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Structure-property relationships in carbon electrochemistry

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A B S T R A C T

Carbonaceous nanomaterials can be a game changing materials in many technological fields, especially in electroanalytical applications. However, there is no consensus on the associations between the structure and electrochemical performance of these nanomaterials – even for the most basic electrochemical properties. This challenge stems from the fact that typically carbonaceous nanomaterials are obtained from various sources and not characterized properly. Therefore, to solve this deadlock we carry out systematic electrochemical characterization for a set of in-house fabricated as well as physicochemically thoroughly characterized carbon nanomaterials. We will then proceed to establish structure – performance associations for these materials. In addition, we will highlight how sensitive the electrochemical performance of these materials can be to small changes in their structural properties. Further, we emphasize the lack of correlation between electrochemical performance of electrode materials as determined using outer sphere redox (OSR) and inner sphere redox (ISR) probes the latter being highly analyte specific. As a first consistent set of electrochemical data obtained by using well characterized carbonaceous nanomaterials, this work will provide solid basis to expand the use of these materials in more complex electroanalytical as well as other applications.

1. Introduction

Carbon is a versatile material, which can be found with various allotropes and structures - stable and metastable. As widely discussed and reported, carbon has many unique properties that allow it to be used in a wide range of applications such as electroanalytical [1], energy storage [2,3] and tribological [4] just to name a few. However, often in-depth characterization is missing, thus making it hard to understand the correlations between the structure of the used materials and their observed properties. Especially in the field of electroanalytical applications, often bold claims about electrocatalytical properties of carbon nanomaterials are stated [5]. Unfortunately, these arguments are generally unsubstantiated based on the actual results presented [5]. In particular, there is a lack of systematic assessment of the structural and basic electrochemical properties of the carbon allotropes used in these often very complex material assemblies [6]. In fact, we argue that it is next to impossible to find from the literature a set of consistent electrochemical characterization of different carbon nanomaterials with known structural and chemical properties. In-depth characterization of all these properties is crucially important if we want to reveal the associations between the structure and electrochemical performance of carbon nanomaterials (and any materials in general).

To provide some examples about these challenges one encounters when trying to establish structure-property relationship for electrochemical performance of carbonaceous nanomaterials it should be noted that the electrochemical properties of these materials are dependent on many different physicochemical factors such as: (i) microstructure at the nanoscale (ratio of edge/basal plains, sp2/sp3 ratio, defects, local structural motifs if amorphous, degree of order), (ii) surface chemistry, especially in case of inner-sphere probes (ISR), (iii) surface cleanliness, specifically when working with electrode materials that have inherently weak electronic coupling to redox probes, such as basal planes of highly oriented pyrolytic graphite (HOPG), (iv) residual metal catalyst (amount, particle size, state of the surface), and (v) roughness/geometry.

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affecting mass transport inducing phenomena such as thin-film effects, spherical diffusion fields or current dispersion. As an example, data from even long used and well established electrode materials, such as glassy carbon (GC), is still contradictory, since the material is very sensitive to fine details of electrode finishing and maintenance between the measurements [7,8]. Hence, for the full potential of these carbon nano-materials to be realized, systematic investigations of their structure-property relationships must be carried out.

In this study, we start with a consistent set of in-house fabricated carbon nanomaterials that have been fully characterized physicochemically in our earlier works [9–17] including amorphous carbon (a-C), tetrahedral amorphous carbon (ta-C), pyrolytic carbon (PyC), carbon nanofibers (CNF), multi-walled carbon nanotubes (MWCNT) and single-walled carbon nanotubes (SWCNT). To maximize the consistency of our set of materials, we have used catalyst free carbon nanomaterials (a-C, ta-C, PyC) or used only Fe catalyst in all cases where metals are needed for the growth (CNF, MWCNT, SWCNT) to allow head-to-head comparison between materials including residual catalyst. Glassy carbon is also included as it is so widely used and acts here as a benchmark comparison between materials including residual catalyst. Glassy carbon nanofibers (CNF), multi-walled carbon nanotubes (MWCNT) and tetrahedral amorphous carbon (ta-C), pyrolytic carbon (PyC), carbon nanofibers (CNF), multi-walled carbon nanotubes (MWCNT) and single-walled carbon nanotubes (SWCNT). To maximize the consistency of our set of materials, we have used catalyst free carbon nanomaterials (a-C, ta-C, PyC) or used only Fe catalyst in all cases where metals are needed for the growth (CNF, MWCNT, SWCNT) to allow head-to-head comparison between materials including residual catalyst. Glassy carbon is also included as it is so widely used and acts here as a benchmark comparison between materials including residual catalyst.

