Efficient OER Catalyst with Low Ir Volume Density Obtained by Homogeneous Deposition of Iridium Oxide Nanoparticles on Macroporous Antimony-Doped Tin Oxide Support

Daniel Böhm,* Michael Beetz, Maximilian Schuster, Kristina Peters, Alexander G. Hufnagel, Markus Döblinger, Bernhard Böller, Thomas Bein, and Dina Fattakhova-Rohlfing*

A multistep synthesis procedure for the homogeneous coating of a complex porous conductive oxide with small Ir nanoparticles is introduced to obtain a highly active electrocatalyst for water oxidation. At first, inverse opal macroporous Sb doped SnO$_2$ (ATO) microparticles with defined pore size, composition, and open-porous morphology are synthesized that reach a conductivity of $\approx 3.6$ S cm$^{-1}$ and are further used as catalyst support. ATO-supported iridium catalysts with a controlled amount of active material are prepared by solvothermal reduction of an IrO$_x$ colloid in the presence of the porous ATO particles, whereby homogeneous coating of the complete outer and inner surface of the particles with nanodispersed metallic Ir is achieved. Thermal oxidation leads to the formation of ATO-supported IrO$_2$ nanoparticles with a void volume fraction of $\approx 89\%$ calculated for catalyst thin films based on scanning transmission electron microscope tomography data and microparticle size distribution. A remarkably low Ir bulk density of $\approx 0.08$ g cm$^{-3}$ for this supported oxide catalyst architecture with 25 wt% Ir is determined. This highly efficient oxygen evolution reaction catalyst reaches a current density of 63 A g$_{Ir}^{-1}$ at an overpotential of 300 mV versus reversible hydrogen electrode, significantly exceeding a commercial TiO$_2$-supported IrO$_2$ reference catalyst under the same measurement conditions.

1. Introduction

Generation of hydrogen via the electrolysis of water is considered one of important pillars of a future sustainable economy. In this way, the renewably generated electricity is converted into hydrogen that can be stored and used when required, either in a fuel cell or to replace petrochemically produced hydrogen as a process feedstock.[1,2] Relatively recent but already advanced proton exchange membrane (PEM) electrolysis technology enjoys an upswing in the industrial and research interest due to its compact design enabling high efficiency, high applicable current density and intermittent operation capability, which makes it an excellent match for decentralized renewable generators with high output fluctuations.[3] However, the large scale application of PEM electrolysis is currently limited by the high cost of its components and in particular iridium used to catalyze the oxygen evolution reaction (OER) process.[4,5] In spite of intensive research on different classes of OER catalysts, iridium oxide remains the only material demonstrating sufficient long-term catalytic activity without stability fading.[6] This is however achieved by a high Ir loading in the electrode assemblies of about 1.5–3 mg cm$^{-2}$ in the state of the art PEM cells.[7–9] Taking into account the cost, scarcity and total availability of Ir, at least a 10-fold decrease in the Ir loading is required.[10] At the same time, a certain thickness of the catalyst layer of several $\mu$m is needed to enable its integration in the cells without the shortcuts in their functionality.[7] In fact, it is not only the decreased loading but the drastic decrease in the Ir volumetric packing density in the electrode assembly with the simultaneous increase in the OER activity that should be targeted to...
make PEM technology economically feasible for the large scale hydrogen generation.

Due to a high economic impact of PEM electrolysis, considerable efforts have been made to improve the performance of Ir-based catalysts. Nanostructuring, and in particular inverse opal morphology with its high void volume were demonstrated to be beneficial for decreasing the catalyst loading in membrane based electrolyzers as has been recently reported by Park et al.\cite{11} and by Faustini et al.\cite{12} for IrO$_2$ or RuIrO$_2$ catalysts, respectively. The critical point in the fabrication of nanostructured Ir-based catalysts is however the simultaneous optimization of the nanomorphology and the catalytic activity, which is strongly influenced even by the subtle changes in phase composition and is sensitive to the fabrication method.

Another established approach is a dispersion of the Ir-based OER catalyst on a nanostructured support, which potentially results in a much larger active surface area for a given amount of catalyst than could be achieved by a solid compact structure.\cite{13-18} TiO$_2$-supported IrO$_2$ has been used for years as dimensionally stable electrodes (DSA) in chlorine-alkali electrolysis\cite{19} and in the state of the art PEM electrolysis.\cite{7,9,20} The major advantages brought by the commercially available supported catalysts are however more an improved mechanical stability and simple processability of the catalyst layers rather than the decrease in Ir loading.

Significant efforts have been made therefore to optimize the morphology of supports by using materials with high surface area, high electric conductivity and high oxidation stability such as mesoporous transparent conductive oxides (TCO). Mesoporous antimony doped tin oxide (ATO)\cite{13,21} indium tin oxide (ITO)\cite{21} fluorine-doped tin oxide (FTO), and niobium-doped titania (NTO)\cite{18,22} coated with a thin iridium active phase have been reported to show the high electrocatalytic activity with a substantially decreased iridium loading. Still, in spite of the progress achieved, the rather small pore size and compact structure of the mesoporous materials put constraints on the homogeneous dispersion of iridium layers and the volumetric density as well as on the gas transport at high current densities. Therefore, a combination of conductivity provided by TCOs with a low volumetric density of macroporous supports can be expected to enable a further decrease in the Ir loading per membrane area on a scale required for large scale application of the PEM technology.\cite{21}

The challenges in the development of supported catalysts are the synthesis of an ideally conductive, corrosion-stable support with the optimized morphology, as well as its conformal coating with a very thin layer of catalyst in a simple and scalable way.

We present a scalable approach to prepare a dimensionally stable OER catalyst with a very low Ir volumetric loading density but very high OER activity. In contrast to previous work on supported catalysts and Ir-based OER catalysts, our multistep synthesis approach allows for an independent optimization of all single components to result in a highly active and stable catalyst. With the introduced synthesis concept the composition (by choice of the transition metal precursor), morphology (by the size of porogen), and conductivity (by the doping level) of the oxidic support, as well as the iridium loading (by the ratio of Ir-precursor to oxidic support) and the active phase (by the oxidation procedure applied on the Ir@oxidic-support) can be tuned individually to enable the development of highly active OER catalysts with high Ir-volume dispersion for future PEM-electrolysis.

2. Results and Discussion

Scheme 1 depicts the synthesis workflow starting from the ultrasonic spray pyrolysis of electrically conducting macroporous antimony-doped tin oxide (Sb:SnO$_2$ or ATO) microparticles templated by poly(methyl methacrylate) (PMMA) (Step I), and an iridium chloride precursor that is oxidized in an aqueous environment to form hydrous IrO$_2$ colloid nanoparticles (Step II). A solvothermal reaction in tert-butanol/methanol/H$_2$O as a key step leads to a reduction of the IrO$_2$ colloid nanoparticles at the oxide microparticle surface (Step III) to form a homogeneous layer of metallic nanoparticles (referred to as Ir fBuOH) of comparable size (<2 nm). The resulting ATO nanoparticle-supported Ir nanoparticle product is referred to as SG$_{280}$Ir-YX, with “SG” abbreviated for sol–gel derived product, subscript (“280” or “120”) representing the PMMA bead diameter (in nm) used for the synthesis of inverse opal microparticles, “Δ” indicating thermally cured ATO scaffold.

Scheme 1. Synthesis of ATO microparticle-supported IrO$_2$ oxygen evolution reaction catalyst. Step I: Synthesis of macroporous oxide microparticles (red) by ultrasonic spray pyrolysis. Step II: Synthesis of IrO$_2$ colloid nanoparticles (green) used for catalyst loading. Step III: Solvothermal loading of oxidic support by reduction of IrO$_2$ to metallic Ir (blue) on the microparticle surface (assigned as “Ir fBuOH”). Step IV: Thermal oxidation of Ir-loaded ATO microparticles leads to the formation of IrO$_2$ nanoparticles (black, assigned as Ir fBuOH Δ) resulting in the final ATO-supported IrO$_2$-based OER catalyst.
particles, “Ir” indicating an Ir nanoparticle loaded product obtained by a solvothermal synthesis and “Y” = 1/2, 1, 2, 3, 4 being a multiplier of the iridium amount “X” on the ATO scaffold theoretically yielding a ≈ 15 wt% Ir content in the composite catalyst (see the Experimental Section and Table S1, Supporting Information, for further details). Thermal oxidation in air (Step IV) leads to the formation of ATO microparticle-supported IrO₂ nanoparticles referred to as SG₂₈₀Δ-IrO₂-YX which represents IrO₂ nanoparticles supported on ATO scaffold particles originating from the thermal oxidation in air.

