Synergetic Effects of Mixed-Metal Polyoxometalates@Carbon-Based Composites as Electrocatalysts for the Oxygen Reduction and the Oxygen Evolution Reactions

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Abstract: The smart choice of polyoxometalates (POMs) and the design of POM@carbon-based composites are promising tools for producing active electrocatalysts for both the oxygen reduction (ORR) and the oxygen evolution reactions (OER). Hence, herein, we report the preparation, characterization and application of three composites based on doped, multi-walled carbon nanotubes (MWNT_N6) and three different POMs (Na12[(FeOH)2·Fe2(As2W15O56)2]·54H2O, Na12[(NiOH)2·Ni2(As2W15O56)2]·54H2O and Na14[(FeOH)2·Ni2(As2W15O56)2]·35H2O) as ORR and OER electrocatalysts in alkaline medium (pH = 13). Overall, the three POM@MWNT_N6 composites showed good ORR performance with onset potentials between 0.80 and 0.81 V vs. RHE and diffusion-limiting current densities ranging from −3.19 to −3.66 mA cm−2. Fe4@MWNT_N6 and Fe2Ni2@MWNT_N6 also showed good stability after 12 h (84% and 80% of initial current). The number of electrons transferred per O2 molecule was close to three, suggesting a mixed regime. Moreover, the Fe2Ni2@MWNT_N6 presented remarkable OER performance with an overpotential of 0.36 V vs. RHE (for j = 10 mA cm−2), a jmax close to 135 mA cm−2 and fast kinetics with a Tafel slope of 45 mV dec−1. More importantly, this electrocatalyst outperformed not only most POM@carbon-based composites reported so far but also the state-of-the-art RuO2 electrocatalyst. Thus, this work represents a step forward towards bifunctional electrocatalysts using less expensive materials.

Keywords: polyoxometalates; oxygen reduction reaction; oxygen evolution reaction; carbon nanotubes; heteroatom doping

1. Introduction

The current environmental and energy crisis has stimulated the demand for viable, sustainable and clean energy solutions for energy storage and conservation. The development of energy storage and conservation devices, such as fuel cells and water-splitting devices, aims to reduce the effects of energy demand [1,2]. The electrochemical processes that occur in these devices are the oxygen reduction reaction (ORR) at the cathode of the fuel cell and the oxygen evolution reaction (OER) at the anode of an electrolytic cell [3,4]. The fuel cell generates energy from O2 and H2, yielding water as a clean by-product, and the electrolytic cell uses electricity to split water into H2 (fuel) and O2 [5,6].

For the ORR, the most active electrocatalysts (ECs) so far are based on noble metals, such as Pt, and, for the OER, the most effective ECs are IrO2 and RuO2. However, these materials have some disadvantages, such as high cost, low abundance and intolerance to fuel crossover (methanol and CO). Besides, these materials do not work in both reactions; for
example, platinum-based materials have poor electrocatalytic activity for the OER because Pt oxidizes easily at large overpotentials [7–9]. So, these limitations and disadvantages have encouraged the growing search for new, more stable and economically viable alternatives. Therefore, possible alternatives to current electrocatalysts include carbon materials (CMs), polyoxometalates (POMs) and their corresponding hybrid materials POMs@CMs.

There are many types of carbon materials, including graphene and carbon nanotubes. These materials have advantages such as a high specific surface area, a symmetrical pore size and structure and a high electric conductivity [10,11], but their electrocatalytic activity may still be improved by doping with different heteroatoms such as nitrogen. The incorporation of nitrogen into the sp² carbon allows the tuning of the electronic properties of pristine carbon materials, giving rise to increased electrochemical performances and catalytic activities [12–14], improved tolerance to fuel crossover and higher versatility for a wide range of reactions [9]. The advantage of having electrocatalysts with high surface area and mesoporosity is that they can facilitate the adsorption of oxygen and, therefore, accelerate the surface reaction [15]. So, these advantages make carbon materials promising candidates for the ORR [12,16–22] and the OER [23–28].

Polyoxometalates, due to their high versatility, have potential applications in diverse areas ranging from catalysis, electroanalytical chemistry and materials science [29]. POMs are metal-oxo anionic clusters, the chemical properties of which can be controlled by transition metal substitution and the counter cation used [30]. They are ideal candidates for electrocatalysis because of their chemical properties, which can be adjusted as required by choosing the appropriate elements [31]. Undoubtedly, one of their most important properties is their ability to undergo reversible multivalent reductions/oxidations, leading to the formation of mixed valence species, which enable them with favorable electrocatalytic properties in relation to other electrochemical processes [32,33]. In recent years, the use of composites based on POMs and carbon nanomaterials as potential ECs for the ORR [34–36] and the OER [37–41] has been explored. The POMs used in this work are from the sandwich-type Dawson family and result from the reaction of a lacunary species \([X_2W_{15}O_{56}]^{12−}\) (where \(X = \text{As, P, Si, Ge, B, Al, ou Ga}\), with M (a d- or f-transition metal) to give the compound \([\text{M}_4(\text{H}_2\text{O})_2(X_2\text{W}_{15}\text{O}_{56})_2]^n^{−}\), in which the metal cluster \(\text{M}_4\text{O}_{14}(\text{H}_2\text{O})_2\) is sandwiched between two lacunary fragments (Scheme 1).

