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Nanoscale engineering to control mass transfer on carbon-based electrodes

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- Outer-sphere redox probe
- Thin-layer diffusion
- Nanofibers

ABSTRACT

Here we use an electrode consisting of carbon nanofibers (CNFs), the lengths and surface population density of which can be effectively controlled. It is shown that (i) a thin liquid layer forms when the thickness of the diffusion layer has a specific ratio to the dimensions of the nanostructured carbon surface. (ii) This leads to a decrease in the peak potential difference and a subsequent increase in the apparent heterogeneous electron transfer (HET) constant, both of which could be interpreted as a result of increased catalytic activity. (iii) However, we show that this explanation is not likely, as our materials are chemically identical, and we use an outer sphere redox (OSR) probe to minimize any specific chemical interactions. On the contrary, (iv) the results clearly show that the observed behavior is caused by a combination of the formation of a thin liquid layer and the increased apparent surface area of the electrodes.

1. Introduction

Carbon nanomaterials are widely used as electrodes for electrochemical detection due to their large surface area, wide potential windows, high sensitivity, and electrical conductivity, properties which arise from their nanoscale dimensions and variable sp3/sp2 hybridization – see, for instance [1]. Due to their easily modified topography, carbon nanomaterials have been shown to exhibit a range of different mass transfer regimes, unlike planar electrodes. Previous studies have indicated that carbon nanotube yarns (CNTY) [2], multi-walled carbon nanotubes (MWCNTs) [3–5], and single-walled carbon nanotubes (SWCNTs) [6,7] can exhibit thin-liquid-layer behavior. Detailed investigations have also demonstrated how this is often mistakenly taken to represent increased electrocatalytic performance of the electrode [8,9]. This occurs because the thin-liquid-layer effect induces the confinement of the analyte within the nanostructure, leading to a decrease in the peak potential separation – phenomena also manifested by increased electrochemical activity [10,11]. The thin-layer electrochemical behavior is only observed under conditions where the diffusion layer thickness and the dimensions of the nanomaterial are in an appropriate ratio [12]. When using cyclic voltammetry, the scan rate provides a method of controlling the thickness of the diffusion layer.

Carbon nanofibers provide an interesting electrode material for a wide variety of electrochemical applications, such as biosensing [13]. The vertical forest-like morphology of CNFs, especially when grown directly on a suitable substrate [14], provides an excellent platform for engineering the electrode response towards different analytes [1]. However, in order to be able to carry out geometrical optimization, one needs to thoroughly understand the effect of the different factors that can be structurally changed to improve sensor performance. To achieve this, geometrical nanostructure parameters, such as length, diameter, and fiber surface density, must be precisely controlled.

Thus, this study elucidates the effect of CNF length and fiber surface population density on the diffusion behavior on the electrodes. Nanofiber length is precisely controlled by the duration of the growth phase during the fabrication process. The use of identical catalyst layers (here Ni) ensures that the resulting structures are chemically identical. In contrast, the use of different adhesion layers (Ti or Cr), induces changes in the nucleation of the fibers, as shown in detail in [15], resulting in CNF forests with different fiber surface population densities. By utilizing this controlled approach to surface morphology modification, we can effectively isolate pure geometrical effects from other parameters, such as surface chemistry or electrical properties, and provide a systematic assessment of geometrical effects on thin-liquid-layer formation on nanostructured carbon-based electrodes. By using only an outer sphere redox probe (Ru(NH3)63+) we can further neglect any major chemical interactions, especially strong adsorption. We will then proceed to use standard kinetic analysis methods to show that the results obtained can be easily interpreted to affect the HET constants of the fibers, although these should remain unaltered due to their identical physicochemical properties.
2. Materials and methods

p-type silicon wafers (Siegert Wafers, Germany) were used as substrates. First, the wafers were coated with adhesive and catalyst metal layers: 20 nm Ti followed by 20 nm Ni for Ti-Ni CNFs, or 80 nm Cr followed by 20 nm Ni for Cr-Ni CNFs. An electron beam evaporator (MASA IM-9912) was used to deposit the metal layers. The chamber pressure was approximately 2 $\text{e}^{-7}$ mbar during evaporation. Subsequently, the wafers were cleaved into smaller pieces, measuring approximately 7 mm $\times$ 7 mm. The PECVD process for CNF growth was carried out as described in the Supplementary Information (SI).

The morphology and geometry of the CNFs were studied using SEM (Zeiss Sigma VP). Length, diameter, and area analyses were carried out using ImageJ. We estimated the average length and diameter by measuring 20 CNFs from the cross-sectional SEM images. Details of the area analysis are given in the SI.