In addition to the catalyst described above, particles with a smaller macropore size were prepared using 120 nm PMMA beads for the ATO microparticle synthesis. The samples are assigned as SG₁₂₀Δ-Ir-YX and SG₁₂₀Δ-IrO₂-YX for supported catalysts before and after thermal oxidation, respectively. As two series of the catalysts show very similar materials properties, mainly the characterization of particles with a larger pore size is shown in the paper, with characterization results of the smaller pore size catalyst series being shown in the supporting information.

Macroporous ATO microparticles depicted in Figure 1 were synthesized using an ultrasonic spray pyrolysis (USP) approach (Scheme 1, Step I, also see Scheme S1 in the Supporting Information and the Experimental Section for further details).[23] PMMA with bead sizes of ≈ 120 and ≈ 280 nm were used as templates to form ordered macroporous[24] ATO particles either from sol gel derived precursor (in the following referred to as SG₁₂₀Δ and SG₂₈₀Δ for 120 and 280 nm PMMA templated particles, respectively) or from presynthesized ATO nanoparticles[25] (referred to as NP₁₂₀Δ). Resulting powders before (SG₁₂₀Δ, SG₂₈₀Δ and NP₁₂₀Δ) and after thermal curing (SG₁₂₀Δ, SG₂₈₀Δ, and NP₁₂₀Δ with “Δ” representing an additional heating step in air after the spray pyrolysis reaction) for the removal of residual carbon as well as undoped reference (SG₂₈₀Δ w/o Sb) were analyzed by X-ray diffraction and Raman spectroscopy (see Figure S1a,c in the Supporting Information) confirming the exclusive formation of the SnO₂ cassiterite phase for undoped and ≈ 4 at% (sol–gel based) and ≈ 5 at% (nanoparticles based) Sb-doped samples. X-ray photoelectron spectroscopy (XPS) (see Figure S3 in the Supporting Information) and energy dispersive X-ray (EDX) analysis (value noted in Figure 1a) point to a Sb doping concentration of 4.3 at% for the SG₂₈₀Δ samples, which is in a good agreement with the Sb content of 4.8 at% in the precursor solution. n-Type doping by antimony is known to increase the conductivity of stoichiometric SnO₂ significantly, with the highest values reported for an Sb-doping level of about 5 at%.[25] Dc measurements for densely compressed pellets return a high specific conductivity of 3.6 S cm⁻¹ for the Sb-doped (SG₂₈₀Δ) SnO₂ microparticle samples, which is an increase by a factor of ≈ 10⁴ compared to a respective undoped sample SG₂₈₀Δ (3.8 × 10⁻⁴ S cm⁻¹).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images reveal the formation of ATO

Figure 1. a–c) Electron microscopy images of macroporous antimony-doped tin oxide microparticles templated with 280 nm PMMA beads (SG₂₈₀Δ). d) Lattice spacings indexed for individual ATO crystallites determined by intensity profiles of crystallites and correlated to d-spacings and orientation according to ICDD card number 00-041-1445 (SnO₂, tetragonal symmetry, a = b = 4.7382(4) Å, c = 3.1871(1) Å, α = β = γ = 90°).
microparticles with a mean diameter of 850 nm and inverse opal morphology with an outer pore opening diameter of 150–190 nm (mean Ø172 nm, N = 191) (Figure 1a,b) and a mean inner pore diameter determined from high resolution (HR)-TEM images of ≈232 nm indicating a shrinkage of the initial pores obtained by the 280 nm PMMA beads by ≈17% during the spray pyrolysis reaction. The pore size of the inverse opal ATO microparticles can be easily tuned by the size of the PMMA beads, as shown in Figures S4 and S5 (Supporting Information) for sol–gel and nanoparticle based ATO microparticles templated with 120 nm PMMA beads. 120 nm PMMA porogen templating thereby results in the formation of pore opening diameters of 55–75 nm (mean Ø65 nm, N = 137) on the outer microparticle surface and mean inner pore diameter of ≈83 nm as shown by electron microscopy translating to a pore shrinkage of ≈30% during the pyrolysis reaction.

According to X-ray diffraction (XRD) and high resolution TEM images, the scaffold is composed of ≈5 nm nanocrystals (Figure 1d and Figure S1, Supporting Information). Nitrogen sorption measurements (Figure S6, Supporting Information) correspond to mainly macroporous adsorbent with minor contribution of microporosity originating from textural porosity of interconnected small crystalline domains.

A Brunauer–Emmett–Teller surface area of 54 and 52 m² g⁻¹ was determined for 120 and 280 nm PMMA templated ATO microparticles, respectively. Direct evidence of macropores of about 70 nm for sample SG₁₂₀A is given by the pore size distribution shown in inset of Figure S6a (Supporting Information), which is in a good agreement with the pore size quantification by SEM and TEM (see Figure S4 in the Supporting Information). The pore size distribution of SG₂₈₀A does not show any porosity beyond a minor amount of micropores which can be explained by a detection limitation of the nitrogen sorption technique with regard to larger macropores (≥80 nm) as present in 280 nm PMMA templated microparticles. However, the visibly open porosity observed by SEM and TEM (Figure 1) in combination with the BET surface area strongly suggest interconnected macropores also for the 280 nm PMMA templated ATO microparticles.

For the synthesis of a highly OER active iridium phase we have introduced a facile synthesis method for ultrasmall colloidal IrOₓ particles (Scheme 1, Step II), which was used as an Ir precursor phase for the solvothermal loading of the oxidic scaffold. The procedure employs the rapid oxidation of an Ir(III)Cl₃ precursor in aqueous solution with KO₂ which was inspired by a synthesis introduced by Sutto for the fabrication of ultrasmall metal oxide nanoparticles.[36]

The as-prepared IrOₓ colloid (Figure 2e,f and Figure S7a, Supporting Information) consists of approximately spherical particles with a mean diameter of ≈2.4 nm as shown by scanning transmission electron microscope (STEM). The electron diffraction pattern (Figure 2f) of the particles only shows a diffuse ring that does not correspond to a distinct crystallographic plane but represents a mean Ir–O atomic distance in this poorly crystalline hydrated material.[37] The hydrous IrOₓ particles are also easily reduced and crystallize in the electron beam evidenced by a visible growth and aggregation of nanoparticles with extended illumination periods (see Figure S8 in the Supporting Information).

Hydrous IrOₓ colloids display a remarkable electrocatalytic performance but a rather limited long-term stability which requires an additional thermal treatment for the transformation to a stable active IrOₓ phase.[38,39] To obtain a more stable unsupported nanosized IrOₓ reference catalyst the precursor colloid was therefore oxidized in air at a moderate temperature of 375 °C to avoid significant particle growth and sintering. Powder X-ray diffraction patterns of the IrOₓ colloid sample (Figure 2a) show a broad peak centered around 33° 2θ that is shifted to 35° 2θ upon heating. According to the XRD line broadening and peak positions, the as-prepared as well as the heated IrOₓ colloid is composed of a nanosized iridium oxide phase presumably differing in the degree of crystallinity and present crystal water causing a slight peak shift.[27] After calcination, aggregated nanoparticles (Figure 2g and Figure S7b, Supporting Information) with a mean particle size of ≈3.0 nm are observed with an electron diffraction pattern (Figure 2h) displaying diffraction rings mainly associated with the tetragonal IrOₓ phase. The increase in crystallinity accompanied by only negligible particle growth can directly be observed by STEM and is furthermore indicated by XRD (Figure 2a). The tetragonal iridium oxide phase of the IrOₓ colloid before and after calcination is further confirmed by Raman spectroscopy (Figure 2b) displaying the characteristic Eg band around 560 cm⁻¹ and a broad peak around 740 cm⁻¹, which is presumably formed by an overlapping B₂g and A₁g band at 728 and 752 cm⁻¹, respectively.[30,31]

For the preparation of the IrOₓ/ATO composite catalyst a solvothermal reaction of the precursor IrOₓ colloid in presence of the porous ATO microparticles scaffold is introduced as integral part of this work to homogeneously coat the accessible surface of a porous support with iridium nanoparticles (Scheme 1, Step III). To obtain an unsupported reference catalyst the solvothermal reaction is simply performed without the presence of the oxidic support.

