



Synthesis and electrocatalytic performance of spherical core-shell tantalum (oxy)nitride@nitrided carbon composites in the oxygen reduction reaction



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ABSTRACT

As part of an ongoing effort to develop novel, highly active and stable Pt-free catalysts for the oxygen reduction reaction (ORR), we here report the synthesis, structural characteristics and electrochemical/electrocatalytic properties of novel core-shell composite materials, consisting of a spherical nitrided carbon core and a tantalum (oxy)nitride shell. The (nitrided) carbon core is supposed to improve the electrical conductivity of the material and the (oxy)nitride shell is intended to protect the core against electrochemical corrosion. Spherical core-shell Ta_xN_y@C_mN_n composite particles were synthesized by sol-gel deposition of tantalum oxide on preformed carbon spheres, which were prepared by hydrothermal carbonization of glucose and subsequent nitriding in ammonia vapor at different temperatures (700 °C – 1150 °C). The influence of the nitriding temperature on the structure and phase composition of the resulting composite particles was evaluated, employing a variety of techniques, including electron microscopy (SEM, TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), elemental analysis, thermogravimetric analysis (TGA), IR spectroscopy and N₂ sorption measurements, and correlated with changes in the electrochemical/electrocatalytic behavior. These core-shell composite materials show a significantly improved ORR activity compared to pure tantalum (oxy)nitrides, in particular upon nitriding at 1000 °C, while the selectivity for the 4-electron pathway to H₂O still requires improvement. The physical origin of the high activity of these materials and contributions from different phases are discussed.

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1. Introduction

The commercial success of polymer electrolyte fuel cells (PEFCs) for direct conversion of chemical into electrical energy will sensitively depend on the further progress in cost reduction and, closely related to that, in enhancing their durability under operating conditions. Among the main factors are the catalysts, which are commonly based on platinum and platinum alloys, both on the anode and on the cathode [1–4]. Therefore, in the long run, alternative catalysts based on noble metal-free, less expensive and

stable materials are highly desirable, in particular for the oxygen reduction reaction at the cathode. A variety of alternative ORR catalysts have been proposed by several groups, including transition metal complexes with porphyrin-type ligands [5,6], iron-based catalysts containing iron cations coordinated by pyridinic nitrogen in graphitic sheets [7], or carbon-based materials doped with different metals or non-metals [8–12]. In particular, nitrogen-doped carbon was found to be highly promising in that respect [8,12]. Various transition metal oxides, such as Ta₂O₅, TiO₂, ZrO₂, etc., were also found to be active towards the ORR [13–15], as well as their nitrided counterparts [16–19]. None of these materials, however, reaches the activity of the Pt based catalysts. Furthermore, the carbon-based or carbon supported catalysts suffer from their sensitivity to corrosive degradation under operating conditions [20], while the activity of the metal oxide based materials, which are mostly stable in both acidic

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and oxidizing environments, is limited by their generally poor electrical conductivity [19,21,22]. An increase of the electric conductivity is possible by nitriding of metal oxides, which can lead to a decreased band gap of the metal oxide semiconductors [23].

As part of an ongoing effort to develop novel, highly active and stable Pt-free ORR catalyst materials [19,24,25], we report here the synthesis, structural characteristics and electrochemical/electrocatalytic properties of novel core-shell composite materials, consisting of a spherical nitrated carbon core and a tantalum (oxy)nitride shell. Metal (oxy)nitrides, and in particular tantalum (oxy)nitrides, have been reported earlier to be active ORR catalysts and to be stable in acidic environment [22,26–29]. Similarly, nitrated carbon was also reported to exhibit a significant ORR activity [8,12]. The nitrated carbon cores are supposed to increase the electrical conductivity of the material. On the other hand, the metal (oxy)nitride shells are expected to protect the nitrated carbon cores against electrochemical corrosion under reaction conditions. Based on the results of a recent study, where we investigated the synthesis and electrochemical/electrocatalytic properties of similar type core-shell particles with a titania (oxy) nitride shell [25], the shell is expected to be mesoporous, allowing transport of O₂ also to the nitrated carbon core. Compared to the titania based analogue, tantalum (oxy)nitrides are rather complex, since they may include a variety of crystal phases with different ORR characteristics [26].

Before presenting and discussing the results of our study, we will briefly summarize previous findings relevant for this work. Ishihara et al. [26] presented TaO_{0.92}N_{1.05} as an ORR-active phase and later attributed the activity to a Ta₃N₅-like TaO_xN_y structure with some surface defects [22]. This work already demonstrates the complexity of determining the active sites in such systems with numerous different phases, phase boundaries and surface compositions. The addition of carbon makes the overall catalytic system even more complex, as shown by Ishihara et al. [17], who stated that the oxidation of a TaCN precursor leads to increased ORR activities. Later, Ohgi et al. [30] and Ishihara et al. [31] attributed the ORR activity to the oxygen-vacancy defects of the Ta₂O₅ resulting from the oxidation of the TaC/TaCN precursors and the formation of electrical conduction pathways introduced by the carbon which are necessary for an efficient ORR activity. Furthermore, the oxidized Ta₃N₅ phase was also discussed as being ORR active [32]. Theoretical studies claim that this activity is based on O-substituted Ta₃N₅ surfaces, which lead to additional states located between conduction and valence band and allow O₂ adsorption [33]. These authors stated that those states weaken the O–O-bond, thereby enhancing the ORR activity. Overall, the previous results indicate that the ORR activity of tantalum (oxy) nitride systems is not a result of a single active phase, but is rather due to the presence of various types of defects.

