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HfN nanoparticles: an Unexplored Catalyst for the Electrocatalytic Oxygen Evolution Reaction

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Abstract: Water electrolysis is one of the most promising methods to produce H₂ and O₂ as high potential fuels. Comparing the two half-reactions, the Oxygen Evolution Reaction (OER) is the more difficult to be optimized and still relies on expensive noble-metal based catalysts such as Ru or Ir. In this paper, we prepared nanoparticles of HfN and Hf₂ONx and tested them for the OER for the first time. The HfN sample, in particular, showed the highest activity, requiring an overpotential of only 358 mV at 10 mA/cm² in Fe-free electrolyte and, above all, exhibiting long-term stability. This result places this system amongst one of the most promising catalysts for OER tested to date, in terms of sustainability, activity and stability. The prepared nanoparticles are small (less than 15 nm in diameter), well-defined in shape and crystalline, and were characterised before and after electrochemical testing also via electron microscopy (EM), Powder X-rays diffraction (PXRD) and X-rays photoelectron-spectroscopy (XPS).

Introduction

Energy production is fundamental to modern society, which relies on it to survive and develop. Current energy production almost entirely relies on burning fossil fuels, which are no longer a sustainable solution. Among reliable alternatives, the production of high potential combustibles (such as H₂) via electrolysis of water (Scheme 1) is one of the most promising methods.

\[ 2\text{H}_2\text{O}(\text{l}) \rightarrow \frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}_2(\text{g}) \]

Scheme 1. The two half-reactions for the water-splitting: H₂ is produced at the cathode (HER) and O₂ at the anode (OER). To ensure an efficient conversion, the process of water splitting requires the use of suitable catalysts, which are, to date, mainly based on noble metals (Pt for HER and IrO₂, or RuO₂ for OER[1-2]), because they offer a lower overpotential (n) compared to other materials and fast kinetics for driving the reaction. While Pt shows ideal activity for HER (close to zero overpotential in acidic conditions), there are no other catalysts that can catalyze OER at such low overpotentials. For example, even the most commonly employed RuO₂ and IrO₂ catalysts perform at overpotentials of a few hundred millivolts[3]. In this respect, OER is more difficult to be optimized compared with HER and despite extensive research, the overpotentials required to sustainably drive the OER are still very high. This has wide reaching implications considering that OER finds broader applications, e.g. in fuel cells and batteries[4]. One fundamental step to be considered for a sustainable and large-scale production of hydrogen from water splitting, besides optimising catalytic activity, is to explore readily available and cost-effective catalysts. Stability is also a key prerequisite and the ideal catalyst must be resistant under the reaction conditions, i.e. it should not undergo passivation or deactivation, and must possess high surface area, conductivity and homogeneity, to ensure an efficient electron transport.