The solvothermal treatment of the IrOₓ colloid in tert-butanol/MeOH/H₂O (with or without the presence of oxidic support material in the reaction) leads to a reduction and formation of metallic iridium nanoparticles, whereby unsupported Ir nanoparticles are referred to as “Ir tBuOH” in the following. The reduction process is indicated by the broad diffraction peak centered at around 41° 2θ corresponding to the cubic Ir phase and the absence of any peaks related to the tetragonal IrOₓ phase or hydrous IrOₓ (Figure 2a and Figure S9a, Supporting Information). HR-TEM and STEM images reveal the formation of crystalline uniform nanoparticles (Ir tBuOH; Figure 2i,j and Figure S7c, Supporting Information) with an average diameter of ≈2.8 nm. The electron diffraction pattern (Figure 2j) indicates the presence of metallic iridium (cubic phase), which is in agreement with the X-ray diffraction (Figure 2a).

The XRD pattern of particles after calcination at 375 °C in air (Ir tBuOHA) shows a broad peak around 33° 2θ, indicating the presence of a nanosized iridium oxide phase (Figure 2a and Figure S9b, Supporting Information). During thermal treatment the metallic nanoparticles undergo a transformation to the tetragonal IrOₓ phase (Ir tBuOHΔ; Figure 2k,l) as confirmed by electron microscopy with broad diffraction rings visible in Figure 2l, which matches well with the X-ray diffraction data.
This process is accompanied only by a minor particle growth to a mean diameter of \( \approx 3.2 \) nm (Figure 2k). The presence of an iridium oxide phase is further confirmed by Raman spectroscopy (Figure 2b) for the calcined metallic Ir nanoparticles (Ir\(_{tBuOH}\Delta\)) sample. However, the Raman spectra of Ir/IrO\(_2\) nanoparticles with reference band at 561 cm\(^{-1}\) (E\(_g\)) and close bands at 728 cm\(^{-1}\) (B\(_{2g}\)) and 752 cm\(^{-1}\) (A\(_{1g}\)) correspond to the tetragonal iridium oxide phase.\(^{[30,31]}\) XPS spectra of c) IrO\(_x\) colloid before and after thermal oxidation and d) iridium nanoparticles (Ir\(_{tBuOH}\)) and IrO\(_2\) nanoparticles (Ir\(_{tBuOH}\Delta\)). An Ir 4f\(_{7/2}\) core electron binding energy of 60.8 eV was assigned to metallic Ir(0) and an Ir 4f\(_{7/2}\) binding energy of 61.9 eV was assigned to Ir(IV)O\(_2\).\(^{[32]}\) Scanning transmission electron microscopy data and e)–i) electron diffraction (ED) patterns of respective Ir/IrO\(_2\) samples. Phase identification and assignment of lattice planes in ED pattern according to literature values.

By comparison, the ratio between the Ir 4f\(_{7/2}\) and Ir 4f\(_{5/2}\) peak is higher in the calcined sample, and we observe a visibly increased peak area and a shifted position of the Ir 4f\(_{7/2}\) and Ir 4f\(_{5/2}\) satellite peaks. The subtle changes in the XPS spectra in combination with the observed small shift in the XRD pattern (Figure 2a) are attributed to an increase in crystallinity with an accompanying loss of crystal-bound water which slightly alters the chemical surrounding of the Ir atoms in the hydrous oxide nanoparticles.

Solvothermal reduction of the IrO\(_x\) colloid nanoparticles in tert-butanol/MeOH/H\(_2\)O causes a shift of the Ir 4f\(_{7/2}\) binding energy to 60.6 eV (Ir\(_{tBuOH}\) in Figure 2d) which is assigned to Ir(0)\(^{[32]}\) and is in agreement with the corresponding X-ray diffraction (Figure 2a). Upon thermal oxidation the Ir 4f\(_{7/2}\) peak shifts again to higher binding energies (61.3 eV) and is therefore assigned to the oxide phase (Ir (+IV)).\(^{[32]}\) However, the Ir 4f spectrum of the final IrO\(_2\) nanoparticles differs from the spectra of the IrO\(_x\) colloid samples shown in Figure 2c. A significantly increased signal intensity, a further shift of the Ir 4f\(_{7/2}\) and Ir 4f\(_{5/2}\) satellite peaks and a slightly increased Ir 4f\(_{5/2}\)
to Ir 4f\textsubscript{7/2}/4f\textsubscript{5/2} ratio are observed. This indicates the formation of a nanoparticle oxide phase, as shown by the diffraction data, with a slightly altered chemical surrounding of the Ir atoms in contrast to the initial hydrous oxide phase. The results can be interpreted as a slightly altered local structure of the oxide phase differing in the degree of crystallinity and the number of defects caused by altered change in the Ir/O ratio over the course of the multistep synthesis. These structural differences not distinguishable in the powder X-ray diffraction data can have a significant impact on the OER activity and stability of the Ir-active phase (see section on electrochemical characterization).

The crucial step in the synthesis of highly active oxide supported catalysts is the homogeneous coating of a complex support morphology with a thin compact layer of iridium nanoparticles. Simple infiltration of the oxidic support with IrO\textsubscript{2} colloid results in a very poor support coverage, with the majority of colloidal nanoparticles remaining in the dispersion. We found, however, that the solvothermal treatment of this mixture in tert-butanol/methanol/H\textsubscript{2}O (step III) leads to a reduction of IrO\textsubscript{2} colloid to metallic Ir nanoparticles of similar size, conformally precipitating on the surface of porous ATO particles. The resulting composite catalyst is termed as SG\textsubscript{280}X-Ir-XY, with Y = 1/2, 1, 2, 3, 4 as a multiplier of the iridium amount declared as “X” which corresponds to an amount of precursor for a theoretical loading of 15 wt% Ir in the supported catalyst. The subcript represents the diameter of the templating porogen PMMA with 280 nm. Analogous results presented in the Supporting Information on ATO microparticles templated by 120 nm PMMA beads demonstrate a successful homogeneous coating of complex porous substrates also with decreased pore size (Figures S10a,c, S11, S12a,b,e,f, and S13 and Table S1, Supporting Information).

The diffractograms of Ir-loaded ATO microparticles templated by 280 nm PMMA beads (Figure S10b, Supporting Information) exhibit peaks associated with the cassiterite (ATO) phase and an additional peak corresponding to the Ir oxide peak that increases in intensity with the amount of (ATO) phase and an additional peak corresponding to the Ir oxide phase. The deposition of a thin layer of IrO\textsubscript{2} nanoparticles onto the parent microparticle support (Figure 1 and Figure S4, Supporting Information) results in a very poor support coverage, with the majority of colloidal nanoparticles remaining in the dispersion. We found, however, that the solvothermal treatment of this mixture in tert-butanol/methanol/H\textsubscript{2}O (step III) leads to a reduction of IrO\textsubscript{2} colloid to metallic Ir nanoparticles of similar size, conformally precipitating on the surface of porous ATO particles. The resulting composite catalyst is termed as SG\textsubscript{280}X-Ir-XY, with Y = 1/2, 1, 2, 3, 4 as a multiplier of the iridium amount declared as “X” which corresponds to an amount of precursor for a theoretical loading of 15 wt% Ir in the supported catalyst. The subscript represents the diameter of the templating porogen PMMA with 280 nm. Analogous results presented in the Supporting Information on ATO microparticles templated by 120 nm PMMA beads demonstrate a successful homogeneous coating of complex porous substrates also with decreased pore size (Figures S10a,c, S11, S12a,b,e,f, and S13 and Table S1, Supporting Information).

