Supported metal oxide nanoparticle electrocatalysts: How immobilization affects catalytic performance

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1. Introduction

The sluggish kinetics of the oxygen evolution reaction (OER) is associated with high overpotential and remain a critical challenge for commercialization of H2 as an energy carrier [1–3]. Although great improvements have been made over the last decades with respect to improved activity and insight into interactions between the catalyst surface and reaction intermediates, there is still need for optimization and a more profound understanding of the influence of the support material [4]. Catalyst supports are known to increase the overall catalytic performance and to yield high mass-based activities due to im-
proved catalyst dispersion, electrolyte accessibility and better conductivity [5]. Nonetheless, different types of catalysts such as metals and metal oxides interact differently with the support, and therefore need to be processed differently to achieve the desired loading and to avoid agglomeration. This is crucial to reach optimal catalytic performance. Extensive research on this topic has been done for noble metal nanoparticles on carbonaceous materials [6–8], while investigations on metal oxides have been neglected with very few exceptions [9–11]. Carbon-based materials have been widely applied as catalyst supports for the oxygen evolution reaction (OER) as well as the oxygen reduction reaction (ORR) due to their low costs, and comparably high surface area [12–18]. Some of the established techniques for the immobilization of metal and metal oxide nanoparticles on a support material are liquid precursor impregnation, more specifically, incipient wetness impreg-
nation using a precursor salt and subsequent processing [7,12,16], chemical-and physical-vapour-deposition [19,20], or electrodeposition [21–23]. Each catalyst dispersion technique results in a distinct nano-
particle (NP) distribution, which influences the measured catalytic activity. For the investigation and application of complex metal oxide nanomaterials, it is highly desirable to be able to separate the synthesis step of the active component from the step where the active component is put on the support while retaining high reproducibility and accessibility. Thereby the benefits of control over material properties such as size, shape and crystal structure can be combined with the full utilization of the carbon support, and avoiding unwanted influences of the support material on these properties such as reduced electro-
catalytically active area.

Herein we present a concise systematic study of how and why dif-
ferent support methods result in distinct particle distributions on a high surface area support. Mn3O4 and Vulcan XC-72R serve as model catalyst and support, respectively. We use a combination of transmission electron microscopy (TEM), inductively coupled plasma - optical emission spectroscopy (ICP-OES), and standard electrochemical characterization to compare and contrast three support procedures with respect to the metal loading, particle distribution, and catalytic activity towards the
To investigate how the chemical immobilization of metal oxide nanoparticles (NPs) on a catalyst support affects the catalytic performance, MnOx NP catalysts were supported on Vulcan XC-72R carbon using three different support protocols, i) a “one-pot” synthesis, ii) a rapid-mixing RM-method, and iii) a “slow-mixing” SM-method, as detailed in the experimental section and shown in Fig. 1. The final metal weight loadings of the individual catalysts on the supports resulting from a nominal target loading of 50 wt.% in all cases are reported in separator for impedance. A catalyst film was drop-casted on the working electrode by following procedure. Catalyst inks were prepared by dispersion of 3–6 mg of catalyst powder in a mixture of 0.796 equivalents Milli-Q water, 0.2 equivalents isopropanol, and 0.004 equivalents Nafion, wherein the equivalents are percentages with respect to the mass of the weighted catalyst. The inks were sonicated for 15 min using a horn-sonifier with constant cooling using an ice water bath. A volume of 10 μL of the resulting ink dispersions were pipetted onto polished glassy carbon (GC) electrodes with a diameter of 5 mm (Pine Instruments). The electrodes were polished using 2 μm followed by 0.05 μm silica polishing solutions (Buehler). The electrodes were rinsed for 5 min with Milli-Q water, acetone, and Milli-Q in a sonication bath. After drop-casting of the catalyst, the GC electrodes were dried for 10 min at 50°C in air to form a thin film of catalyst.

Transmission Electron microscopy (TEM) was performed using a FEI Tecnai G2 20 S-TWIN with LaB6 cathode, 200 kV accelerating voltage, and resolution limit of 0.24 nm. For preparation, the catalyst suspension was deposited onto a lacey carbon coated Cu TEM grids (300 mesh) and dried in air. The microscope was equipped with an energy-dispersive x-ray spectroscopy (EDX) unit and an EDAX r-TEM SUTW detector.