Atomic force microscopy (AFM) measurements of the bare substrates were carried out using a Dimension Icon AFM (Bruker Inc) in ScanAsyst mode, using a ScanAsyst-Air tip (Bruker Inc) with a nominal tip radius of 2 nm. Measurements were performed in air at room temperature. Details of the analysis are given in the SI.

Electrochemical investigations were carried out using both conventional cyclic voltammetry (CV) and a RDE configuration. Experiments were conducted with a Gamry Reference 600 $+$ potentiostat. A three-electrode cell was used with an Ag/AgCl reference electrode (Radiometer Analytical) and a Pt wire (Goodfellow) counter electrode. The solutions were purged with N$_2$ for at least 30 min before the experiments. All the measurements were carried out at room temperature in a Faraday cage with dynamic uncompensated resistance compensation. Experiments were conducted in 1 mM Ru(NH$_3$)$_6^{2+/3+}$, where hexaamineruthenium(III) chloride (Sigma-Aldrich) was dissolved in 1 M KCl (Merck Suprapur, pH 6.8). Details of the analysis are included in the SI.

3. Results

Fig. 1 shows the overall morphology of the CNF samples. It can be clearly seen that the length of the fibers is affected by the growth time, whereas the diameter and fiber surface density are largely unaffected for a specific interlayer metallurgy. The characteristic values of the CNF forest for each electrode type are listed in Table 1.

Based on the AFM measurements, the Cr-Ni substrates had significantly larger roughness values than the Ti-Ni substrates (Fig. 2).

From the electroanalytical point of view, it is practical to define a potential window where the analyte signal can still be measured i.e., analyte oxidation/reduction has not been overrun by HER and OER. This analytical potential window is defined using a self-chosen threshold current value (here $\pm$ 150 $\mu$A/cm$^2$). Overall, one can see the potential window becoming narrower as the CNF length increases, regardless of the chosen metal substrate. This is simply caused by the increase in the available CNF area and the resulting higher pseudofaradaic contribution to the background current. In the case of carbonaceous nanomaterials,

![Cross-sectional SEM images of CNF samples prepared using different growth times (1, 5 and 30 min). The left-hand column shows samples grown on Ti-Ni and the right-hand column samples grown on Cr-Ni. Note that the structure cannot be regarded as porous as the electrolyte can flow down to the substrate through the CNF forest.](image-url)

<table>
<thead>
<tr>
<th>Sample type</th>
<th>CNF diameter (nm)</th>
<th>CNF length (nm)</th>
<th>% Surface covered by Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-Ni 1 min</td>
<td>N/A</td>
<td>$-50$</td>
<td>$50$</td>
</tr>
<tr>
<td>Ti-Ni 1 min</td>
<td>N/A</td>
<td>$-50$</td>
<td>$37$</td>
</tr>
<tr>
<td>Cr-Ni 5 min</td>
<td>$71 \pm 49$</td>
<td>$221 \pm 61$</td>
<td>N/A</td>
</tr>
<tr>
<td>Ti-Ni 5 min</td>
<td>$66 \pm 51$</td>
<td>$361 \pm 131$</td>
<td></td>
</tr>
<tr>
<td>Cr-Ni 30 min</td>
<td>$69 \pm 27$</td>
<td>$915 \pm 257$</td>
<td></td>
</tr>
<tr>
<td>Ti-Ni 30 min</td>
<td>$84 \pm 43$</td>
<td>$873 \pm 181$</td>
<td></td>
</tr>
</tbody>
</table>
the capacitance, as determined by CV, is typically considered to be of the pseudocapacitance type, owing to the rich surface chemistry of these materials that inevitably provides faradaic contributions to the measured values. Again, the values scale with increasing CNF length (Table 2).

The experiments to determine the apparent HET changes were carried out using the outer-sphere redox probe Ru(NH$_3$)$_6^{3+/2+}$ to focus solely on the geometrical structural effects. We emphasize that the actual HET constant should be identical for fibers of different lengths and all apparent changes should be the result of geometrical effects. Electrodes with long carbon nanofibers (on both Cr-Ni and Ti-Ni substrates) have symmetrical peaks that indicate some degree of thin-layer formation (Fig. 3A, B, D, E), as we can exclude specific adsorption in our model system. On the other hand, electrodes without a nanostructured surface generate peak shapes typical of diffusion-controlled behavior (Fig. 3C, F).