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As indicated by scanning electron microscopy and EDX, Ir- (Figure S12a–d, Supporting Information) and IrO\textsubscript{2} (Figure S12e–h, Supporting Information) nanoparticle-coated ATO microparticles after solvothermal loading do not show a visible difference in shape or morphology as compared to the parent microparticle support (Figure 1 and Figure S4, Supporting Information). Also, the presence of chloride ions in the solvothermal reaction introduced by the IrCl\textsubscript{3} precursor has no significant impact on the microparticle phase (Figure S1b, Supporting Information), composition (Figure S2e, Supporting Information) or conductivity (Figure S2e,f, Supporting Information). EDX (Figure S12a,c,e,g, Supporting Information) confirms the presence of iridium, which is homogeneously distributed on the microparticle scale. The loading of ATO microparticles with iridium nanoparticles and the oxidation state of the active Ir phase were also investigated by XPS (Figure S14, Supporting Information), which confirms the formation of a metallic Ir phase (Figure S14a, Supporting Information) upon solvothermal treatment in the presence of ATO microparticles as shown for unsupported nanoparticles (Figure 2d) which underwent the same synthesis procedure. Calcination also leads to the formation of the respective oxide phase (Figure S14a, Supporting Information and Figure 2d).

Table S1 (Supporting Information) summarizes the theoretical and experimentally determined Ir fractions in the ATO microparticle-supported Ir and IrO\textsubscript{2} nanoparticle materials. The measured values deviate only slightly from the theoretical ones with the exception of the highly Ir-loaded sample ATO-SG\textsubscript{280}/IrO\textsubscript{2}-4X. The reason for the smaller loading capacity of the large-pore ATO microparticles at high iridium amounts (“4X” sample with theoretical loading of 43 wt% Ir) compared to the ATO-SG\textsubscript{120}/IrO\textsubscript{2} series is expected to be caused by the slightly smaller surface area available for particle adhesion. In summary, a near quantitative adsorption of the supplied iridium on the ATO scaffold could be realized for a broad range (7 to \(\approx\)40 wt% Ir) of ATO/Ir ratios by our solvothermal loading method.

For a more detailed analysis of the spatial IrO\textsubscript{2} distribution on the macroporous ATO microparticles, high resolution transmission electron microscopy with energy-dispersive X-ray spectroscopy analysis and elemental distribution mapping was performed as shown in Figure 3. The overview images (Figure 3a,b) of the microparticles show that the morphology and pore structure of the unloaded particles has been maintained. The lattice spacings derived from electron diffraction patterns of individual ATO/IrO\textsubscript{2} particles (Figure 3d) indicate the exclusive presence of the cassiterite (ATO) and tetragonal IrO\textsubscript{2} phase. The deposition of a thin layer of IrO\textsubscript{2} nanoparticles on the inner ATO surface is shown by the lattice fringes visible in the high resolution TEM images, which can be assigned to the cassiterite and IrO\textsubscript{2} phase for individual nanocrystals (Figure 3c). Furthermore, the inner pore diameter of IrO\textsubscript{2}-loaded 280 nm PMMA-templated particles could be quantified to \(\approx\)216 nm (\(\Phi\) inner pore diameter, \(N = 14\)) according to HR-TEM images as shown in Figure 3 versus \(\approx\)71 nm (\(\Phi\) inner pore diameter, \(N = 6\)) for 120 nm PMMA templated microparticles (Figure S13b, Supporting Information). As the inner pore diameter of unloaded ATO microparticles is \(\approx\)232 nm (\(\Phi\) inner pore diameter, \(N = 27\)) and \(\approx\)83 nm (\(\Phi\) inner pore diameter, \(N = 13\), Supporting Information) for SG\textsubscript{280}Δ and SG\textsubscript{120}Δ, respectively, a mean thickness of the IrO\textsubscript{2} nanoparticle catalyst coating of \(\approx\)16 nm (ATO-SG\textsubscript{120}IrO\textsubscript{2}-2X) and \(\approx\)12 nm (ATO-SG\textsubscript{120}Δ-IrO\textsubscript{2}-2X) can be calculated. The reduction of the mean pore diameter is caused by a layer of nanocrystals of about 3 nm diameter (see Figure 2) that can be identified in the HR-TEM images of both samples (Figure 3c and Figure S13c, Supporting Information), which is in good agreement with the crystallite domain size derived from X-ray diffraction data (Figure 2a).
The active material layer on the ATO microparticle surface is therefore built up from an average of two to three IrO₂ nanoparticles for ≈25 wt% Ir loaded microparticles.

EDX elemental mappings of outer ATO pores was performed (Figure 3e and Figure S13e, Supporting Information) for Ir coated ATO with both pore sizes. For both samples a colocalization of the Sn-L, Sb-L, and Ir-L signal was observed. As the Ir-L signal extends beyond the areas of high tin and antimony concentration, we infer a homogeneous coating of the ATO surface with IrO₂.

The distribution and interconnection of ATO, IrO₂ and void volume within this composite catalyst is of critical importance for the OER activity and its possible application in membrane based electrolysers and was therefore studied by the 3D reconstruction of a representative, fully processed particle by means of STEM tomography (see the Experimental Section and Figure S15–S18, Supporting Information). The reconstruction for a 280 nm PMMA templated ATO-based particle is shown in Figure 4. Due to the higher electron scattering efficiency of high-atomic-number atoms (Z-contrast), a strong contrast between Sn and Ir is observed in high-angle annular dark-field (HAADF) imaging. The employed tomography algorithms were used to render a discrete 3D reconstruction, in which the volume occupied by ATO and IrO₂ is represented by orange and violet colors, respectively. Figure 4a shows the combined 3D intensity volume of ATO and IrO₂ reconstructed from a series of HAADF-STEM images recorded at different tilt angles. Figure 4b,c shows the extracted 3D intensity volume of the ATO scaffold and the loaded IrO₂ nanoparticle layer, respectively. The 3D intensity volume of IrO₂ (Figure 4c) follows the geometry of the ATO scaffold (Figure 4b). A calculated particle cross-section, shown in Figure 4d, confirms the homogeneous coverage of the total internal pore surface with IrO₂.

The porosity and the volume dispersion of iridium could also be extracted from the 3D particle reconstruction. For the specific SG₂₈₀ₐ-IrO₂-2X particle with ≈25 wt% iridium, a void volume of 84.4% including ATO as void and 59.7% excluding ATO as void was determined (Figure S18, Supporting Information). To calculate the volume dispersion of iridium in a catalyst film of ATO microparticle-supported IrO₂ nanoparticles expected in a membrane-electrode assembly of a PEM electrolyzer, the porosity of individual microparticles as well as the packing density of the microparticles have to be taken into account.

The void volume present in a catalyst film of spherical microparticles can be approximated by a random closed packing model[13] to reach 34 vol% for the experimentally determined particle size distribution (for further details and calculation, see Figure S19 in the Supporting Information). This results in an iridium volume fraction of 10.3 vol% in a catalyst film composed of SG₂₈₀ₐ-IrO₂-2X particles with ≈25 wt% iridium loading. The resulting Ir density of ≈0.08 gIr cm⁻³ of bulk catalyst powder is much lower than the ≈1.5 gIr cm⁻³ determined for a commercial IrO₂/TiO₂ reference catalyst. Thus, when employed in a PEM electrolyzer, a supported catalyst synthesized by the introduced procedure enables the preparation of a continuous, porous anode catalyst layer with a significantly lowered Ir loading than possible with commercial catalysts.

Electrochemical characterization was performed to assess the performance of macroporous ATO microparticle-supported iridium oxide nanoparticles as an oxygen evolution reaction catalyst in acidic media. For the experiments shown in Figure 5a,b (120 and 280 nm PMMA-templated ATO microparticles, respectively), thin films of the catalyst particles drop-cast onto Au-coated quartz crystal microbalance (QCM) sensors were used as working electrodes. The amount of iridium on the QCM chips was obtained from the absolute mass deposited onto the sensors and the iridium fraction determined by EDX measurements of the catalyst film (for Ir fractions of ATO supported catalysts see Table S1 in the Supporting Information). The morphology of thin films of unsupported IrO₂ nanoparticle reference catalysts “Irₙ colloidΔ” and “Ir tBuOHΔ” were investigated by SEM together with their unheated precursor phases “Irₙ colloid” and “Ir tBuOH” as shown in Figure S20 (Supporting Information).