With this aim, several classes of materials based on non-noble metals have been explored, including their alloys (e.g. Ni-Mo)[5,6], oxides and chlorocenogenes[7-9], and in very few cases metal carbides (MC) and nitrides (MN). Among these compounds, MN possess the highest electronic conductivity and stability under harsh conditions[10]. MN, as well as MC, are part of the family of metal nitrides and possess high thermal and chemical resistance, good mechanical properties and high melting point, alongside metallic behaviour (e.g. good electronic conductivity) and obviously catalytic activity. The catalytic activity of some metal nitrides is similar to that of some noble metals[11] and some of them were found to be active not only for HER (e.g. Mo₂C[12], Mo₂N[13] and Co₉N[14]) or OER (e.g. Ni₅N and Fe₅N[15-18], Co₉N[11] and Mn₃N₂[16]), but also for the reverse electrochemical processes such as oxygen reduction reaction (ORR), the cathode reaction in the fuel cells[17-18]. In some cases, however, the material is unstable or the synthesis requires toxic ammonia flow, hindering the production on a large scale. Among metal nitrides, Hf-based nitrides are one of the less explored in catalysis and electrocatalysis. So far, only HfON has been tested with promising results towards ORR[19,20] and HER[21], but not in OER. To the best of our knowledge, no studies on hafnium nitride (HfN) have been reported. This is surprising considering that HfN is also a metallic ceramic with high melting point (>3300°C) and low electrical resistivity (27 μΩ·cm)[22]. Furthermore, it is expected to have chemical and physical properties similar to Zr-based materials, which was recently addressed as a high performing electro-catalyst from theoretical studies[23]. In addition, Hf is readily available and more abundant than Ru and Ir. For example, the price of Hf in 2010 was $563 per kilogram[24], while Ru was $8500 per kilogram and Ir is $47500 per kilogram[25]. One of the
reasons behind the lack of studies for HfN might be related to the synthetic challenge related to its nanoparticles preparation. In fact, only works on HfN films (using CVD and ALD) are known[25] and no reports have been published on the formation of nanoparticles or nanofibers. Although useful for film preparation, neither ALD nor CVD allows large-scale productions. In this contribution, we present a sustainable synthesis of both HfN and Hf₂ON₂ nanoparticles and related application for the OER. The sol-gel based procedure used (known as Urea-Glass-Route, UGR)[26,27] allows the easy preparation of both the metal oxynitride (Hf₂ON₂) and the pure nitride phase (HfN) in form of well-defined and small particles (15 and 10 nm for Hf₂ON₂ and HfN, respectively), with relatively high surface area (>40 m²/g). The change in composition is accompanied by a reduction of particles size, while reaction conditions (such as temperature and metal/urea molar ratio, R) have a significant effect on the morphology of the final material. Electrochemical tests have shown significantly improved performance using HfN over Hf₂ON₂ and HfO₂ with an overpotential of 391 mV at 10 mA/cm² and a Tafel slope of 94 mV/dec in Fe-free 1M NaOH electrolyte. Long-term chronopotentiometry tests (up to 24h) evidence good stability of the catalyst. These results place HfN amongst the best OER noble metal-free and iron contamination-free electro-catalysts tested so far. To the best of our knowledge, this is the first time that HfN and Hf₂ON₂ were prepared at the nanoscale and tested for OER.

Results and Discussion

Phase attribution on all prepared samples was ascertained by XRD analysis. Figure 1 shows the XRD patterns of samples prepared at different ratios and heat treatments. The pattern nicely matches that of expected Hf₂ON₂ for samples prepared with a urea/metal molar ratio R=3, and HfN for samples prepared with ratios R>10. This difference in composition is also reflected by a difference in colour (as shown in the experimental part): light grey for the oxy-nitride phase and darker grey for the nitride.

The possibility to address the synthesis to metal nitride over the metal oxynitride phase by changing R and/or reaction temperature is a peculiarity of the UGR and was also observed for other systems[28,29]. The reaction temperature not only affects the crystallinity of the final material but also the purity. For samples treated at T=900°C, traces of HfN can be observed in the Hf₂ON₂ phase, and vice versa, while a higher reaction temperature (T=1200°C) leads to pure HfN. The absence of the main graphitic peak from XRD pattern (expected around 26 degrees[30]) confirms the amorphous nature of the residual carbon observed from elemental analysis (Table 1). In all cases this was not found to be detrimental for the electrochemical performance of the active Hf-based material. The results of elemental analysis reported in Table 1 also show a slight nitrogen deficiency in the HfN samples (wt %<6%), compared to the theoretical value (7.23%) while the C% could be due to the formation of amorphous carbon during the synthesis, as previously observed when using the UGR[26]. The crystallite size as obtained via Debye-Scherrer analysis shows smaller size for HfN nanoparticles and results are reported in Table 1.

Table 1. Experimental details of some representative samples obtained by varying R and heating at different temperatures under nitrogen flow. Values of nominal diameter, as well as Elemental Analysis (EA) data and surface area are reported.

