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Accelerated fuel cell tests of anodic Pt/Ru catalyst via identical location TEM: New aspects of degradation behavior

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ABSTRACT

In the present work the stability, chemical composition and structure of a Pt/Ru catalyst alloy with a nominal ratio of 1/1 is investigated. The same catalyst particles are analyzed before and after potential cycling experiments using identical location transmission electron microscopy. The experiments were performed at room temperature at $[0-1.0] V_{RHE}$ and $[0-1.2] V_{RHE}$ to simulate conditions occurring during ramping up of fuel cells. With decreasing maximum potential value a higher stability is found. Dissolution and dealloying are identified to be the main degradation mechanisms during potential cycling with Ru being dissolved preferably. Also agglomeration and Ostwald ripening are taking place, the frequency decreasing the longer the experiment is performed. Advanced in-depth analysis of potential-dependent reshaping mechanisms are performed by calculating the three-dimensional volume of single particles both in the as-prepared state and after potential cycling experiments using electron tomography data. Evaluation of the volume-specific change of the accessible surface area of the catalyst helps to understand fuel cell performance deterioration.

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Introduction

Catalyst design is an important aspect in the continuously growing field of fuel cell application [1]. Long-term stability

and activity of the nanoparticles are considered to be among the key challenges to guarantee performance continuity over an extended lifetime. The most prevalent catalyst system for polymer-electrolyte-membrane fuel cells is based on platinum nanoparticles dispersed on a carbon support (Pt/C).

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When applied as catalyst for a fuel cell anode, where the hydrogen oxidation reaction (HOR) occurs, different degradation mechanisms take place [2]. In the case of the catalyst support, carbon corrosion is frequently reported to occur [2–5]. A collapse of the basic framework of the carbon support results in a reduced porosity and hence mass transport limitations for the reactants. Macroscopically this can be seen in a diminishing fuel cell performance [6]. To circumvent corrosion, other support materials like metal oxides have been tested [7–11]. Not only the support material but also the highly dispersed catalyst nanoparticles are subject to diverse degradation mechanisms. The most frequently reported phenomena are particle dissolution, agglomeration, Ostwald ripening and particle detachment [2,12–17]. Particle dissolution is one of the main degradation mechanisms taking place during fuel cell operation [18,19]. On the atomic level, only atoms in the outermost surface shell can dissolve and their specific dissolution rate was found to be more or less independent of the particles' diameter [20]. However, since already in a 2 nm sized particle about 50% of the atoms are located in the outermost surface layer, smaller particles generally vanish faster than bigger ones [18]. The dissolved catalyst species can either leave the fuel cell in the water stream or redeposit at different locations of the fuel cell's electrode or membrane. Several studies report the presence of catalyst nanoparticles in the ionomer after fuel cell operation. These particles were redeposited by cross-leaking hydrogen [21–29]. Also, when the dissolved atoms redeposit on neighboring particles, Ostwald ripening is taking place. Small, energetically disfavored particles decrease in size while bigger particles grow further. The driving force of this process is the reduction of the surface energy since the fraction of atoms on the surface decreases with increasing particle size. The overall increase in particle size during fuel cell operation [30] can be also described by agglomeration. In this process, minimum two nanoparticles coalesce to form one bigger sized particle. The mechanism depends on the particles' distance and support properties. Hence, either previously separated particles actively move together [2] or a shrinkage of the carbon support as a result of corrosion [31] is taking place to meet this requirement. A further degradation mechanism, particle detachment, involves particles that detach from the carbon support as a whole. This can occur as a consequence of carbon corrosion. By use of a bimetallic catalyst, dealloying can take place additionally [32–36]. It is defined as selective dissolution of the less noble component when a certain potential threshold value is exceeded. Surface atoms dissolve first and as such expose underlying atoms of the second component. The result is an enrichment of the more noble metal on the surface of the particle. This can be either beneficial or harmful, depending on whether the metal composition on the particle's surface is important for the designated purpose of the catalyst. Meier et al. [2] reported that the degradation mechanisms depend on the metal-support interaction and the composition of the support but concluded that the weighting of these phenomena is not possible. To prove the occurrence of different particle degradation mechanisms and track changes of single particles, identical location transmission electron microscopy (IL-TEM) was employed [14,15]. TEM investigations and

electrochemical tests are performed on the same location by using a TEM finder grid. The particles are studied in the as-prepared state and after an accelerated degradation protocol (ADP). The ADP typically consists of accelerated cyclic voltammetry (high scan rates) to simulate fuel cell start-stop operation in a standard three-compartment electrochemical cell [5]. Sequential TEM investigations of the previously measured, electrochemically altered catalyst reveal particle-specific degradation mechanisms [5,14,15].

The work in hand focusses on a high-surface-area carbon (HSAC) supported Pt/Ru based catalyst alloy which is applied as anode in high-temperature polymer-electrolyte-membrane fuel cells (HT-PEMFCs). The Pt/Ru system is the most frequently used alloy to enhance the carbon monoxide (CO) tolerance of Pt [37–42]. Depending on the overpotential applied, two mechanisms are proposed: At higher potentials water activation on Ru sites on the surface of the Pt/Ru based particle is taking place. A maximum activity was found when the Pt/Ru ratio was set to 1, as this is frequently reported to be the most active composition due to the maximum achievable number of Pt–Ru pairs on the particles' surface [39,40,43,44]. However other studies reveal a Pt/Ru ratio of 3/1 to exhibit the best CO tolerance [45]. At lower potentials Ru is reported to induce electronic changes on Pt. The reduced electron density in the Pt 5d band weakens the Pt–CO interaction (ligand effect) [40,45–48]. While pure Pt is known to adopt the face centered cubic (fcc) lattice, Ru crystallizes in the hexagonal close packed lattice (hcp) [49]. The crystal structure of the alloy is depending on the ratio of Pt/Ru used. According to Yamada et al. [50] an alloy exhibiting a Pt/Ru ratio of 1/1 will adopt the Pt fcc lattice, where half of the Pt sites in the crystal lattice are occupied by Ru atoms. When the Pt/Ru ratio is decreased to 1/2, the solubility limit of Ru in the Pt fcc phase is exceeded and concomitantly, both a Pt–Ru fcc phase and a Ru(-Pt) hcp phase are formed [50]. This explanation conforms to the Pt–Ru bulk phase diagram where a miscibility gap is present at higher Ru contents [51]. Besides Pt/Ru alloyed catalyst species, also Ru-core Pt-shell particles were in the focus of several research activities [42,52–55].

During regular fuel cell operation, the anode potential typically ranges from 0.0 V_{RHE} to a maximum of ca. 0.5 V_{RHE} . However, prior to operation, air can diffuse into the anode compartment resulting in a rise of the initial potential to an air open circuit voltage of ca. 1.0 V_{RHE} [56]. These conditions are applied in the present work to investigate the occurring degradation mechanisms during ramping up of the fuel cell, starting from room temperature. Moreover, during start-stop cycling, cell reversal can occur when a fuel cell stack is loaded but the anode is not supplied with enough fuel. In this case, the amount of current drawn from the fuel cell exceeds the amount that can be produced. As a result the anode potential increases up to values which are even more positive than the cathode potential and subsequently the cell voltage reverses [57–59]. According to Taniguchi et al. [57] several minutes in the cell reversal condition are sufficient to cause severe damage on the anode catalyst. Thereby, depending on the hydrogen stoichiometry supplied, the anode potential can vary in a wide range. Liang et al. [58] presented a study where

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