Figure 3. Transmission electron micrographs and EDX mapping of IrO₂ nanoparticles supported on macroporous ATO microparticles templated with 280 nm PMMA beads. a–c) Electron micrographs, d) electron diffraction pattern, and e) STEM/EDX elemental mapping of an outer pore. ATO microparticles with IrO₂ loadings of 25 wt% Ir (ATO-SG₂₈₀ₐ-IrO₂-2X). Phase identification and assignment of lattice spacings in d) electron diffraction pattern and c) high resolution TEM image according to literature values. SnO₂ (cassiterite) pattern: ICDD card number 00-041-1445 IrO₂ pattern: ICDD card number 00-015-0870.
Ir-mass based OER currents for an overpotential of 300 mV for 120 and 280 nm PMMA-templated ATO based catalysts in Figure 5a,b, respectively, show a similar maximum in activity for the 2X samples (55 A g\(^{-1}\) for ATO-SG120\textsubscript{2X} and 63.5 A g\(^{-1}\) for ATO-SG280\textsubscript{2X} after 10 CV cycles, respectively) that correspond to a Ir loading of \(\approx 25\) wt\%. The slightly higher performance of the 280 nm PMMA templated supported catalyst is thereby attributed to a better dispersion of the IrO\(_2\) nanoparticles on the internal surface of the porous microparticle. Higher Ir loadings of up to 40 wt\% do not further increase the noble metal mass-based OER activity but rather resulted in a decrease. On the other hand, low Ir loadings of up to 15 wt\% Ir for ATO-SG\textsubscript{120}\textsubscript{2X} and ATO-SG\textsubscript{280}\textsubscript{2X} exhibit activities of only 8.4 and 24.3 A g\(^{-1}\), respectively. Compared to the unsupported IrO\(_2\) nanoparticle (Ir\textsubscript{BuOH}) reference catalyst from the same synthesis, a 4- and 4.6-fold increase versus the most active ATO-SG\textsubscript{120} \textsubscript{2X} and ATO-SG\textsubscript{280}\textsubscript{2X} sample could be observed. A comparable difference is observed for unsupported calcined IrO\(_2\) from the colloid synthesis (IrO\(_2\) colloid\textsubscript{A}). The best-performing ATO-supported samples with \(\approx 25\) wt\% Ir have a 7.3-fold (ATO-SG\textsubscript{120}\textsubscript{2X} and ATO-SG\textsubscript{280}\textsubscript{2X}) higher Ir mass-based activity at \(\eta_{OER} = 300\) mV than an industrial TiO\(_2\)-supported Ir\textsubscript{2} catalyst composed of IrO\(_2\) nanocrystals with domain sizes of \(\approx 4\) nm (according to XRD analysis) on a nanocrystalline TiO\(_2\) scaffold (Figure S21, Supporting Information) with a stated Ir loading of 75 wt\% (Elyst Ir75, Umicore, Germany).\(^{[34]}\) The significantly higher mass-based activity of the IrO\(_2\)/ATO versus the IrO\(_2\)/TiO\(_2\) supported reference catalyst may at first be explained by an optimized dispersion of IrO\(_2\) nanoparticles on the surface of the macroporous ATO resulting in a high catalytically accessible surface area. A further beneficial effect of the open macroporous morphology is an optimized mass transport through the catalyst layer enabling high current densities (Figure S22e,f, Supporting Information) without a limitation through pore clogging by evolving oxygen, which is a possible scenario for a micro- or mesoporous structure composed of aggregated nanoparticles.

IrO\(_2\) nanoparticles oxidized at a temperature of 375 °C show a similar size of crystalline domains of tetragonal IrO\(_2\) phase (=2–3 nm) as the reference catalyst (=4 nm), but a lower crystallinity (Figure 2a and Figure S21, Supporting Information). According to Geiger et al., IrO\(_2\) heated at \(\approx 375\) °C is not fully crystalline but at the upper temperature range of an intermediate phase between the amorphous IrO\(_2\) and thermal IrO\(_2\) with an increased intrinsic activity compared to the thermal oxide phase at the expense of a lower conductivity.\(^{[35]}\)

For comparison with the literature, the best performing ATO supported Ir-based catalyst reported to our knowledge are high surface area (=260 m\(^2\) g\(^{-1}\)) mesoporous-ATO sup-

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**Figure 4.** STEM-based tomography with 3D intensity volume reconstruction of IrO\(_2\) nanoparticles supported on macroporous ATO microparticles templated by 280 nm PMMA (=25 wt\% Ir). a) Total (ATO and IrO\(_2\)) 3D intensity volume derived from particle reprojection. b) Extracted ATO 3D intensity volume from a complete particle. c) Extracted IrO\(_2\) 3D intensity volume from a complete particle. d) Extracted cross section of an IrO\(_2\)-coated ATO microparticle from the 3D intensity volume.
ported core–shell IrNi\textsubscript{x}@IrO\textsubscript{x} nanoparticles prepared by Nong et al., which were obtained by electrochemical leaching of respective supported IrNi\textsubscript{x} nanoparticles. The composite catalyst with a loading of \textasciitilde19 wt% Ir exhibits an OER activity of \textasciitilde90 A g\textsubscript{Ir}\textsuperscript{\textendash1} at an overpotential of 280 mV.\cite{14} The reported 30\% higher initial activity of this catalyst as compared to our best performing sample is however obtained for a more compact structure, with a high volumetric Ir performance density disadvantageous for the application in PEM electrolyzers. Besides ATO supported catalysts, recently a nanostructured porous NTO with remarkably high conductivity of \textasciitilde440 S cm\textsuperscript{\textendash1} was introduced by Hufnagel et al. to support a \textasciitilde1 nm thin IrO\textsubscript{2} coating based on atomic layer deposition. The thin film catalyst with a low Ir-loading of \textasciitilde8 wt\% thereby showed an onset potential of \textasciitilde250 mV and an OER activity of \textasciitilde654 A g\textsubscript{Ir}\textsuperscript{\textendash1} at an overpotential of 460 mV, as compared to an onset potential of \textasciitilde215 mV and an activity of over 3200 A g\textsubscript{Ir}\textsuperscript{\textendash1} for our catalyst at a slightly lower overpotential of 420 mV.\cite{36} In comparison, our catalyst shows a significantly higher mass based activity of \textasciitilde1100 A g\textsubscript{Ir}\textsuperscript{\textendash1} at a slightly higher overpotential of 380 mV.

The decreased activity of our introduced ATO-supported samples with low loading (8 and 15 wt\% Ir) is attributed to an incomplete layer of IrO\textsubscript{2} nanoparticles on the porous ATO microparticle, whereas a complete layer is formed at 25 wt\% Ir. As the conductivity of the ATO scaffold (\textasciitilde3.6 S cm\textsuperscript{\textendash1}, Figure S2, Supporting Information) is lower than that of a layer of IrO\textsubscript{2} nanoparticles of similar particle size (\textasciitilde26 S cm\textsuperscript{\textendash1}),\cite{37} the absence of a continuous conducting pathway through the IrO\textsubscript{2} layer limits the performance. For the case of a the poor