Basic electrochemical characterization is carried out for all these materials. Then we proceed, to a certain extent, to connect observed performance to their known physicochemical structure. We begin by defining point of total zero charge (ptzc) and open circuit potential (OCP) for all the materials in (i) perchloric acid, which is known to be an inert electrolyte without serious complications arising from adsorption and (ii) phosphate buffered saline (PBS) with pH 2.5, 7.4 and 12 as it is so widely used as a buffer solution in the context of bioelectrochemical applications of carbonaceous nanomaterials. The PBS solutions were also used for defining solvent and analytical potential windows as well as capacitance of carbon nanomaterials with cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). After these steps, two outer-sphere redox (OSR) couples Ru(NH₂)₆³⁺/²⁻ and IrC₂⁻/²⁻ with very different formal potentials are used to probe heterogeneous electron transfer (HET) kinetics on different carbon nanomaterials with CV. In addition, charge transfer resistance (Rct), double-layer capacitance (Cdl) and HET are obtained with Ru(NH₂)₆³⁺/²⁻ using EIS. Finally, inner-sphere redox (ISR) probe dopamine (DA) is used to initially assess the effect of differences in physicochemical properties of carbonaceous nanomaterials to reactions kinetics occurring via the inner sphere route. DA is used here because it is widely applied as a model ISR molecule as well as owing to extensive earlier studies on electrochemical detection of DA with carbon nanomaterials that gives us a wealth of data for comparison purposes [5,18–20]. Finally, it should be noted that while results for solvent windows, ptzc and HET of surface insensitive OSR probes are rather general in their nature, the results for ISR probes are highly redox system specific because of the strong chemical interactions with the electrode surface.

2. Materials and methods

2.1. Material fabrication

Amorphous carbon was deposited with a pulsed filtered cathodic vacuum arc (p-FCVA). Prior to a-C deposition, Ti adhesion underlayer was deposited by direct current magnetron sputtering in the same system without breaking vacuum. 20 nm Ti and 7 nm a-C films were deposited on boron-doped p-type silicon (100) prime wafers (<0.005 Qcm, Siegent Wafer) and microscope glass slides Menzel in a vacuum chamber evacuated to base pressures below 5 × 10⁻⁷ Torr using a CTI cryogenic CTI 8F cryopump. The p-FCVA system uses a toroidal 45° bent electromagnetic filter, with a pulse-forming network unit of 2.6 mF charged to −400 V (pulse current 650 A, 1 Hz). Substrate was placed on a 17 rpm rotating holder at 220 mm working distance at room temperature. The source material for the carbon plasma was a graphite rod of 6.35 mm diameter and purity of 99.995% (Goodfellow). For Ti sputtering the following deposition parameters were used: discharge power fixed at 100 W, total pressure of 5 mTorr, Ar gas flow rate of 29 sccm, and 220 mm working distance. The Ti target was cleaned by pre-sputtering of 120 s prior to all depositions. 15 nm ta-C film with Ti underlayer was deposited as described above. In the case of ta-C deposition time of carbon was changed to obtain thicker film. With increasing film thickness, the bulk contribution (rich in sp²) to the signal increases and that of the surfaces (rich in sp³) decreases, resulting in an overall increase in the volume content of sp³ of the film [21]. Thus, the film is referred as tetrahedral amorphous carbon.

Pyrolytic carbon was fabricated by pyrolysis of negative photoactive polymer SU-8-50 (Microchem). Briefly, the pyrolysis was carried out in a horizontal tube furnace (Nabertherm RS 170/1000/13) in nitrogen atmosphere. Pressure was maintained at 1 atm throughout the process. First, a pre-heating step was carried out at 300 °C for 40 min. After this step, temperature was increased to 900 °C for 60 min to pyrolyze SU-8. At both steps 200 °C/min ramp speed was used. More detailed information about the fabrication process can be found from Ref. [22].

Carbon nanofibers were grown on 7 nm a-C film with 20 nm Fe underlayer as a catalyst. Films were deposited as described above. The p-FCVA arc source assembly used for the deposition consists of two separate cathodes (carbon and iron) surrounded by a common anode body. Software running on National Instruments hardware controls the triggering of either cathode with the pulse-forming network to result in a pulse of either carbon or iron plasma incident on substrate. The source material for iron plasma is an iron rod of 6.35 mm diameter and purity of 99.99% (Goodfellow). CNFs were fabricated in a cold-wall plasma enhanced chemical vapor deposition (PECVD) reactor (Aixtron, Black Magic, UK). The chamber pressure was pumped below <1 Pa and then heated to 400 °C by a ramp speed of 250 °C/min. At this temperature samples were annealed for 3 min before the growth process. After this step, the chamber was filled with NH₃ (100 sccm) reducing gas while maintaining the pressure at 10 Pa and increasing the temperature to 600 °C with a ramp speed of 300 °C/min. After the temperature had reached 575 °C, carbon precursor CH₂ was introduced to the chamber (30 sccm) and 150 W DC plasma ignited. At the same time NH₃ flow was increased to 125 sccm. After a 30 min growth phase, the chamber pressure was maintained below 20 Pa while cooling down the reactor with argon (2000 sccm).