The peak separation values for samples grown for 1 and 30 min show no significant differences at 10 mV/s (Table 3). However, the values drop considerably for samples grown for 30 min at scan rates ranging from 0.01 to 1 V/s but increase again with a further increase in the scan rate, owing to kinetic limitations (Fig. 4). The peak separation value is smallest at scan rates ranging from 0.4 to 1 V/s for the electrodes with the longest fibers.

The slope of log $I_{pa}$ – log $v$ for long Ti-Ni CNFs is ~ 0.5, indicating diffusion-controlled behavior (Fig. S12) [17]. On the other hand, long Cr-Ni CNFs have slightly higher slopes (~0.54), demonstrating diffusion-controlled behavior with a small contribution from thin-layer diffusion. The slopes for the plain electrodes are below 0.5 (0.45 and 0.42 for Cr-Ni and Ti-Ni substrates, respectively), indicating the presence of some additional limitations to the overall reaction kinetics on top of pure semi-infinite linear diffusion. As discussed above, the observed behavior appears to be restricted to a certain (rather narrow) scan rate region. Thus, to elaborate on this further, separate plots were made for low and high scan rates and these are shown in Fig S13. We also carried out background subtraction and assessed whether that would affect the log $I_{pa}$ – log $v$ plots (Fig. S14), but no significant improvement in revealing thin-liquid-layer formation was observed with either approach. Note that none of the slope values was even close to one, which is the expected value for pure thin-liquid-layer behavior. Hence, the use of log $I_{pa}$ – log $v$ plots is not very effective in revealing (modest) thin-liquid-layer effects.

Next, we calculated the theoretical peak current values using the Randles–Sevcik equation (for justification of its use see Fig. S12) and compared that value to the measured current values for each electrode type (Table S11). The measured anodic peak current values for the CNF electrodes are similar to the theoretical ones at small scan rates (0.01–0.05 V/s). At intermediate scan rates (0.2–1 V/s), the experimental currents are somewhat smaller than the theoretical ones. We argue that this is owing to the formation of a thin liquid layer, which produces smaller currents than semi-infinite diffusion, thus decreasing the overall measured current [12]. Further, the range of scan rates at which these phenomena are observed is consistent with the range where the $\Delta E_p$ values were lower than the ideal values. A similar decrease in the experimental current values is also observed for plain electrodes for a different range of scan rates (>1 V/s), but this is caused by the sluggish electron transfer kinetics as the $\Delta E_p$ values are seen to increase significantly.

Finally, we proceeded to carry out RDE measurements to see if the apparent kinetic effects would be observed using this approach. The Levich plot (Fig. 5) shows that the electrodes without a nanostructured surface (substrates) have shallower slopes than the materials with structural features, but there is no significant difference between the materials (Cr-Ni or Ti-Ni). Specifically, the nanostructured electrodes have different slopes depending on the length of the CNFs: long carbon nanofibers have the steepest slopes. Also, none of the lines go through the origin, indicating kinetic limitations on top of diffusion control and providing grounds for using Koutecky–Levich, even though the CVs show reversible behavior.

The rotating disk electrode set-up is commonly used to characterize the electron transfer kinetics of nanostructured electrodes by utilizing Koutecky–Levich analyses. The estimated thickness of the diffusion layer is ~ 6–25 µm, as shown in Table S12. The electrodes fabricated on Ti-Ni substrates had in general slightly faster apparent overall kinetics (i.e.

Table 2

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Cr-Ni CNFs</th>
<th>Ti-Ni CNFs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.51 ± 0.04</td>
<td>2.71 ± 0.02</td>
</tr>
<tr>
<td>5</td>
<td>1.56 ± 0.04</td>
<td>2.78 ± 0.02</td>
</tr>
<tr>
<td>30</td>
<td>2.51 ± 0.04</td>
<td>2.79 ± 0.02</td>
</tr>
</tbody>
</table>

The rotating disk electrode set-up is commonly used to characterize the electron transfer kinetics of nanostructured electrodes by utilizing Koutecky–Levich analyses. The estimated thickness of the diffusion layer is ~ 6–25 µm, as shown in Table S12. The electrodes fabricated on Ti-Ni substrates had in general slightly faster apparent overall kinetics (i.e.
higher kinetic currents and thus larger HETs, Table 4) than those grown using Cr-Ni substrates, according to the Koutecky–Levich analysis (Fig. S17). Out of all the electrodes, the bare Ti-Ni substrate had the fastest apparent overall kinetics. It should be noted that we use the simple Koutecky–Levich equation (as well as the Nicholson approach to determine HETs from CV) to identify the main trends in the overall kinetic behavior. To obtain quantitative values for HET constants, more sophisticated analytical or numerical approaches, such as those described in [18,19], should be used.

