by Lee et al. [29]. In the present work, 3 g of TTAB was dissolved in 50 ml of de-ionized and deoxygenated water. Subsequently, 43 mg of K_2PtCl_4 was dissolved in 15 ml of de-ionized and deoxygenated water and added drop wise. The above mixture was kept in a water bath at 50 °C until the solution became clear. Finally, 60 mg of $NaBH_4$ was dissolved in 15 ml of de-ionized and deoxygenated water and added to the solution. During the reaction process, the solution was stirred and kept under a constant flow of hydrogen and a temperature of 50 °C for 5 h. Subsequently, the solution was cooled and large aggregates were removed by centrifuging the solution at 6000 rpm for 30 min. Finally, the smaller NPs were separated by centrifuging at 15,000 rpm for 15 min. Particles were re-dispersed and re-centrifuged to remove the excess of surfactant. The obtained Pt NPs were ultrasonically dispersed along with 200 mg of Vulcan carbon, and the resulting slurry was filtered and dried.

The resulting TTAB@Pt/C catalyst and the commercial Pt/C catalysts (HiSPEC 3000, Alfa Aesar) were further characterized by TEM and XPS. TEM was performed with a FEI CM20 (FEI, Eindhoven, The Netherlands) instrument operating at 200 kV acceleration voltage with a LaB_6 filament. For sample preparation, a small amount of the powder was dispersed in ethanol using ultrasonic dispersion and one drop was transferred to a standard holey carbon film-covered copper grid. Images were recorded with a CCD camera (KeenView G2, Olympus Soft Imaging Solutions GmbH, Münster, Germany) mounted at the bottom of the electron microscope. Images were acquired with a resolution of 1.32 pixels per nm. XPS were done at the HESGM beamline at BESSY II (Helmholtz Zentrum Berlin, Germany) [30]. The sample powders were pressed into indium foil and mounted on a stainless steel sample holder. XPS data were recorded at an incidence angle of 45° using linearly polarized light. XPS spectra are measured with different excitation energies using the Scienta R3000 analyser. After a survey scan, C1s, Br3d, and Pt4f regions were measured in detail. The spectra were analyzed with the software XPSPEAK 4.1. The background was corrected by the Shirley method, and the peaks were fitted by Voigt profiles.

2.2. Preparation and testing of catalysts coated membranes

The CCMs were fabricated using a modified air brush technique developed by Wilson et al. [31]. Initially, 200 mg of Vulcan XC72 was ultrasonically dispersed in 5 ml of a water-isopropanol solution (3:2) containing 1.5 ml of Nafion (5 wt%) solution. Subsequently, 1 ml of unsupported Pt NPs (TTAB@PtNPs) dissolved in water, which were synthesized as described above using 43 mg K_2-$PtCl_4$ and 3 mg TTAB, was added. The Pt loading of the dried TTAB@PtNPs/C catalyst was determined to be 7.3 wt%. The ink was sprayed onto a Nafion 117 membrane using an air brush pistol. For this, the Nafion membrane was mounted on a heated vacuum table and covered by a corresponding 5×5 cm^2 stainless steel template. While spraying, the vacuum table was heated up to about 108 °C. On the other side of the CCM a commercial Pt catalyst from Johnson Matthey (20 wt% Pt on Carbon, HiSPEC 3000) was sprayed. A second CCM with both sides sprayed with the commercial catalyst was prepared for comparison. For the electrodes with the commercial Pt/C catalyst, 200 mg of the catalyst powder was ultrasonically dispersed in 5 ml of water-isopropanol solution (3:2) containing 1.5 ml of Nafion (5 wt%) solution. The total amount of Pt used for the electrodes under investigation was