In these studies, we synthetized new composite materials based on multi-walled carbon nanotubes doped with nitrogen (MWCNT_N6) and Wells–Dawson sandwich polyoxometalates with M = Fe, Ni and both metals (Fe₂Ni₂) in order to understand the in-

![Scheme 1. Two-step formation of mixed, sandwich-type Dawson family derivatives, \([\text{M}_2\text{M'}_2(X_2\text{W}_{15}\text{O}_{56})_2]^{n−}\).](image)
fluence of the metal on the electrochemical performances towards both the ORR and the OER processes.

2. Experimental Section

2.1. Materials and Methods

Sodium acetate (99.5%, Merck, Algés, Portugal), acetic acid (100%, Merck, Algés, Portugal) and potassium hydroxide (99.99%, Sigma-Aldrich, Algés, Portugal) were used as received. Multi-walled carbon nanotubes (sample denoted as MWCNT) were commercially obtained from Nanocyl S.A., ref. 3100 MWCNT (>95% carbon purity; 9.5 nm average diameter, Sambreville, Belgium). Pt/C 20 wt% (HiSPEC® 3000, Alfa Aesar, Kandel, Germany), Nafion 117® (5 wt% in lower aliphatic alcohols and water, Aldrich, Algés, Portugal), isopropanol (99.5%, Aldrich, Algés, Portugal) and methanol (anhydrous, VWR, Amadora, Portugal) were also used directly. Ultra-pure water (18.2 MΩ cm at 25 °C, Interlab, Lisboa, Portugal) was used to prepare the solutions for materials synthesis and the electrolyte for the ORR tests. The materials prepared were characterized prior to their application through XPS and SEM/EDX, and the apparatus and the detailed methods used are described in the Supplementary Materials file.

Regarding the electrocatalytic tests, a PGSTAT 302N potentiostat (Autolab, Utrecht, The Netherlands) controlled by NOVA 2.1 was used. All details concerning the electrodes and the electrode preparation and modification are depicted in the file.

2.2. Materials Preparation

The tungstoarsenates Na$_{12}$[(FeOH)$_2$)$_2$Fe$_2$(As$_2$W$_{15}$O$_{56}$)$_2$·54H$_2$O (Fe$_4$), Na$_{12}$[(NiOH)$_2$]Ni$_2$(As$_2$W$_{15}$O$_{56}$)$_2$·54H$_2$O (Ni$_4$) and Na$_{14}$[(FeOH)$_2$]$_2$Ni$_2$(As$_2$W$_{15}$O$_{56}$)$_2$·55H$_2$O (Fe$_2$Ni$_2$) were prepared according to already described procedures [42–44].

The incorporation of nitrogen onto the pristine MWCNT was accomplished through mechanical treatment in ball-milling Retsch MM200 equipment using melamine as the precursor, followed by adequate thermal treatment under N$_2$ flow. Briefly, 0.60 g of MWCNT was mixed with 0.26 g of nitrogen using the melamine precursor, and the mixture was ball-milled for 5 h at a constant frequency of 15 vibrations s$^{-1}$. Then, the resulting material was subjected to a thermal treatment under N$_2$ flow (100 cm$^3$ min$^{-1}$) at a rate of 10 °C min$^{-1}$ until it reached 600 °C, kept at that temperature for 1 h, cooled to room temperature under nitrogen atmosphere and stored in a desiccator.

The POM@MWCNT_N6 composites were then prepared through the immobilization of the three POMs onto the previously prepared MWCNT_N6. The immobilization of the POMs was achieved as follows: a 5 mL acetate buffer solution (pH = 4.0) containing 50 mg of POM was added to a 20 mL acetate buffer solution (pH = 4.0) containing 50 mg of MWCNT_N6. The mixture was dispersed for 15 min in an ultrasonic bath and then left to stir for 2 h at 400 rpm. Afterwards, the resulting composites were filtered, washed and left to dry at 60 °C under vacuum overnight. The composites were labelled as Fe$_4$@MWCNT_N6, Ni$_4$@MWCNT_N6 and Fe$_2$Ni$_2$@MWCNT_N6.