The main difference between our materials and the ones of Ota et al. is that we use composite materials based on a combination of a highly structured nitrated carbon core and a tantalum (oxy) nitride shell, while most previous studies either used modified tantalum oxide/(oxy)nitride based compounds which are supported on carbon [17,30,31] or sputtered TaO_xN_y films [22,27,34]. Recently, also carbon nanotubes were used as support [32,35].

In the following, we will first describe the synthesis of the (oxy) nitride core-shell materials as well as the experimental procedures and instrumentation employed for their characterization (Section 2). Next we present results of the synthesis and physical characterization of the resulting catalyst materials (Section 3.1). The results of the electrochemical characterization, both in acid and alkaline electrolyte, will follow in Section 3.2. In Section 3.3 we will focus on the performance of these materials in the ORR (Section 3.3.1) and compare this with the ORR performance of

related materials (Section 3.3.2). Next, we tested their stability under operating condition, evaluating the loss of ORR activity during simulated start-stop cycles (Section 3.3.3), followed by a discussion of the active phase(s) of the materials (Section 3.3.4). Finally, the main conclusions derived from this work are summarized in Section 4.

2. Experimental

2.1. Synthesis of uniform tantalum (oxy)nitride@nitrated carbon spheres

165 mL of a 0.75 M solution of glucose in aqua dest. was hydrothermally treated at 165 °C for 10.5 h [36]. The resulting spherical carbon particles were washed three times with 200 mL aqua dest. and ethanol each, centrifuged and dried.

A homogeneous tantalum oxide shell was deposited by sol-gel processing of tantalum alkoxides in the stable colloidal solution of the as-synthesized carbon spheres, following a modified procedure reported by Ming et al. [37]. A colloidal solution of carbon spheres (1.915 g) in ethanol abs. (210 mL) was prepared by ultrasonic treatment (2.5 h). Tantalum(V) butoxide (3.29 g) dissolved in ethanol abs. (40 mL) was first added dropwise to this colloidal solution, followed by homogenization for 1.5 h. Aqua dest. (200 mL) was added (1 mL min⁻¹) while stirring, followed by ageing of the reaction solution for 24 h. Subsequent solvothermal treatment at 210 °C for 16 h led to spherical tantalum oxide@carbon particles. The product was washed twice with 100 mL ethanol, centrifuged and dried.

The tantalum oxide@carbon spheres were subjected to ammonia nitriding leading to tantalum (oxy)nitride@nitrated carbon composites: After placing 400 mg of the as-synthesized tantalum oxide@carbon composite in the tube furnace and flushing with argon, the sample was heated to the desired reaction temperature (different temperatures between 700 °C and 1150 °C in 150 °C steps). The NH₃ flow during the heat-up phase was adjusted such that the overall volume of the gas stream during this phase was equal to half of the volume of the furnace tube (12 L). When reaching the reaction temperature, the NH₃ flow was adjusted to 2.5 NL h⁻¹. The sample was kept under these conditions for 2 h. (Note that in this work ‘oxynitride’ will indicate compounds containing both oxygen and nitrogen, whereas ‘(oxy)nitrides’ will stand for the class of materials formed during nitriding of the oxides, which will either be oxynitrides or nitrides.) In the following, the tantalum (oxy)nitride@nitrated carbon spheres are labelled as TaON@CN, independent of the O:N and C:N ratios. For specific materials, the reaction temperature is stated by a number added to that label (700–1150 = 700 °C – 1150 °C), the non-nitrated tantalum oxide@carbon spheres are denoted as TaO@C-RT. In addition to the composites, Ta₂O₅ powder (Alfa Aesar) was nitrated for comparison and labelled TaO_xN_y-a, with a indicating the nitriding temperature (TaO_xN_y rather than TaON to indicate the difference to the TaON phase).

2.2. Characterization of uniform tantalum (oxy)nitride@nitrated carbon spheres

Bright field transmission electron microscopy (BF-TEM) images were taken with a JEOL1400 instrument equipped with a CCD camera. For sample preparation, a droplet of ethanol (Merck Emsure) solution containing the material powder (ca. 1 mg mL⁻¹) was deposited on a carbonized Cu grid (Plano, Mesh 300), followed by evaporation of the ethanol. The energy dispersive X-ray spectroscopy (EDS) maps were acquired with a JEOL JEM-F200 high-resolution transmission electron microscope equipped with a cold field emission electron source at 200 kV in STEM (scanning

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