<table>
<thead>
<tr>
<th>Name</th>
<th>Main Phase (side product)</th>
<th>Nominal diameter [nm]</th>
<th>EA [wt %]</th>
<th>Surface area [m²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf R=3 900°C</td>
<td>Hf₂ON₂</td>
<td>46</td>
<td>7.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Hf R=10 900°C</td>
<td>HfN (Hf₂ON₂)</td>
<td>-</td>
<td>5.6</td>
<td>14.2</td>
</tr>
<tr>
<td>Hf R=16 900°C</td>
<td>HfN</td>
<td>20</td>
<td>5.8</td>
<td>21.2</td>
</tr>
<tr>
<td>Hf R=3 1200°C</td>
<td>Hf₂ON₂</td>
<td>69</td>
<td>5.7</td>
<td>3.8</td>
</tr>
<tr>
<td>Hf R=10 1200°C</td>
<td>HfN (Hf₂ON₂)</td>
<td>-</td>
<td>4.8</td>
<td>17.4</td>
</tr>
<tr>
<td>Hf R=16 1200°C</td>
<td>HfN</td>
<td>25</td>
<td>4.6</td>
<td>26.0</td>
</tr>
</tbody>
</table>

Crystal structures of HfN, Hf₂ON₂ and HfO₂ are reported in figure 2 (HfN is cubic, with unit cell parameter of 4.5120 Å, Hf₂ON₂ has unit cell parameter of 10.0634 Å[31]).

![Figure 1. XRD patterns of samples prepared with different molar ratios (R=3, 10 and 16) and treated at 900°C (left) and 1200°C (right), respectively. The reference pattern of Hf₂ON₂ (ICDD: 00-050-1171, red vertical lines) and HfN (ICDD: 03-065-5056, dashed black lines) are also reported for comparison.](image-url)
To investigate the sample’s morphology, larger scale homogeneity and particle dimensions, SEM and TEM analysis were performed. SEM images of Hf$_2$ON$_2$ prepared with an initial ratio R=3 and treated at 900°C show clusters of uniform size and cube-like shape (Figure 3.A). The "edged" nature of the particles was also shown in some TEM images, where hexagonal shape nanoparticles are occasionally observed (highlighted in red in Figure 3.B). According to TEM, together with smaller nanoparticles (10-20 nm in diameter), clusters of bigger particles (50-60 nm) were also observed. TEM analysis confirmed the smaller size of the HfN nanoparticles over the Hf$_2$ON$_2$ ones (Figure 3.B-D and Figure SI.1) while SEM images of the same sample (Figure 3.C), display a needle-like shape, where nanoparticles seem to growth alongside a preferential orientation (2D structure).

A closer examination of the TEM results performed on the same sample (Figure 3.D) evidenced the presence of small, core-shell interconnected nanoparticles. Overall, it can be concluded that the reaction conditions not only influence the final composition, but also the size and morphology of the final material. To further explore this point, additional samples were prepared with intermediate ratios, for which the TEM and SEM analysis were performed. From R=10 till R=16 the nanoparticles shape transforms from needle-like (R=10) to rod-plate like (R=12) to a layered structure for higher R (R=16) as shown in Figure 4. From this figure, it can be also observed that the 2D structure, with the preferential growth direction, is completely lost for R=16, as also confirmed by TEM (Figure 5.A). An HR-TEM study also reveals a core-shell nature of the particles synthesised at 1200°C with R=16 (Figure 5.B), where the crystalline core shows the (1-11) and (200) lattice planes for HfN (Figure 5.C) while the shell is amorphous. It must be noted that the shell is not observed for R<10 or lower reaction temperature (T<900°C).

XPS confirmed that the surface layer was oxygen-rich, which may be left after the conversion of the oxy-nitride phase in to the nitride one. The surface elemental composition (in wt.%) is reported in Table 2, while a comparison of XPS spectra bands for the Hf 4f, N 1s, C 1s and O 1s regions for each of the samples is shown in Figure 6. The fitted spectra, survey scans and peak assignment tables are shown in the supporting information (Figure SI.2-6 and Table SI.1-4).