Figure 5. Electrochemical characterization of IrO\textsubscript{2} nanoparticles supported on macroporous ATO microparticles. Iridium mass-based catalytic activity of IrO\textsubscript{2} nanoparticle-loaded microparticles templated by a) 120 nm (ATO-SG\textsubscript{120}A\textendashIrO\textsubscript{2}) and b) 280 nm (ATO-SG\textsubscript{280}A\textendashIrO\textsubscript{2}) PMMA for \textasciitilde\eta\textsubscript{OER} = 300 mV. c\textendash f) Rotating disc electrode (RDE) measurements of IrO\textsubscript{2} nanoparticles (Ir-tBuOH\textsubscript{Δ} colloid, blue), 25 wt\% Ir loaded ATO (ATO-SG\textsubscript{280}A\textendashIrO\textsubscript{2}−2X, gray) and commercial TiO\textsubscript{2}-supported IrO\textsubscript{2} with 75 wt\% Ir loading (IrO\textsubscript{2}/TiO\textsubscript{2}−Elvest Ir75, red). c) 75th scan cycle of RDE measurement with scan rate of 5 mV s\textsuperscript{\textendash1}. d) Extracted overpotentials (\textasciitilde\eta\textsubscript{OER}) for each cycle required for 1 mA cm\textsuperscript{\textendash2}. Cyclic voltammograms e) before and f) after 75 RDE cycles at a scan rate of 50 mV s\textsuperscript{\textendash1}. Chronopotentiometry measurements at g) j = 10 mA cm\textsuperscript{\textendash2} over 120 min and h) 20 h on FTO substrates with catalyst loading of 15 \textmu g\textsubscript{Ir}.
conductive TiO₂ support, Bernsmeyer et al. have correlated catalyst conductivity for different Ir contents with the OER activity. They have demonstrated that the high performance values can be reached only for Ir loadings exceeding ~25 wt% Ir, while below this threshold value practically no activity was observed. Furthermore, a minimum in the electrical conductivity of ~1.0 × 10⁻³ S cm⁻¹ in the catalyst films is suggested to eliminate negative effects of slow electron transport on the catalytic performance. [38] The conductivity of the ATO scaffold used in our work exceeds this conductivity limit (as opposed to TiO₂), which explains the considerably high OER performance of our composite catalysts even at low Ir contents of 8 wt% and 15 wt%. To further investigate the slightly reduced performance of low Ir loaded (<25 wt% Ir) catalyst, the trend in the conductivity of loosely compressed powders of IrO₂/ATO catalyst with varying Ir content as well as the IrO₂/TiO₂ reference catalyst were measured (Figure S22 and Table S2, Supporting Information). The conductivity of the ATO/IrO₂ composite catalyst is rather low for low Ir loadings of 8 and 15 wt% Ir (1.00 × 10⁻⁶ and 1.79 × 10⁻⁵ S cm⁻¹, respectively). The electrocatalytic activity of the samples is however very high, with the values equaling or even exceeding those of the commercial IrO₂/TiO₂ reference catalyst with much higher Ir loading (75 wt%) and much higher conductivity. The conductivity of the ATO/IrO₂ composite powders rises to 1.16 × 10⁻² S cm⁻¹ for the 25 wt% Ir sample (SG120Δ-IrO₂-2X). Higher iridium contents of 33 and 40 wt% further increase the conductivity up to a value of 0.88 S cm⁻¹. In comparison, a value of 4.42 S cm⁻¹ was determined for the commercial IrO₂/TiO₂ reference catalyst with 75 wt% Ir under same measurement conditions. Due to the low compressive force applied by the in house constructed d-c conductivity measurement setup (Figure S23, Supporting Information) and thus limited contact between particles across the powder-pellet thickness, the absolute values are expected to be significantly underestimated. However, the measurements performed in similar conditions enable to estimate a trend among the equally prepared samples series (Table S2, Supporting Information). As can be seen from the measured values, for the samples with Ir loading beyond 25 wt% (percolation threshold) the conductivity mainly depends on the Ir content, showing nearly linear dependence on the Ir loading. However, for the samples with very low Ir loadings below 25 wt% the conductivity of the support becomes a decisive factor, providing for a high electrocatalytic activity even without a direct contact between the IrO₂ nanoparticles. In total, there is no a linear correlation between the electrical conductivity and the electrocatalytic activity, as the commercial IrO₂/TiO₂ reference catalyst featuring the highest conductivity shows the lowest electrocatalytic activity among the investigated series.

The effect of limited conductivity in the low-iridium-loading samples (1/2X and 1X with 8 and 15 wt% Ir, respectively) becomes pronounced at higher current densities as shown in Figure S22 (Supporting Information). However, at low overpotentials of \( \eta_{\text{OER}} < 380 \text{ mV} \), even samples with low Ir loading possess an Ir mass-based activity comparable to the industrial TiO₂-supported reference despite a significantly reduced Ir content.

To investigate OER kinetics, rotating disc electrode (RDE) measurements of selected catalyst samples were performed under controlled reaction conditions (1600 rpm, 60 °C, O₂-purged electrolyte). The TiO₂-supported IrO₂ reference (Elyst Ir75) exhibits an overpotential of 258 mV, Ir /BuOHΔ requires a slightly lower overpotential of 250 mV and the ATO nanoparticle-supported IrO₂ nanoparticles require only an overpotential of 215 mV to reach an OER current of 1 mA cm⁻² in the 75th scan cycle (Figure 5c,d and for more details, see Figure S24 in the Supporting Information). The RDE performance data thus confirm the synthesis of highly OER-active IrO₂ nanoparticles by the multistep synthesis introduced in this work and furthermore emphasize the importance of a nanostructured conductive support that can enhance the catalytic activity due to a high volume dispersion of the active iridium oxide nanoparticle phase.

To investigate possible electrochemical side reactions, cyclic voltammograms of ATO-supported IrO₂ were recorded over a broad potential range between the hydrogen evolution reaction (HER) and OER onset potentials (0.05–1.52 V vs RHE) before and after each RDE activity measurement (Figure 5e,f, respectively). For all samples a very broad redox peak centered around 0.8 V versus RHE attributed to the Ir(III)/Ir(IV) redox reaction [39,40] can be observed with increasing intensities in the order TiO₂/IrO₂ reference <Ir /BuOHΔ <ATO-SG280Δ-IrO₂-2X. After the RDE activity measurements, the intensity of the aforementioned feature has notably increased for all samples (for more details, see Figures S24 and S25 in the Supporting Information). We assign this increase to a redox surface activation of the crystalline (thermal) iridium oxide in the first few cycles [41] with the formation of a highly catalytically active surface hydroxide layer. [42] This results in an increase in OER activity as seen by a decline of the required overpotentials during the early CV cycles in Figure 5d or by a shift of the CV curves shown in Figure S24 (Supporting Information).

Finally, the short (Figure 5g: 120 min) and intermediate term (Figure 5h: 20 h) corrosion behavior of the IrO₂ nanoparticle-based supported catalyst was investigated by chronopotentiometry measurements at a current density of 10 mA cm⁻². Unsupported IrO₂ nanoparticles (Ir /BuOH Δ) display a required potential of 1.72 V versus RHE remaining constant over the measurement period. For ATO-supported particles (ATO-SG280Δ-IrO₂-2X) the potential is lower by ~70 mV at 1.65 V versus RHE. The TiO₂-supported reference catalyst (Elyst Ir75) shows a slight increase in the potential over the measurement period up to 1.72 V versus RHE after 120 min, matching that of unsupported IrO₂ nanoparticles. However, intermediate term measurements show the same trend for unsupported as well as ATO-supported IrO₂ nanoparticles, with only a slight increase in potential to 1.74 and 1.66 V versus RHE after 20 h, respectively. In contrast to the catalyst particles with the conducting ATO support, the potential of TiO₂-supported IrO₂ reference catalyst constantly rises with time and reaches the highest measured end potential with 1.77 V versus RHE after 20 h in the chronopotentiometric measurement, which indicates a lower activity and stability as compared to the IrO₂ nanoparticle catalysts introduced in this work. Small differences in the absolute potential obtained by the 120 min versus 20 h measurement period indicated by an offset of the V-t curves are thereby attributed to slightly varying amounts of catalyst coated onto the FTO substrate.
of the slope of the curves as visible for the TiO/IrO₂ reference however may originate from a slightly altered catalyst dissolution during the two different experiments, as manifested by a detachment of active material from the electrode. Electron microscopy of catalyst samples after OER measurements (Figure S26, Supporting Information) further confirms a rather stable iridium content in the electrodes for a chronopotentiometric current density of 10 mA cm⁻² (20 h) and 100 mA cm⁻² (1.5 h), amounting to 24 and 23 wt% Ir, respectively, for the ATO-SG₂₈₀₀-IrO₂-2X sample with an initial Ir-loading of 25 wt%. Contrarily, analysis of the antimony content indicates a leaching process during the OER at the applied potentials shown by a reduction from initially ≈4.3 at% Sb (Figure 1a) to below 3 at% Sb after the OER experiments (Figure S26, Supporting Information).