3. Results and Discussion

3.1. Electrocatalysts Characterization

3.1.1. X-ray Photoelectron Spectroscopy

All materials were analyzed by XPS to study their composition. The surface atomic percentages of each element for all the materials are presented in Table 1.
Table 1. XPS relative surface atomic percentages for all the materials \(^a\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1s</th>
<th>O1s</th>
<th>N1s</th>
<th>Na1s</th>
<th>Fe2p</th>
<th>Ni2p</th>
<th>As3p</th>
<th>W4f</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>98.84</td>
<td>1.16</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MWCNT_N6</td>
<td>94.39</td>
<td>3.70</td>
<td>1.91</td>
<td>0.76</td>
<td>0.05</td>
<td>-</td>
<td>0.05</td>
<td>0.55</td>
</tr>
<tr>
<td>Fe(_4@MWCNT)_N6</td>
<td>90.62</td>
<td>6.76</td>
<td>1.21</td>
<td>0.76</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.55</td>
</tr>
<tr>
<td>Ni(_4@MWCNT)_N6</td>
<td>90.29</td>
<td>6.77</td>
<td>1.57</td>
<td>0.66</td>
<td>-</td>
<td>0.06</td>
<td>0.07</td>
<td>0.57</td>
</tr>
<tr>
<td>Fe(_2Ni_2@MWCNT)_N6</td>
<td>92.88</td>
<td>5.00</td>
<td>1.31</td>
<td>0.41</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>0.32</td>
</tr>
</tbody>
</table>

\(^a\) Determined by the areas of the respective bands in the high-resolution XPS spectra.

As can be seen in Table 1, the presence of nitrogen in the doped material (MWCNT_N6) was confirmed, indicating that the doping procedure was successful, and the composite materials atomic percentages also revealed that the POM was present. There was a significant oxygen percentage increase after the POM immobilization, asserting the POM presence in the composite materials. After the POM immobilization, there was also a decrease of the N1s’ atomic percentage in the composite materials. Considering that XPS is a surface technique that analyzes depths up to 10 nm, the presence of the POM at the surface of the materials may have hindered the nitrogen detection. The N1s high-resolution XPS spectra of the N-containing prepared materials are shown in Figure 1, and the relative atomic percentages of nitrogen obtained in different chemical environments are presented in Table 2. The high-resolution XPS N1s spectra of the N-containing prepared materials were deconvoluted into three main peaks and assigned to pyridinic N (≈398.9 eV), pyrrolic N (≈400.6 eV) and quaternary N (≈402.8 eV) [45–47]. For the MWCNT_N6, a fourth peak at 405.5 eV was found and attributed to nitrogen oxide and/or nitrate species [45].

Figure 1. Deconvoluted N1s high-resolution spectra of MWCNT_N6-based materials (green: pyridinic N; pink: pyrrolic N; olive: quaternary N; gray: N-oxides/nitrates).
Table 2. Relative atomic percentages of nitrogen obtained from the XPS high-resolution N1s spectra of the prepared carbon materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>% N (\approx 398.9) eV (Pyridinic N)</th>
<th>% N (\approx 400.6) eV (Pyrrolic N)</th>
<th>% N (\approx 402.8) eV (Quaternary N)</th>
<th>% N (\approx 405.5) eV (N-Oxides)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT_N6</td>
<td>49.3</td>
<td>30.9</td>
<td>10.9</td>
<td>8.9</td>
</tr>
<tr>
<td>Fe(_4)@MWCNT_N6</td>
<td>49.8</td>
<td>44.3</td>
<td>5.9</td>
<td>-</td>
</tr>
<tr>
<td>Ni(_4)@MWCNT_N6</td>
<td>45.6</td>
<td>40.2</td>
<td>14.2</td>
<td>-</td>
</tr>
<tr>
<td>Fe(_2)Ni(_2)@MWCNT_N6</td>
<td>57.0</td>
<td>36.6</td>
<td>6.4</td>
<td>-</td>
</tr>
</tbody>
</table>