Table 2. Elemental composition from XPS in wt.% for the samples HfO$_2$, HfN and Hf$_2$ON$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>O 1s</th>
<th>N 1s</th>
<th>Hf 4f</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfO$_2$</td>
<td>16.88</td>
<td>2.23</td>
<td>45.9</td>
</tr>
<tr>
<td>Hf$_2$ON$_2$</td>
<td>14.95</td>
<td>4.04</td>
<td>48.61</td>
</tr>
<tr>
<td>HfN</td>
<td>9.05</td>
<td>2.79</td>
<td>14.76</td>
</tr>
</tbody>
</table>
HfO$_2$ was confirmed from photoelectron peaks at 16.35 and 16.88 eV (Hf 4f7/2) agreeing well with previous characterisation results$^{[22]}$. Lattice oxygen was also confirmed at 530.29 eV (O 1s spectra)$^{[22]}$. A more reduced Hf species was observed in the oxynitride sample, with peaks at 14.66 and 16.01 eV corresponding to Hf-N and Hf-O respectively$^{[33,34]}$. The formation of the oxynitride phase was further established from the analysis of the core level N 1s spectra, where peaks in the 395-397 eV region were observed, corresponding to new Hf-N bonds$^{[33,34]}$. The HfN sample also showed oxidized Hf 4f7/2 (16.65 eV) and N 1s at 401.34 eV, with the peak at 398.73 eV assigned to the overlap of the Hf 4p plasmon. This is consistent with the oxygen-rich outer shell of the nanoparticles, as observed by TEM on samples prepared with higher urea/metal molar ratio (R). However, following etching of the sample under argon ion bombardment, the carbonaceous species was removed, and a new peak at 396.80 eV was deconvoluted, corresponding to Hf-N$^{[33,34]}$. The binding energy of the Hf 4f peak also shifted from 16.65 eV to 15.59 eV, further signifying the reduced Hf-N species$^{[33,34]}$.

**Electrochemical testing.** The electrocatalytic performance was examined for both Hf$_2$ON$_2$ and HfN. Commercial HfO$_2$ and RuO$_2$ were also tested to compare the OER activity. The OER activity in Fe-free electrolyte was initially tested in order to avoid iron contaminations on the working electrode, which would affect the results. This is a very important point to be considered, since it was reported that even small impurities of iron have an enormous effect on the OER activity of the catalysts$^{[36]}$. In fact, a plethora of OER catalysts reported so far are tested in non-purified electrolytes containing traces of Fe impurities but this does not allow to determine the actual catalytic activity of the material under investigation. Initially, the samples were deposited on glassy carbon electrodes to measure the intrinsic OER activities. CVs were repeated until a reproducible voltammogram was obtained. In addition, commercial RuO$_2$, a benchmark catalyst for OER$^{[40]}$, was used to compare the activity of our catalysts. The overpotential needed to achieve 10 mA/cm$^2$ current density was used as a parameter to compare different catalysts studied, herein. As shown in figure 8A, RuO$_2$ requires, as expected, lowest overpotential (321 mV) to achieve 10 mA/cm$^2$ catalytic current, followed by HfN (504 mV), HfO$_2$ (497.7 mV at 1 mA/cm$^2$) and Hf$_2$ON$_2$ (577 mV at 8 mA/cm$^2$). The overpotential values are in line with those observed for widely studied Ni(OH)$_2$ catalyst measured in Fe-free electrolytes$^{[36]}$. The lower overpotential of HfN compared to Hf$_2$ON$_2$ and HfO$_2$ can be attributed to better electrical conductivity of HfN$^{[22]}$, which results in efficient charge transport. Tafel analysis was performed to gain insights on the mechanism underlying OER on our catalysts (figure 8B). The Tafel slope values are summarized in Table 3 which lie in the range of 130-300 mV/dec range for HfN and Hf$_2$ON$_2$ while a value of 385 mV/dec was obtained for HfO$_2$. Next, we proceeded to measure the OER activity of our catalysts in normal commercially available NaOH electrolyte, which contains traces of Fe impurities, as this would be the obvious electrolyte of choice for commercial alkaline electrolyseres. Figure 8C reports the CVs of the catalysts measured in 1M NaOH electrolyte (non-purified). As can be seen, the OER current densities increased substantially for HfN and Hf$_2$ON$_2$, while HfO$_2$ showed similar activity. The Tafel plots are reported in figure 8D and the slope values reported in table 4 indicate improved OER kinetics over HfN in the normal electrolyte. This is in line with the improvement observed for previously studied Ni(OH)$_2$ catalysts$^{[36]}$.
orders of magnitude lower than that of HfN, indicating lower ECSA of the former (see figure SI. 8). This, combined with the insulating nature of HfO₂, might be the cause for the lowest OER activity of HfO₂. This highlights that the catalyst having high conductivity with high ECSA is required to achieve high OER activity and that presence of Fe impurity only cannot guarantee the high OER activity.