4. Discussion

There are slight differences in the limiting values of the analytical potential windows between the substrates (Cr-Ni and Ti-Ni) in different solvents, but when CNFs are grown on the surface these differences diminish. Especially for the longest CNFs, the analytical windows are
practically identical, highlighting the dominating role of carbon. CNFs grown on Cr-Ni substrates show, in general, slightly higher pseudocapacitance values than CNFs grown on Ti-Ni substrates, which is also observed in the pseudocapacitance values of the substrates without any CNFs. The higher values for the Cr-Ni CNFs are expected to be caused by the higher surface population density of the fibers, whereas the difference between the planar samples likely originates from the difference in roughness between the Cr-Ni and Ti-Ni substrates (Fig. 2). The increase in pseudocapacitance with increasing carbon nanofiber length is caused by the increase in the reactive carbon surface area.

Thin-liquid-layer formation was observed to occur at medium scan rates (0.1–1 V/s) on electrodes with nanofibers grown for 5 and 30 min, whereas it was absent in the case of 1 min CNFs or planar substrates. This is because the thickness of the diffusion layer within this scan rate regime has a suitable magnitude compared to the length of the CNFs to facilitate the formation of a thin liquid layer. From the calculated ratios of diffusion layer thickness to fiber length (Table 5), the most significant decrease in the $\Delta E_p$ value is seen in the range where the ratio is less than 30:1 but is still high enough for the concentration to be constant within the thin layer volume [12]. At higher scan rates the thickness of the diffusion layer approaches the length of the long CNFs but will still be in a favorable region for short CNFs. This is reflected in the fact that the $\Delta E_p$ values of short CNFs become smaller than those of long CNFs at scan rates over 10 V/s and approaching 100 V/s.

Finally, the RDE results did not show any marked differences in the apparent HET values. In fact, the bare substrates appeared to have the fastest kinetics. Thus, under RDE conditions the formation of any type of thin liquid layer is minimized with these samples. This may be rationalized by looking at the morphology of the CNF forest in Fig. 1. Even though there are many fibers on the surface of the electrode, the electrolyte can still flow quite freely between the fibers towards the surface (z-direction) and past them along the x-y direction, enabling enhanced mass transport to eliminate most of the stagnant liquid layer next to the surface. Nevertheless, RDE should be used with caution on non-planar surfaces as discussed in [20]. Further, in our case, the increased area of the CNF electrodes was not large enough to be seen as apparent kinetic effects in RDE [21]. Small variations in mass transfer as a function of fiber length are expected and most likely caused by the different flow conditions adjacent to the electrode substrate (bare vs fiber) as shown by the changes in the slopes of CNFs with different lengths.

### 5. Conclusions

We show that by precisely controlling the dimensions of chemically identical carbonaceous nanomaterials, it is possible to induce thin-liquid-layer formation by controlling the thickness of the diffusion layer. By using the outer sphere redox probe as our analyte, we exclude any complications from chemical interactions. We note that the geometrical effects on peak potential separation in cyclic voltammetry can be easily interpreted as a result of increased electrocatalysis if
proper caution is not observed. Further, as thin-liquid-layer formation is observed only within a certain range of scan rates, it may not be easily detected from the slope of the log (i) – log (ν) plot taken from a wider range of scan rates. We also show by using the RDE measurements that the geometrical effects are seen as changes in the apparent diffusion coefficient, but no significant variation in the HET constant is observed.

CRediT authorship contribution statement

Laura Ferrer Pascual: Investigation, Writing – original draft, Formal analysis, Writing – review & editing, Visualization. Ishan Pande: Resources, Writing – original draft. Ayesha Kousar: Writing – original draft. Tomi Laurila: Investigation, Formal analysis, Writing – original draft. Samuel Rantataro: Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2022.107328.

References


Table 5

<table>
<thead>
<tr>
<th>Scan rate (V/s)</th>
<th>Ratio of diffusion layer thickness to length of CNFs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Long Cr-Ni CNFs</td>
</tr>
<tr>
<td>0.01</td>
<td>255</td>
</tr>
<tr>
<td>0.05</td>
<td>114</td>
</tr>
<tr>
<td>0.1</td>
<td>81</td>
</tr>
<tr>
<td>0.2</td>
<td>57</td>
</tr>
<tr>
<td>0.4</td>
<td>40</td>
</tr>
<tr>
<td>1</td>
<td>26</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
</tr>
<tr>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>100</td>
<td>2.5</td>
</tr>
<tr>
<td>300</td>
<td>1.5</td>
</tr>
</tbody>
</table>

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Appendix A. Supplementary data

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