For fabricating multi-walled carbon nanotubes, 4 nm of Fe catalyst was first sputtered on the 7 nm a-C surfaces. The coated substrates were then heated to 550 °C in a cold-wall chemical vapor deposition (CVD) reactor (Aixtron, Black Magic, UK) to reduce the catalyst (in NH₃ at a flow rate of 250 sccm and pressure of 10 mbar) for 1 min. After the reduction step, the reactor chamber was first evacuated to 0.2 mbar, and then subsequently filled with N₂ buffer (250 sccm). When the pressure was stabilized back to 10 mbar, C₂H₂ was introduced to the chamber at flow rate of 25 sccm for 10 min to grow the carbon nanotubes at 550 °C.

Single-walled carbon nanotubes were fabricated with a high-temperature floating catalyst CVD. Growth was done in a laminar flow reactor. In this process a ferrocene precursor is introduced into a carbon monoxide atmosphere, where it thermally decomposes to Fe nanoparticles due to a high temperature. Subsequently, these Fe particles catalyze the growth of SWCNTs by decomposing carbon monoxide. In the end of the process, SWCNTs grown in the gas phase are collected using a membrane filter. The floating catalyst CVD fabrication process is described in more detail in Refs. [23,24].

Glassy carbon was obtained from Goodfellow (VC00-RD-000115).

2.2. Scanning electron microscopy

Imaging of carbon nanomaterials was performed with Zeiss Sigma VP and Hitachi-4700 scanning electron microscopes (SEM) at 15 or 20 kV.
accelerating voltage.

2.3. Electrochemical characterisation

Electrodes prepared from carbon nanomaterials fabricated on silicon (a-C, ta-C, PyC, CNF, MWCNT) were done by placing a piece of sample on top of a conductive copper clap (double sided FR 4 glass fiber substrate with thickness of 0.3 mm). The sample was enclosed with inert PTFE-tape (Saint-Gobain Performance Plastics CHR 2255–2) with a 3 mm hole (radius = 1.5 mm), which was placed on top of the carbon sample to define the working area of the electrode and isolate the copper from the electrolyte. The contact between substrate and carbon sample was enhanced by scraping the backside of the carbon sample with a piece of copper.

SWCNT were prepared by press-transferring a smaller piece of network onto a glass substrate (Thermo Scientific, ISO 8037/I) and densified with a drop of 99.5 wt.-% ethanol (Altea). A conductive pad was painted with silver paint (Electrolube). Sample was covered with inert PTFE-tape with a 3 mm hole. More detailed description of SWCNT preparation can be found from Ref. [15].

GC rod with diameter of 3 mm was polished between every measurement with a 0.05 μm alumina polishing suspension (Struers) for 3 min, then sonicated in deionized water for 5 min. After sonication GC was rinsed with DIW and transferred to the electrochemical cell with a thin layer of water on the surface to avoid oxidation.

All measurements were carried out with Gamry Reference 600-i potentiostat. 3-electrode setup was used for all experiments with Pt wire (Goodfellow) counter and Ag/AgCl (±0.199 V vs. SHE, Radiometer Analytical) reference electrode. Preparation of carbon working electrodes was done as described above. All measurements were conducted in a Faraday cage at room temperature. All measurements were repeated at least 3 times with different electrodes. Cyclic voltammograms and Nyquist plots presented here are individual measurements, but are representative data for each carbon nanomaterial. The contact resistance of carbon working electrodes was monitored with the potentiostat to ensure good contact and confirm that the resistance does not vary significantly between different carbon samples to allow comparison between the materials.

2.3.1. Cyclic voltammetry

The CV measurements were carried out in several different solutions. pH dependence of potential window was measured in blank 10 mM phosphate-buffered saline solution with pH 2.5, 7.4 and 12. Stock solution of PBS pH 7.4 was prepared and pH was adjusted with HCl and NaOH. Pseudocapacitance, \( C_{\text{pseudo}} \), was also evaluated from the potential window measurements at three different potential values with following equation:

\[
C_{\text{pseudo}} = \frac{(i_a - i_c)}{2 \cdot v}
\]  

(1)

where \( i_a \) and \( i_c \) are anodic and cathodic background currents with scan rate of \( v \).