This is further supported by our electrochemical impedance spectroscopy (EIS) measurements. Nyquist plots of the impedance data are reported in figure 9, both for the purified and normal electrolyte. All the catalysts studied herein exhibit a single semicircle, which is related to the charge transfer resistance (Rct) associated with OER process. The size of the semicircle in the low-frequency range increases from HfN-Hf₂O₂-HfO₂, indicating that OER is most favoured on HfN electrodes and least favoured on HfO₂ electrodes[38]. Furthermore, in normal electrolytes, the trend in Rct values remains the same while the values decrease considerably in all the cases as shown in Table 4. This further highlights the efficient OER over HfN in both purified and normal electrolytes.

Figure 9. Nyquist plots of HfN, Hf₂O₂ and HfO₂ at 1.72V vs RHE in A) purified 1M NaOH and B) in normal 1M NaOH.

In order to further maximize the OER catalytic activity of HfN, we deposited the catalyst ink on Ni foam, a support with uniform three-dimensional network, high surface area and good electron transport[29]. As can be seen from the polarization curves reported in Figure 10, OER currents improved significantly in both purified and normal electrolytes. The HfN-NF catalyst achieves 10 mA/cm² of OER current at an overpotential of only 391 mV in purified electrolyte, while in the normal electrolyte this value further improves to 358 mV. The Tafel slope values also improve in both cases indicating better kinetics of OER on HfN on porous 3D NF substrate. The overpotential values obtained here are comparable to those of the widely studied Ni and Co-based catalysts and could be further improved by increasing ECSA of the HfN catalyst[37]. A comparison of the overpotential and Tafel slope values for the tested HfN with other nitrides-based catalysts reported in literature and tested in similar conditions is reported in figure SI.6.

Table 3. Over potential, Tafel slope and average Cd values for the HfN, Hf₂O₂, and HfO₂ catalysts, tested with different supports both in the normal and in the purified electrolyte.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Over potential (mV) at 10 mA/cm²</th>
<th>Tafel slope (mV/dec)</th>
<th>Average C_d (mF/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfN (GC) purified electrolyte</td>
<td>504 mV</td>
<td>295</td>
<td>0.0013</td>
</tr>
<tr>
<td>HfN (GC) normal electrolyte</td>
<td>436 mV</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>Hf₂O₂ (GC) purified electrolyte</td>
<td>577 mV (at 8mA/cm²)</td>
<td>139</td>
<td>0.0014</td>
</tr>
<tr>
<td>Hf₂O₂ (GC) normal electrolyte</td>
<td>557 mV</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>HfO₂ (GC) purified electrolyte</td>
<td>497 mV (at 1mA/cm²)</td>
<td>385</td>
<td>3.9*10⁻⁵</td>
</tr>
<tr>
<td>HfO₂ (GC) normal electrolyte</td>
<td>585 mV (at 5mA/cm²)</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>HfN (NF) purified electrolyte</td>
<td>391 mV</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>HfN (NF) normal electrolyte</td>
<td>358 mV</td>
<td>85</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Charge transfer resistance values for the HfN, Hf₂O₂, and HfO₂ catalysts, both in the normal and in 1M NaOH purified electrolyte.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rct (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Purified electrolyte</td>
</tr>
<tr>
<td>HfN</td>
<td>110</td>
</tr>
<tr>
<td>Hf₂O₂</td>
<td>505</td>
</tr>
<tr>
<td>HfO₂</td>
<td>2039</td>
</tr>
</tbody>
</table>

Finally, the stability of the HfN catalyst was measured under OER operating conditions at a constant applied current density of 10 mA/cm² for 24h as reported in figure 11. From this figure, it can be appreciated that the potential required to maintain the applied current density remains nearly constant through the 24h indicating excellent stability of our HfN catalyst.
The catalyst ink was prepared via UGR, using a mixed flow of N₂Ag/AgCl. The morphology (via TEM) and composition (via PXRD) of the HfN catalyst was examined after the stability tests. As shown in figure S1.9-11 and table S1.5, no significant changes were observed, further confirming the stability of our HfN catalyst.