The C1s high-resolution spectra of all the materials are shown in Figure S1 and were deconvoluted as follows: a main peak at 284.6 eV was assigned to sp\(^2\) C, characteristic of graphitic structures; a peak at 285.2 eV corresponded to the sp\(^3\) C hybridization; a peak at 285.9 eV was attributed to C–N; a peak at 286.9 eV was ascribed to C in C–O–C; a peak at 288.2 eV was assigned to C in C=O; a peak at 289.3 eV corresponded to C in O=C=O; and a peak at 290.7 eV was attributed to \(\pi-\pi^*\) transitions \[48\]. For the MWCNT_N6, the deconvolution of the O1s high-resolution XPS spectrum (Figure S2) was not possible, but, still, the peak at 532.7 eV had the contribution of O in the C=O, COOH and C–OH groups. On the other hand, in the O1s spectra of all POM-containing materials (Figure S2), it was possible to identify a peak at 531.1 eV, associated with O in the C=O and COOH groups, and a second peak at 533.0 eV, attributed to O in the C–OH groups \[49,50\]. The peak at lower binding energies also had the contribution of O in O=W arising from the presence of the polyoxometalate. The Fe2p high-resolution spectra of Fe\(_4\)@MWCNT_N6 and Fe\(_2\)Ni\(_2\)@MWCNT_N6 showed a peak at 710.8 eV corresponding to 2p\(^3/2\) (Figures S3 and S5). The corresponding 2p\(^1/2\) was difficult to attribute due to the low signal-to-noise ratio. The same difficulty was encountered in the deconvolution of the Ni2p spectra. Both Ni\(_4\)@MWCNT_N6 and Fe\(_2\)Ni\(_2\)@MWCNT_N6 showed a peak at \(\approx 856.5\) eV, assigned to 2p\(^3/2\) (Figures S4 and S5). All POM-containing materials also showed the presence of arsenic and tungsten, but, since As3d and W4f appeared in the same region, the percentage of arsenic was estimated from the As3p high-resolution spectra, which presented one peak at \(\approx 145\) eV. In the W4f high-resolution spectra, the peaks could be resolved as 4f\(^7/2\) and 4f\(^5/2\) doublets that appeared at \(\approx 36.0\) eV and \(\approx 38.2\) eV, respectively \[3\]. The signal of Na1s for the three POM-containing materials was due to the presence of the POM counter cations in the final compounds.

3.1.2. Scanning Electron Microscopy

The morphology of the three composites prepared was assessed by SEM. Figure 2 shows the SEM images for Fe\(_2\)Ni\(_2\)@MWCNT_N6 at two magnifications, while the corresponding images for Fe\(_4\)@MWCNT_N6 and Ni\(_4\)@MWCNT_N6 are depicted in Figure S6. The SEM images at lower magnification (\(\times 5000\)) show a roughened texture, while, under higher magnification (\(\times 50,000\)), it is possible to observe the carbon nanotubes. An EDX elemental mapping analysis (Figure 3, Figures S7 and S8) was further conducted to assess the presence and distribution of the POMs in the composites. The EDX spectra showed the presence of C and O from the carbon materials and As, W and O from the POMs. The presence of Fe was also observed for Fe\(_4\)@MWCNT_N6 (Figure S7) and Fe\(_2\)Ni\(_2\)@MWCNT_N6, and the presence of Ni was observed for Ni\(_4\)@MWCNT_N6 (Figure S8) and Fe\(_2\)Ni\(_2\)@MWCNT_N6. The elemental mapping analysis also revealed a homogeneous distribution of all the elements throughout the composites, suggesting a uniform immobilization of the polyoxometalates throughout the MWCNT_N6.
3.2. Electrochemical Performance of the Electrocatalysts towards the ORR

Initially, the ORR electrocatalytic performances of Fe$_4$@MWCNT$_6$, Ni$_4$@MWCNT$_6$ and Fe$_2$Ni$_2$@MWCNT$_6$ were assessed by cyclic voltammetry (CV) in KOH saturated with nitrogen and with oxygen. The CVs of the three prepared composites are depicted in Figure S9, where it can be clearly observed that, when oxygen is absent no peak can be
detected, whereas, in O$_2$-saturated electrolyte, all composites present an irreversible reduction peak corresponding to the reduction of oxygen at $E_{pc}$ = 0.74, 0.75 and 0.75 V vs. RHE for Fe$_4$@MWCNT$_{N6}$, Ni$_4$@MWCNT$_{N6}$ and Fe$_2$Ni$_2$@MWCNT$_{N6}$, respectively. Pt/C and MWCNT$_{N6}$ were also evaluated in the same experimental conditions, presenting the ORR peak at $E_{pc}$ = 0.86 and 0.76 V vs. RHE, respectively.