The stability of ATO as a catalyst support for proton exchange membrane fuel cells has been discussed in the literature.⁴³⁻⁴⁵ Surface segregation of antimony caused by the preparation method⁴³ or by potential cycling⁴⁵ were discussed to lead to Sb-dissolution in an acidic environment. This results in a reduced conductivity of the surface of the obtained core–shell structure that can directly affect the electrocatalytic performance of attached catalyst nanoparticles.⁴⁵ Geiger et al.⁴⁶ recently investigated the corrosion stability of tin-oxide based catalysts (ATO, ITO, FTO) in acidic media and under applied potentials. They could show that these materials (dopants and SnO₂ host structure) possess a critical dissolution rate under cathodic potential. But also the anodic potential range for the thermodynamic stability of ATO is reported to be limited to theoretically 1.1 V versus RHE with measured critical Sb- and related Sn-dissolution upon anodic polarization,⁴⁶ rendering the material inappropriate for an industrial long-term application at high potentials and current densities.

For an adoption of this model system for industrial use a new oxidation stable conductive oxide support such as fluorine-doped tin oxide (corrosion stable up to 2.7 V vs RHE)⁴⁶ or niobium-doped TiO₂ may therefore be employed.

The overall high Ir mass-based activity of the synthesized iridium oxide catalyst is attributed to the small size of the spherical IrO₂ nanoparticles obtained by the synthesis approach and the low-temperature calcination that is known to result in an increased fraction of high-surface-energy crystal facets and defects which are associated with high OER activity.⁴⁷ However, the key factor for increased OER activity is the high Ir volume dispersion resulting from the homogeneous coating of nanoparticles onto the surface of the ordered porous conducting support. Catalysts prepared by the introduced multistep synthesis procedure provide two complementary current transmission pathways from the electrode contact to the reaction interface and thereby limit the series resistance and ensure electrical contact to nanoparticles of the catalytically active phase.

The comparably small mass-specific charge for the corresponding redox feature of the IrO₂/TiO₂ reference is attributed to a higher degree of crystallinity and slightly larger crystalline domain sizes of the thermal oxide resulting in a comparably low redox-active surface area with iridium being stable in the +IV oxidation state. The unsupported IrO₂ nanoparticles (Ir fBuOHΔ) as well as the ATO-supported nanoparticles (ATO-SG₂₈₀₀-IrO₂-2X) oxidized at a low temperature possess small crystalline domains (Figures 2 and 3) and a moderate degree of crystallinity (as shown in Figure 2a and Figure S10, Supporting Information), therefore exhibiting an increased redox-active surface. For the well-dispersed IrO₂ nanoparticles on the porous ATO scaffold the accessible redox-active surface area is further increased as indicated by the increased mass-specific charge (Figure 5e,f).

3. Conclusion

This work introduces a multistep synthesis procedure for the homogeneous decoration of complex porous Sb-doped SnO₂ structures as an example for a conductive oxidic OER catalyst support for iridium nanoparticles in the range of 2–3 nm. Detailed structural characterization of the synthesized inverse opal macroporous ATO-microparticle/IrO₂ model catalyst system thereby shows how to independently tune the morphology, porosity, and conductivity of an oxide support material through the ultrasonic spray pyrolysis of a sol–gel or nanoparticle precursor. Furthermore, the ATO/IrO₂ catalyst was thoroughly investigated by high-resolution (S)TEM imaging, which allowed for a detailed analysis of the catalyst particle distribution within the porous 3D structure by means of STEM tomography. An approximation of the iridium volume dispersion in a thin film of porous microparticles returns a roughly 18 times lower iridium volume density than for a TiO₂-supported reference catalyst; this would allow for the fabrication of PEM electrolyzer anodes with strongly reduced Ir loading and retention of the film thickness required for electrolyzer operation.

The ATO-microparticle/IrO₂ catalyst with 25 wt% Ir furthermore shows improved OER activity and stability compared to similarly prepared pure IrO₂ nanoparticles, presumably due to the homogeneous dispersion and stabilization of the small IrO₂ particles on the ATO surface. The model catalyst system shown here significantly outperformed an industrial TiO₂-supported IrO₂ catalyst in Ir mass-based OER activity, underlining the advantage of a suitable oxide support morphology and a homogeneous distribution of the active material on a conductive support.

On the other hand, even lower iridium loadings (≤15 wt% Ir) on the macroporous microparticle scaffold result in considerably lower catalytic performance, suggesting a major current transport pathway through the iridium oxide nanoparticle layer which is lacking in samples with a very low Ir-loading in which the nanoparticles do not form a continuous layer. This emphasizes the need for a highly conductive support to effectively contact isolated catalyst nanoparticles. Overall, this study shows that combining iridium oxide nanoparticles with a suitable conductive and rationally designed porous oxide promises to be a suitable approach toward highly active anodes for PEM electrolyzers with drastically reduced iridium loading and increased long term stability.

4. Experimental Section

Synthesis of Macroporous ATO Microparticles (Oxidic Catalyst Support) by Spray Drying: The synthesis of macroporous ATO microparticles by USP is based on the USP synthesis of macroporous silica particles with
polymer bead templating initially proposed by Iskandar et al.[49] and later modified by Hieda et al.[51] to obtain macroporous (Sb-doped) SnO2 microparticles.

For the synthesis of sol–gel based macroporous antimony doped tin-oxide microparticles, first antimony (III) acetate (224 µmol/67 mg, SIGMA-ALDRICH, 99.99% trace metals basis) was dissolved in ethanol (4 mL) by stirring for 1 h. The antimony solution was slowly added to 1.14 g (4.376 mmol) tin (IV) chloride (SIGMA-ALDRICH, 98% purity) under constant stirring. Possibly precipitated solids were dissolved by further stirring and by using an ultrasonic bath for 5 min. Finally, an aqueous PMMA bead colloid (120 or 280 nm, respectively) was added to the precursor solution to obtain a final polymer bead content of 5.85 wt% and a total metal–salt concentration of 180 × 10−3 M. The synthesis of PMMA beads with mean diameters of 280 and 120 nm was conducted according to the emulsion polymerization route described elsewhere resulting in an aqueous colloidal solution[49,50] (see the Supporting Information for further details).

The in-house constructed spray pyrolysis setup consists of a T-shaped high-temperature polypropylene discharge pipe system (OSTENDORF KUNSTSTOFFE) that connects the carrier gas flow (laboratory pressured air) at a flow rate of ~60 L h−1 to a 45 cm long quartz tube (25 mm diameter) placed in a single zone tube furnace (EUROTHERM 2404 temperature controller) with a temperature set point of 615 °C (609 °C oven temperature). The lower part of the pipe system including the precursor solution was sealed with a thin three-layer polyethylene cling film (TOPPITS) versus a water filled beaker with a 1.7 MHz FULOON 24V DC (700 mA, max. 400 mL aerosol h−1) household ultrasonic nebulizer (SHENZEN KULETONG TECHNOLOGY CO LTD) placed inside. Aerogel collection was achieved with an in-house constructed filter system with polytetrafluoroethylene (PTFE) inset (50 mm diameter RCT-BIOFIL-PX-SU, 0.65 µm thickness, REICHELT filter system with polytetrafluoroethylene (PTFE) insert (50 mm diameter). The product was redispersed in a few mL bidistilled H2O and freeze-dried using an ALPHA 1-4 machine (MARTIN CHRIST GERFRIERTECKNUNGENSLAGEN GMBH). Obtained powders of Ir nanoparticles loaded onto ATO scaffolds were characterized, used for the preparation of electrodes and further electrochemical measurements or calcined to obtain IrOx nanoparticle coated porous ATO scaffold. Calcination of Ir nanoparticles and Ir-NP@porous-ATO-microparticles (solvothermally treated IrOx colloid) was performed in a NABERTHERM laboratory oven (model N15/65SFA) at 375 °C in air with a heating rate of 1.9 °C min−1 and a dwell time of 1 h.