Conclusions

Well-defined and small nanoparticles of HfO₂ and HfN were prepared and tested for the first time for OER. An extensive characterization was made before and after testing, using powder XRD, SEM, HR-TEM and XPS. The OER performance of HfO₂ and HfN were compared in Fe-free purified and normal electrolyte (1M NaOH), using both glassy carbon and nickel foam as supports, to determine the actual catalytic activity of the materials under investigation. HfN showed the best activity, attributed to its high electrical conductivity, favoring an efficient charge transport. The HfN catalyst achieved, 10 mA/cm² of OER current at an overpotential of only 391 mV and 358 mV in purified and normal electrolyte, respectively, with a Tafel slope of 84 and 85 mV/dec.

Experimental Section

Nanoparticles preparation. In a typical experiment, hafnium (IV) chloride (HfCl₄, VWR 98.9%)/methanol solutions (1.24M) were prepared and added with suitable amounts of urea (CO(NH)₂, Sigma Aldrich 99%) to reach a final urea/HfCl₄ molar ratio (R) from 1 to 16. Mixtures were stirred till a clear, viscous yet transparent solution was observed (Fig.12 A). The gel-like precursor was then thermally treated under N₂ flow up to 1200°C for 3 h and thereafter cooled to room temperature. The final product was a fine powder, light grey for samples treated up to 900°C (Fig.12 B) and dark grey for the ones treated up to 1200°C (Fig.12 C). For comparison, HfO₂ was also prepared via UGR, using a mixed flow of N₂ and air. The usefullness of the UGR to prepare metal oxides was also previously reported[40].

Electrochemical measurements. The prepared HfN and HfO₂ were tested for OER using IVIUM Compactstat potentiostat and their performances compared with those of commercial HfO₂ (Sigma Aldrich, 98%) and RuO₂ (Sigma Aldrich, 99.9%). The catalyst ink was prepared grounding in a mortar 2.5 mg of the powder catalyst and then adding 100 microliters of NaNO₃ solution, 0.25% in ethanol (5 wt % in lower aliphatic alcohols and 15−20% water, Sigma Aldrich). For the catalysts deposited on glassy carbon substrates, conductive carbon black was added (carbon black super P Alfa-Aesar, 99%-). The ink was ultrasonicated for 30 min and then dropcast with different loadings on different electrode support, e.g. glassy carbon (3 mm diameter) and nickel foam (Sigma Aldrich, 95%, foam), thickness 1.6 mm, bulk density 0.45g/cm³, porosity 95%) and allowed to dry at room temperature in ambient air. The loading for each catalyst was optimized to obtain maximum OER activity. The best ink loading was found to be 5 μl for HfO₂ (1.96mg/cm²), 10 μl for HfN (4.57mg/cm²) and 20 μl for HfO₂ (7.8 mg/cm²). OER measurements were conducted using a three-electrode cell set-up, using a double junction Ag/AgCl (3.8 M KCl) as a reference electrode and platinum wire as counter electrode. Cyclic voltammetry (CV) measurements were performed in 1M NaOH electrolyte (Sigma Aldrich, >98%, diluted with Milli-Q water, 18.2 mΩcm at 25°C) at room temperature in the range of 0-0.8 V (vs Ag/AgCl) with a scan rate of 5mV/second. Impedance measurements were performed in the frequency range from 0.1 Hz to 1 MHz. All data were IR-corrected using IR correction function of IVIUM software. The potentials were converted to RHE (reversible hydrogen electrode) scale by using the following formula: E_RHE=E_0^Ag/AgCl + E_Ag/AgCl + (0.059 x pH). Long-term stability measurement was conducted by chronopotentiometry at an applied current density of 10 mA/cm².
Acknowledgements

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Keywords: hafnium nitride, hafnium oxide, hafnium oxynitride, nanoparticles, nitrides, oxygen evolution reaction (OER), Urea Glass Route.

HfN nanoparticles prepared via UGR are highly active and stable electro-catalyst for the water splitting semi-reaction OER (Oxygen Evolution Reaction). The results presented place HfN amongst one of the most promising catalysts for OER tested to date, in term of sustainability, activity and stability.