Further evaluation of the ORR electrocatalytic performances of the prepared composites was conducted by linear sweep voltammetry (LSV) in the same electrolyte saturated in both N$_2$ and O$_2$. The LSVs at 1600 rpm of MWCNT$_{N6}$, Fe$_4$@MWCNT$_{N6}$, Ni$_4$@MWCNT$_{N6}$, Fe$_2$Ni$_2$@MWCNT$_{N6}$ and Pt/C are shown in Figure 4a, and the key ORR parameters are depicted in Table 3. It is important to note that these LSVs correspond to those in O$_2$-saturated KOH after subtraction of the blanks (corresponding LSVs in N$_2$-saturated KOH). As can be observed, Fe$_4$@MWCNT$_{N6}$ and Ni$_4$@MWCNT$_{N6}$ presented practically identical diffusion-limiting current density values ($j_L = -3.19$ and $-3.20$ mA cm$^{-2}$, respectively) while, for Fe$_2$Ni$_2$@MWCNT$_{N6}$, the value increased to $j_L = -3.66$ mA cm$^{-2}$. These values are somewhat far from that obtained for Pt/C ($-4.68$ mA cm$^{-2}$); still, it is clear that the introduction of POMs produced an improvement in the $j_L$ values leading to an increase of $\approx 20\%$ for Fe$_4$@MWCNT$_{N6}$ and Ni$_4$@MWCNT$_{N6}$ and $37\%$ for Fe$_2$Ni$_2$@MWCNT$_{N6}$ when compared with the MWCNT$_{N6}$.

Figure 4. ORR LSV curves obtained in KOH (0.1 M) saturated with O$_2$ for MWCNT$_{N6}$, Fe$_4$@MWCNT$_{N6}$, Ni$_4$@MWCNT$_{N6}$, Fe$_2$Ni$_2$@MWCNT$_{N6}$ and Pt/C at 1600 rpm and 0.005 V s$^{-1}$ (a), $n_{O2}$ at several potential values (b), ORR Tafel plots (c) and chronoamperometric responses in KOH (0.1 M) saturated with O$_2$ at 1600 rpm for 43,200 s (d).
<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{\text{onset}}$ (5% Total)</th>
<th>$E_{\text{onset}}$ ($j = 0.1$ mA cm$^{-2}$)</th>
<th>$j_L$ (mA cm$^{-2}$)</th>
<th>Tafel (mV dec$^{-1}$)</th>
<th>$n_{O_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>0.91</td>
<td>0.94</td>
<td>−4.68</td>
<td>87.7</td>
<td>4.0</td>
</tr>
<tr>
<td>MWCNT_N6</td>
<td>0.81</td>
<td>0.81</td>
<td>−2.67</td>
<td>37.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Fe$_4$@MWCNT_N6</td>
<td>0.80</td>
<td>0.81</td>
<td>−3.19</td>
<td>35.4</td>
<td>2.9</td>
</tr>
<tr>
<td>Ni$_4$@MWCNT_N6</td>
<td>0.80</td>
<td>0.80</td>
<td>−3.20</td>
<td>34.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Fe$_2$Ni$_2$@MWCNT_N6</td>
<td>0.81</td>
<td>0.80</td>
<td>−3.66</td>
<td>37.9</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Even though the $E_{\text{onset}}$ can be determined by different methods [31,51,52], we assumed the potential corresponded to 5% of the diffusion-limiting current density. The values for all materials were similar (0.80–0.81 V vs. RHE), while, for Pt/C, a value of 0.91 V vs. RHE was obtained.

The number of electrons transferred per O$_2$ molecule ($n_{O_2}$) was estimated by applying the Koutecky–Levich equation to the LSVs (Figure S10) acquired at different rotation speeds (400 to 3000 rpm). Figure 4b shows the $n_{O_2}$ values vs. the applied potential, and Figure S11 shows the K–L plots. As can be observed, the values of $j^{-1}$ increased with increasing $\omega^{-1/2}$, suggesting a first-order electrocatalytic O$_2$ reduction with respect to the concentration of dissolved oxygen. Moreover, the K–L plots of the three POM@MWCNT_N6 composites prepared presented different slopes, indicating a dependency of $n_{O_2}$ on the applied potential. The mean $n_{O_2}$ value obtained for Fe$_4$@MWCNT_N6, Ni$_4$@MWCNT_N6 and Fe$_2$Ni$_2$@MWCNT_N6 was 2.9, 2.7 and 3.2, respectively, while, for Pt/C, a value of 4.0 was obtained. The ORR process, in alkaline medium, can proceed through either an indirect (2-electrons) pathway or a direct (4-electrons) one. The first involves the reduction of O$_2$ to HO$_2^-$ and then the intermediate’s reduction to H$_2$O/HO$^-$, while, in the second, O$_2$ is directly reduced to H$_2$O/HO$^-$ [31]. Therefore, the results obtained for the three POM@MWCNT_N6 composites suggest a mixed regime. Similar behavior was already reported for other POM@carbon-based materials [3]. On the other hand, Pt/C was involved in a direct process with $n_{O_2} = 4.0$.