Physicochemical Characterization: Wide-angle X-ray diffraction analysis was carried out in transmission mode using a STOE STADI P diffractometer with Cu Kα radiation (λ = 1.5406 Å) and a Ge(111) single crystal monochromator equipped with a DEXTORS solid state strip detector Mythen 1K. Powder XRD patterns of the samples were collected with an omega-2theta scan in the 2θ range from 5° to 90° with a step size of 1° and fixed integration time of 25–35 s per step and a resolution of 0.05°. The size of the crystalline domains was calculated from the XRD patterns for the Ir 111 (ICDD#00-006-0598), IrO2 112 (ICDD#00-015-0870), and SnO2 110 (ICDD#00-041-1445) reflection, respectively, using the Scherrer equation.

Raman spectroscopy was carried out using a LabRAM HR UV–Vis (HORIBA JOBIN YVON) Raman Microscope (OLYMPUS BX41) with a SYMPHONY CCD detection system and a He–Ne laser (λ = 633 nm). Spectra were recorded using a lens with a 10-fold magnification in the range from 100 to 1000 cm−1 with filters of OD 0.3–0.6. Spectrum accumulation mode was used with integration times of 30 s per spectrum and 600 cycles. The data acquisition was carried out with LabSpec software.

HR-TEM and HAADF-STEM images as well as electron diffraction patterns were recorded using a FEI Titan Themis 80-300 transmission electron microscope with aberration correction of the probe-forming lenses operated at 120 kV or 300 kV, respectively. EDX was performed using a SuperX windowless, four quadrant Silicon drift detector with a solid angle of 0.7 sr. TEM specimens were prepared by dispersing IrOx colloids, catalyst nanoparticles, or Ir loaded ATO microparticles respectively in a 1:1 (v:v) ratio of water to ethanol and depositing them on a carbon-film coated copper grid, followed by drying in air.

HAADF-STEM tilt series of 29 images for TEM tomography were recorded in 5° steps from −70° to +70°. For a reconstruction of the 3D intensity volume and a presentation of different phases of Ir and ATO, respectively, a masked simultaneous iterative reconstruction technique (SIRT) with further refinement by a discrete algebraic reconstruction technique (DART) were employed (see the Supporting Information for further details).

SEM images were obtained with a FEI Helios Nanolab G3 UC scanning electron microscope equipped with a field emission gun operated at 3–5 kV. SEM specimens were prepared by dispersing dried catalyst nanoparticles, microparticles, and composites in a 1:1 v/v water to ethanol ratio on FTO or Si substrates that were glued onto a glass slide before coating with a 200 nm thick carbon film.
stainless-steel sample holder with silver lacquer. EDX measurements were performed at an operating voltage of 20 kV with a X-Max® Silicon Drift Detector with 80 mm² detector area (OXFORD INSTRUMENTS) and AZTec acquisition software (OXFORD INSTRUMENTS).

For the analysis of the porosity of the samples, the calcined samples were degassed for 12 h at 120 °C under vacuum. Nitrogen sorption measurements were performed on a QUANTACHROME Autosorb-1 instrument at the boiling point of liquid nitrogen (77 K). The specific surface area was determined with the Brunauer–Emmett–Teller (BET) method at p/p₀ = 0.05–0.2. The pore size distribution was calculated using a nonlocal DFT equilibrium model for silica with cylindrical pores. XPS analysis was conducted with the non-monochromated Mg Kα radiation of a VSW T10 X-ray source and a VSW HA100 hemispherical analyzer. For the XPS measurements the nanoparticles were drop-casted on silicon substrates in air bevor the transfer to the UHV chamber. Peaks were fitted using a convolution of a Doniach–Šunjic type[53] and a Gaussian function with linear background subtraction. If possible, the carbon 1s peak was calibrated to 284.8 eV to compensate for charging effects. An Ir 4f½ core electron binding energy of 60.8 eV was assigned to metallic Ir(0) and an Ir 4f½ binding energy of 61.9 eV was assigned to Ir(IV)[32].

Conductivity measurements of macroporous ATO microparticles were carried out on an HMS 3000 apparatus (ECOPAIA) in the Van der Pauw geometry (5 mm separation of electrodes). Powder samples were measured in form of pellets that were compressed for 10 min at 150 kg cm⁻². Conductivity measurements of ATO/IrO₂ and commercial TiO₂ supported reference catalyst were conducted due to restrictions on sample volume on an in-house constructed dc-conductivity measurements cell on loosely compressed powders by recording I–V curves between −5 to +5 V by an AUTOLAB 302N.

Electrochemical Characterization: Unsupported IrO₂ and IrO₂ nanoparticles and ATO supported IrO₂ nanoparticles were dispersed in 1:1 (v/v) H₂O to isopropanol and drop-casted onto conducting FTO glass or Au-coated QCM sensors (14 mm, 5 and 10 MHz AT-cut Cr/Au crystals from KGV QUARTZ CRYSTAL TECHNOLOGY GmbH and QUARTZ PRO AB). Electrodes were masked with PTFE tape to leave a circular electrode area of 0.196 and 0.126 cm², respectively. Prior to each measurement, the samples were either dried at 60 °C or calcined at 375 °C in air. The frequency of uncoated and coated QCM sensor crystals was determined with a QCM200 5 MHz measurement system (STANFORD RESEARCH SYSTEMS INC.) and an openQCM 5/10 MHz AT-cut crystals, respectively. Mass loadings on QCM chips were calculated according to the Sauerbrey equation[54] from determined frequency differences δf, an overlapping electrode area A of 0.196 cm² and a sensitivity factor G of 56.6 and 4.4 Hz µg⁻¹ cm² for 5 and 10 MHz AT-cut crystals, respectively.

All electrochemical measurements at room temperature were carried out in a three-electrode setup with a quartz cell filled with 20 ml 0.5 M H₂SO₄ (SIGMA-ALDRICH, Titirup volumetric standard) as electrolyte using an PGSTAT302N potentiostat/galvanostat (METROHM AUTOLAB B.V.) equipped with a FRA32 M impedance analyzer (METROHM AUTOLAB B.V.) and an in-house constructed glass/silicone cell with Luggin-capillary for the reference electrode compartment. Electrolyte temperature of 60 °C was maintained by an oil bath with external stirrer and monitored with an immersed silicone coated K-element temperature sensor. The Nernst potential for water oxidation was kept constant by continuous O₂ (AIR LIQUIDE, AlphaCaz 2 N Purity) purging of the electrolyte (0.5 M H₂SO₄, SIGMA-ALDRICH, Titirup volumetric standard). Catalyst loadings of 50 µg cm⁻² (10 µg polished per disc) were drop-casted on cleaned glassy carbon discs and dried at 60 °C before applying 10 µL of a 1:100 dilution of a Nafion perfluorinated resin solution (SIGMA-ALDRICH, 5 wt% in lower aliphatic alcohols and water (15–20% water)) in a H₂O/PrOH mixture (1:1 v/v).

The electrolyte resistance was determined before and after each RDE measurement in the high frequency region of recorded impedance spectra at 0.5 V versus RHE. Due to low current densities reached in the measurement protocol and repeatedly low electrolyte resistance values around 5 Ω, an iR drop correction of the recorded data was not performed. The applied measurement protocol consisted of 75 LSV cycles starting from 1.0 V versus RHE. The upper vertex potential was defined to be at a current density of j = 1 mA cm⁻² (iabs = 0.2 mA, A = 0.196 cm²). Reported current densities were determined from the mean value of capacity current (mean value in potential region 1.0–1.23 V vs RHE) corrected anodic and cathode scans for a given overpotential nOER of the respective scan cycle. Extracted overpotentials nOER for each cycle required to reach an OER current of 1 mA cm⁻² were corrected for the capacitive current and calculated as a mean of anodic and cathodic scan.

Additional cyclic voltammetry measurements over the potential range of 0.05–1.52 V versus RHE were performed during RDE measurements to identify redox active features and to compare the electrocatalytically active surface area of catalyst samples. 3 cyclic voltammograms at a scan rate of 50 mV s⁻¹ were therefore recorded prior to each RDE measurement (as described above), after 50 and after 75 RDE LSV cycles.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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