3. Results and discussion

To investigate how the chemical immobilization of metal oxide nanoparticles (NPs) on a catalyst support affects the catalytic performance, MnOx NP catalysts were supported on Vulcan XC-72R carbon using three different support protocols, i) a “one-pot” synthesis, ii) a rapid-mixing RM-method, and iii) a “slow-mixing” SM-method, as detailed in the experimental section and shown in Fig. 1. The final metal weight loadings of the individual catalysts on the supports resulting from a nominal target loading of 50 wt.% in all cases are reported in
Fig. 2. Metal loadings of Mn$_3$O$_4$ oxide NPs supported on Vulcan XC-72 r according to “one-pot” synthesis, RM (rapid-mixing) method, and SM (slow-mixing) method. The error bars show the standard deviation of repetitive measurements. The target loadings were ~50 wt. % for all methods.

As indicated by the error bars, the “one-pot” synthesis where the NPs were nucleated on the carbon support during synthesis, were quite reproducible, yet resulted in a lower loading, close to 7.5%, in comparison to the RM-method and SM-method, for which the NPs were loaded on the support after their synthesis. In contrast, the rapid-mixing method II RM) resulted in a large variation of NP loadings, showing the lack of control over the final loading using this supporting approach. The slow-mixing (SM-method) gave the most reproducible results with a final loading of 20 wt. %. In all cases, the final catalyst weight loadings were half or less of the target loading. Thus, data suggest that supporting the Mn$_3$O$_4$ NPs as pre-formed particles yields in higher weight loadings compared to the “one-pot” synthesis approach. In order to evaluate activity-relevant parameters such as mean particle size and the nanoparticle morphology distribution on the support for the three different support methods, we conducted transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX). Fig. 3 displays TEM micrographs of representative areas for the respective support methods. The EDX measurements confirmed that no other metals than manganese were present in the samples (see SI Fig.S3). In the samples prepared with the “one-pot” synthesis, large rectangular shaped NPs with a diameter of several hundred nm are visible, as well as smaller spherical particles with a diameter of ~17 nm (Fig. 3a, b). The large particles are another reasonable explanation for the low final metal loading obtained in the “one-pot” synthesis. Large particles have a smaller relative contact area with the support compared to smaller particles and are more likely to be partially washed out during the cleaning procedures.

This suggests that small nanoparticles are more likely to be dispersed in high final weight loadings. The reason for larger particles on the carbon support observed in the “one-pot” synthesis may possibly be due to an early-stage nucleation of the oxide NPs when the carbon support is present in the reaction, owing to the fact that longer reaction times may result in larger nanoparticles. Another possibility are ripening effects on the support during synthesis. This would however need further investigations to clarify. We speculate that the smaller particles present in the “one-pot” support method (see Fig. 3a, b) initially nucleated independent of the carbon support.

The samples prepared with the RM-method have a poor particle distribution with large areas showing significant agglomeration of NPs, as well as areas with very low NP coverage (Fig. 3c, d). The NPs are spherical with an average diameter of 6.2 nm and a narrow size distribution. The sample prepared with the SM-method show a uniform distribution of metal oxide NPs (Fig. 3e, f) with only few areas of agglomerated NPs similar to those predominant in the samples prepared with the RM-method. The size and shape of the NPs supported using the SM-method were nearly identical to the particles prepared by the RM-method, as expected the NPs were synthesized prior to deposition. Thus we find that the SM-method is the only viable support approach that results in a low degree of particle agglomeration or areas with low coverage of metal oxide NPs. This shows that slow addition of the particles to dispersed carbon support is important to obtain optimal and uniform NP distribution. We can attribute this to the slower interaction at higher dilution, where the particles are more likely to attach to the support and not to a nearby NP upon a change in the surrounding solvent.

To optimize the SM-support procedure even further, we explored the effect of the duration of the mixing step at different target loadings. The results are presented in Fig. 4. The dashed line through the origin represents the trend for complete immobilization of the inserted metal oxide NPs on the support (100% support yield). The final loadings were obtained from ICP-OES measurements.