The Tafel plots (Figure 4c) were obtained from the LSV data in Figure 4a in 0.1 M KOH saturated with O$_2$ at 1600 rpm. The Tafel slopes obtained between $E = 1.00$ and 0.76 V vs. RHE were 37.2, 35.3, 34.7, 37.9 and 87.7 mV dec$^{-1}$ for MWCNT_N6, Fe$_4$@MWCNT_N6, Ni$_4$@MWCNT_N6, Fe$_2$Ni$_2$@MWCNT_N6 and Pt/C, respectively. These values suggest that oxygen molecules were easily adsorbed and activated at the surface of these materials and that conversion of MOO$^-$ to MOOH ruled the overall reaction rate (M stands for an empty site on the electrocatalyst surface) [53].

To obtain more insights about the effect of the immobilization of different POMs on the intrinsic ORR activity, the current density values were normalized to the corresponding double-layer capacitances (Figure S12) considered as an approximation of the electrochemically active surface areas (ECSAs). By applying this correction, it was possible to discard the influence of surface areas both from the support (MWCNT_N6) and the final composite (POM@MWCNT_N6). The similar nature of the materials evaluated in this work and the number of accessible electrocatalytically active sites for a particular electrocatalyst [54]. The $C_{dl}$ values obtained were 1.4, 9.0, 9.3, 2.6 and 6.3 µF cm$^{-2}$ for MWCNT_N6, Fe$_4$@MWCNT_N6, Ni$_4$@MWCNT_N6, Fe$_2$Ni$_2$@MWCNT_N6 and Pt/C, respectively. As can be observed in Figure S12, the electroactive surface area had a significant
impact on the ORR performance. These studies suggest that the immobilization of Fe₄ and Ni₄ onto the MWCNT_N6 may not be advantageous as both these composite materials presented the lowest performance. Oppositely, the Fe₂Ni₂@MWCNT_N6 performed better than the MWCNT_N6 alone and even better than Pt/C in terms of the ŒJ values. Additionally, there was a clear synergetic effect in the Fe₂Ni₂@MWCNT_N6 as this composite had a huge increase of the ORR activity when compared with the materials containing POMs with only one type of transition metal (Fe₄@MWCNT_N6 and Ni₄@MWCNT_N6). This suggests that the presence of mixed transition metals may be the solution to improve performance.

The stability of MWCNT_N6, Fe₄@MWCNT_N6, Ni₄@MWCNT_N6, Fe₂Ni₂@MWCNT_N6 and Pt/C was also evaluated, as this is an important parameter when evaluating the performance of an electrocatalyst. This was assessed by chronoamperometry at E = 0.50 V vs. RHE for 12 h in oxygen-saturated alkaline electrolyte, and the results are depicted in Figure 4d. The Pt/C electrocatalyst showed a good stability by retaining 86% of its initial current density after 12 h. The Fe₄@MWCNT_N6 composite presented the best retaining percentage of 84%, followed by Fe₂Ni₂@MWCNT_N6 (80%), Ni₄@MWCNT_N6 (65%) and MWCNT_N6 (19%).

3.3. Electrochemical Performance of the Electrocatalysts towards the OER

The prepared electrocatalysts were also evaluated towards the OER in alkaline media, and the LSVs are depicted in Figure 5a, while the most important parameters are presented in Table 4. One of the parameters that is commonly determined to evaluate the OER electrocatalyst’s performance is the potential that is needed to reach j = 10 mA cm⁻², a value corresponding to the current density anticipated at the electrode in a solar water-splitting device (under sunlight) with an efficiency of 10% [31]. Thus, generally, the overpotential (η₁₀) at j = 10 mA cm⁻² is taken as a reference point. As observed, the three POM@MWCNT_N6 composites presented relatively low η₁₀ values of 0.58, 0.46 and 0.36 V for Fe₄@MWCNT_N6, Ni₄@MWCNT_N6 and Fe₂Ni₂@MWCNT_N6, respectively. This last composite also presented the highest current density at Eₚ = 1.86 V vs. RHE (134.6 mA cm⁻²), being much higher than the values obtained for Fe₄@MWCNT_N6 (13.7 mA cm⁻²) and Ni₄@MWCNT_N6 (30.9 mA cm⁻²). These results suggest that a possible synergetic effect occurs when the POM presents both metals (Fe and Ni). The incorporation of Fe possibly helps in activating the electrochemical processes of Ni (well-known active oxygen evolution center), leading to an enhanced electrocatalytic activity but, at the same time, improves the conductivity of the composite material.

Figure 5. LSV OER curves (a) and Tafel plots (b) of Fe₄@MWCNT_N6, Ni₄@MWCNT_N6 and Fe₂Ni₂@MWCNT_N6.
Table 4. The OER performance parameters for all the materials tested.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{10}$</th>
<th>$\eta_{10}$ ($j = 0.1 \text{ mA cm}^{-2}$)</th>
<th>$j_{\text{max}}$ (mA cm$^{-2}$)</th>
<th>Tafel (mV dec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuO$_2$</td>
<td>-</td>
<td>-</td>
<td>4.14</td>
<td>118</td>
</tr>
<tr>
<td>Fe$_4$@MWCNT_N6</td>
<td>1.81</td>
<td>0.58</td>
<td>13.2</td>
<td>102</td>
</tr>
<tr>
<td>Ni$_4$@MWCNT_N6</td>
<td>1.69</td>
<td>0.46</td>
<td>30.9</td>
<td>54</td>
</tr>
<tr>
<td>Fe$_2$Ni$_2$@MWCNT_N6</td>
<td>1.59</td>
<td>0.36</td>
<td>134.6</td>
<td>45</td>
</tr>
</tbody>
</table>

Table 4. The OER performance parameters for all the materials tested.

The Tafel slopes were determined using the LSVs from Figure 5a, and the Tafel plots are shown in Figure 5b. Fe$_2$Ni$_2$@MWCNT_N6 presented the lowest Tafel slope (45 mV dec$^{-1}$), followed by Ni$_4$@MWCNT_N6 (54 mV dec$^{-1}$) and Fe$_4$@MWCNT_N6 (102 mV dec$^{-1}$), suggesting faster kinetics for the first two composites. All these metrics are increasingly close to those collected in the bibliography (obtained under similar testing conditions) for the expensive, state-of-the-art references: RuO$_2$ with $\eta_{10} = 0.30$ V, Tafel slope = 65 mV dec$^{-1}$ and IrO$_2$ with $\eta_{10} = 0.36$ V and Tafel slope = 82 mV dec$^{-1}$ [55]. Still, we evaluated the performance of commercial RuO$_2$ under the same experimental conditions. However, our OER results were very far from those reported [56–58]. According to the literature, the preparation method has a huge influence on the OER performances of both IrO$_2$ and RuO$_2$ [57,58]. In addition, the electrocatalysts electroactive surface also has an influence on their electrocatalytic performances. Therefore, as for the ORR, the OER current densities were normalized to the corresponding double-layer capacitances (Figure S16). This correction highlights even more that Fe$_2$Ni$_2$@MWCNT_N6 was the best performing composite for the OER from all the materials tested, including the RuO$_2$. Our results with Ni$_4$@MWCNT_N6 and Fe$_4$@MWCNT_N6 are comparable with those reported in the literature (Table S1) for other POM-containing composites, but Fe$_2$Ni$_2$@MWCNT_N6 outperformed all, even the Co-containing POMs well known for their good OER activities [59–62]. Compared with other metal-oxide-containing composites, our results outperformed some [63–65], but others presented even lower overpotentials (0.28–0.32 V) [66–68].

The stability of the three electrocatalysts prepared was assessed by chronoamperometry, and the results are collected in Figure S17. All plots show the characteristic, local current density drops originated by oxygen bubble formation on the electrode surface. For the Ni$_4$@MWCNT_N6 composite, previous current density values were partially recovered with bubble release, and this electrocatalyst showed a good stability with a current retention of 87% after 12 h at a fixed potential of 0.50 V vs. RHE. For the Fe$_4$@MWCNT_N6, there was an initial increase in the current, but then it showed the typical behavior, presenting a current retention of 80%. Unfortunately, the Fe$_2$Ni$_2$@MWCNT_N6 composite presented the worst performance in terms of stability, with a current retention of 64% after the same 12 h.

4. Conclusions

Three POM@MWCNT_N6 composites based on [M$_4$(H$_2$O)$_2$(W$_{15}$O$_{56}$)$_2$]$^-$ with M$_4$ = Fe$_4$, Ni$_4$ and Fe$_2$Ni$_2$ were successfully prepared by a simple and scalable strategy without the need for linker molecules. The prepared composites showed good, intrinsic electrocatalytic activity toward the ORR, but a mixed regime was observed instead of the envisaged selectivity for the 4-electron process. Still, the Fe$_2$Ni$_2$@MWCNT_N6 showed the best performance with a $\eta_{10} = 3.2$ and a diffusion-limiting current density of $-3.66$ mA cm$^{-2}$. Additionally, Fe$_4$@MWCNT_N6 and Fe$_2$Ni$_2$@MWCNT_N6 also showed good stability.