The duration of the mixing step has a larger influence at low catalyst loadings, at which the loadings approaches the target loadings. However, a mixing time of 30 min was required to reach 100% support yield. At target loadings above 20 wt. %, saturation behavior is limiting the final loadings to a value close to 20 wt. %, hence after 30 min and 60 min agitation time the final loadings converge. Except for low loadings (~10 wt. %) the final metal loadings do not reach the target loadings, which shows incomplete support of the oxide NPs.

From the electrochemical characterization procedure described in the experimental section above, the metal loadings are correlated with mass-based activities for the oxygen evolution reaction (OER). The OER activities evaluated at different loadings are presented in Fig. 5. All activities were calculated with respect to the total mass of metal on the carbon support. The iR-corrected OER activities (current densities) were extracted from CVs recorded at a slow scan-rate (6 mV/s) at a potential of 1.63 V vs. RHE. The metal-free Vulcan support was measured as a control sample, however showed negligible activities, confirming that the observed activity resulted from the Mn$_3$O$_4$ NPs. The corresponding voltammograms are displayed in Fig. S4.

The "one-pot" synthesis samples were in a very small loading range between 7% and 9 wt.%. Higher loadings were not achieved using this method, independent of the initial target loading. The catalysts prepared by this method showed significantly varying activities, which can be attributed to the broad range in particle size and the ratio of smaller particles to those of several hundred nm diameter. Therefore, the number of accessible surface sites varies. The samples prepared with the "one-pot" synthesis showed lowest as well as an intermediate OER activity when compared with the RM-and SM-method. The SM-method showed highest activity at comparable loadings. This is consistent with the TEM images where we noted that large and/or agglomerated particles in general were associated with a lower catalytic performance. Samples prepared using the RM-method were in line with these arguments and showed a decrease in activity with increased final loadings (from 5 to 20 wt. %). For the samples prepared with the SM-method, we observed a similar decrease in mass-based activity with increased metal loadings, however with significantly higher activities for all investigated target loadings.

We confirmed a linear trend of increased mass-based activity with lower metal loadings within the range of investigated loadings. This clearly evidences that the OER activity is highly sensitive to the metal loading on the support. Higher loadings apparently result in lower mass-based activities if particles are not distributed in an optimal way on the support.

A loading of 20 wt.% is a common target loading in electrocatalytic applications [14], whereas according to our results the most optimal loading with respect to activity is closer to ~10 wt. %. It is favourable for the catalytic activity to have fewer particles deposited on the carbon support (lower loadings) mainly because of the consequential lower amount of agglomerated particles. Immobilization of NPs on the
support, which are isolated from other particles generally results in higher accessible surface area, and according to our study, this correlates to a higher overall catalytic OER activity. This is why the activity is superior using the slow-mixing (SM-method) in comparison to rapid mixing (RM-method). Considering the TEM images, for the support methods “one-pot” and RM-method, this trend is accompanied with respectively the formation of large particles or very agglomerates immobilization.

In conclusion, the comparability by normalization to electrochemical surface area (ECSA) is not feasible for high surface support materials. In order to evaluate the mass activity of these immobilized materials amongst different studies, a harmonized, reproducible supporting procedure, is crucial. Our study shows that precise control over the loadings of the catalytically active component on the support is an absolute necessity to accurately assess and compare catalytic activities amongst supported metal oxide nanoparticles, and we demonstrate simple guidelines how to gain this control.

Fig. 3. Bright-Field TEM micrographs of representative areas for samples prepared via the “one-pot” synthesis (a, b; 8 wt. %), RM-method (c, d; 23 wt. %) and SM-method (e, f; 19 wt. %).
loadings. Lower metal loadings (around 10 wt. %) generally resulted in higher mass-based OER activities. We demonstrated that control over the support of the metal oxide NPs can be introduced by carefully selecting the support method and is crucial to tune the catalytic performance of the metal oxide NP catalysts.

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Declarations of interest

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Appendix A. Supplementary data

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References