Most importantly, Fe$_2$Ni$_2$@MWCNT_N6 presented a remarkable OER performance, outperforming most of the reported results for other composites based on POMs and carbon materials and reaching an overpotential of 0.36 V vs. RHE (for $j = 10$ mA cm$^{-2}$) and a current density of 135 mA cm$^{-2}$ at $E_p = 1.86$ V vs. RHE. Moreover, in the same experimental conditions, it surpassed the state-of-the-art RuO$_2$ electrocatalyst. Surprisingly, the results were much better than those for the composites containing POMs with just one type of
transition metal in the equatorial plane, which suggests a possible synergistic effect between the two types of metal resulting in an improvement of the electrochemical performances.

Future studies with POMs containing other transition metals will be conducted to confirm these findings but also to unravel the overall reaction mechanisms.

**Supplementary Materials:** The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/catal12040440/s1](https://www.mdpi.com/article/10.3390/catal12040440/s1). Figure S1. Deconvoluted C1s high-resolution spectra of the MWCNT_N6-based materials; Figure S2. Deconvoluted O1s high-resolution spectra of the MWCNT_N6-based materials; Figure S3. Deconvoluted high-resolution spectra for Fe4@MWCNT_N6: Na1s (a), Fe2p (b), As3p (c) and W4f (d); Figure S4. Deconvoluted high-resolution spectra for Ni4@MWCNT_N6: Na1s (a), Ni2p (b), As3p (c) and W4f (d); Figure S5. Deconvoluted high-resolution spectra for Fe2Ni2@MWCNT_N6: Na1s (a), Fe2p (b), Ni2p (c), As3p (d) and W4f (e); Figure S6. SEM images of Fe4@MWCNT_N6 and Ni4@MWCNT_N6 at ×5000 (a,b) and ×50,000 (c,d) magnification; Figure S7. SEM and EDX elemental mapping images of Fe4@MWCNT_N6 at ×2500 magnification; Figure S8. SEM and EDX elemental mapping images of Ni4@MWCNT_N6 at ×2500 magnification; Figure S9. CVs of MWCNT_N6 (a), Fe4@MWCNT_N6 (b), Ni4@MWCNT_N6 (c), Fe2Ni2@MWCNT_N6 (d) and Pt/C (e) in N2−(dash line) and O2-saturated (red line) 0.1 M KOH at 5 mV s−1; Figure S10. ORR LSVs of MWCNT_N6 (a), Fe4@MWCNT_N6 (b), Ni4@MWCNT_N6 (c), Fe2Ni2@MWCNT_N6 (d) and Pt/C (e) acquired at different rotation rates in O2-saturated 0.1 M KOH solution at 5 mV s−1; Figure S11. Koutecky–Levich (K-L) plots of MWCNT_N6 (a), Fe4@MWCNT_N6 (b), Ni4@MWCNT_N6 (c) and Fe2Ni2@MWCNT_N6 (d) in N2-saturated KOH (0.1 M); Figure S14. CVs at different scan rates of Pt/C and RuO2 in N2-saturated KOH (0.1 M); Figure S15. Current density scan rate linear fitting plots for all materials. Numeric values correspond to the double-layer capacitances (Cdl) for each material; Figure S16. OER LSV curves obtained in KOH (0.1 M) saturated with N2 at 1600 rpm and 0.005 V s−1 with current densities normalized to the respective double-layer capacitance values; Figure S13. CVs at different scan rates for MWCNT_N6 (a), Fe4@MWCNT_N6 (b), Ni4@MWCNT_N6 (c) and Fe2Ni2@MWCNT_N6 (d) in N2-saturated KOH (0.1 M); Figure S14. CVs at different scan rates of Pt/C and RuO2 in N2-saturated KOH (0.1 M); Figure S15. Current density scan rate linear fitting plots for all materials. Numeric values correspond to the double-layer capacitances (Cdl) for each material; Figure S16. OER LSV curves obtained in KOH (0.1 M) saturated with N2 at 1600 rpm and 0.005 V s−1 with current densities normalized to the respective double-layer capacitance values; Figure S17. Chronoamperometric responses in KOH (0.1 M) saturated with N2 at 1600 rpm for 43,200 s; Table S1. Comparison of the OER electrochemical performance (overpotentials (η10) and current density (j)) for POM-based composite materials reported in literature [6,41,54,63–77].

**Author Contributions:** The synthesis and characterization of POMs were performed by I.-M.M. and A.-L.T.; doped MWCNT by B.J.; and composite materials by I.S.M. The electrocatalytic experiments were conducted by D.M.F. and I.S.M. The research was supervised by D.M.F., P.d.O. and C.F.; and I.S.M. and D.M.F. were responsible for writing up the manuscript, which was proofread by D.M.F. and P.d.O. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare that they have no conflict of interest.

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