Outer-sphere redox probes Ru(NH\textsubscript{3})\textsubscript{6}^{2+/3+} and IrCl\textsubscript{6}^{3-/2-} with 1 mM concentration in 1 M KCl (Merck Suprapur, pH 6.8) prepared from hexamamineruthenium(III) chloride (Sigma-Aldrich) and potassium hexachloroiridate(IV) (Aldrich) were used for probing the electron transfer kinetics of the carbon electrodes. 100 μM dopamine in 10 mM PBS (pH 7.4) prepared from dopamine hydrochloride (Sigma) was used as an inner-sphere probe. In the case of DA, electrolyte was purged with N\textsubscript{2} for 30 min prior to DA solution preparation.

Following parameters were obtained from OSR measurements: (i) the standard heterogeneous rate constant \( k^0 \), (ii) the kinetic parameter \( \Lambda \) proposed by Matsuda and Ayabe and (iii) effective surface area \( A_{\text{eff}} \). \( k^0 \) was calculated using the Nicholson method [25] and \( A_{\text{eff}} \) obtained from Randles-Sevčík equation [26,27]. The parameter \( \Lambda \) distinguishes reversible, quasi-reversible and irreversible cases with following limits [28]:

Reversible: \( \Lambda \geq 15 \times 10^{-3} \geq 0.3 \times (nv)^{0.5} \ \text{cm} \ \text{s}^{-1} \)

Quasi-reversible: \( 15 > \Lambda > 10^{-3} \times 0.3 \times 12 > k^0 \times 2 \times 10^{-5} (nv)^{0.5} \ \text{cm} \ \text{s}^{-1} \)

Irreversible: \( \Lambda \leq 10^{-3} k^0 \leq 2 \times 10^{-5} (nv)^{0.5} \ \text{cm} \ \text{s}^{-1} \)

where \( n \) is the number of electrons and \( v \) the scan rate.

2.3.2. Electrochemical impedance spectroscopy

The potential of zero total charge was evaluated by measuring differential capacitance, \( C_{\text{diff}} \), with single frequency EIS in 0.01 M HClO\textsubscript{4} (Merck, pH 1) and undiluted PBS with pH of 2.5, 7.4 and 12. Measurements were carried out with following procedure: (i) First open circuit potential (OCP) was recorded for 30 min, where potential of the system was monitored as function of time without applying any external voltage, (ii) then sequence of single frequency EIS was executed using a macro build with Gamry Sequence Wizard, where measurements were carried out from cathodic to anodic direction with increase of 25 or 50 mV. A delay of 5 s was set between every measurement. If less systematic approach was carried out for materials investigated here, it was found relatively difficult to obtain parabolic curve for differential capacitance evaluated from following equation [29]:

\[
C_{\text{diff}} = \frac{(2 \pi A f Z^\prime)^{-1}}{Z''}
\]  

(2)

where \( A \) is the geometrical area of the electrode, \( f \) the frequency and \( Z'' \) imaginary part of the impedance. For all measurements \( f = 700 \) Hz and AC signal amplitude 15 mV. It should be noted that Eq. (2) presents a very simple model for the \( C_{\text{diff}} \), which does not apply for all the materials investigated here. However, Eq. (2) is not used for determining true values of \( C_{\text{diff}} \) for the carbon nanomaterials. It is utilized for defining the potential where \( C_{\text{diff}} \) reaches its minimum i.e. potential that corresponds to the potential of total zero charge.

EIS with frequency range from 0.1 Hz to 100 kHz was conducted in PBS with 3 different pH as well as in 5 mM Ru(NH\textsubscript{3})\textsubscript{6}^{2+} in 1 M KCl. The amplitude of AC signal was 15 mV. In the case of Ru(NH\textsubscript{3})\textsubscript{6}^{2+} DC bias was set to the formal potential of the redox couple defined with CV (−0.165 V vs. Ag/AgCl), whereas in PBS DC bias was set to 0 V vs. Ag/AgCl in every pH. The only exception was CNF in pH 2.5, where DC bias = 0.38 V due to Fe dissolution process taking place around 0 V [30].

![Fig. 1. Randles equivalent circuits used for fitting EIS data obtained in A) PBS and B) 5 mM Ru(NH\textsubscript{3})\textsubscript{6}^{2+}/3-](image-url)
The EIS data obtained in PBS was fitted with Randles equivalent circuit (Fig. 1A), where solution resistance ($R_s$) is in series with a parallel circuit composed of a charge transfer resistance ($R_{ct}$) and a constant phase element (CPE). When fitting Ru(NH$_3$)$_6^{3+}$ data a Warburg element ($W$) is added in series with $R_{ct}$ (Fig. 1B). In both equivalent circuits CPE replaces the double-layer capacitance ($C_{dl}$) as in real experiments the double layer rarely behaves like an ideal capacitor. The constant phase exponent $\alpha$ (0 < $\alpha$ < 1) is used to describe CPE’s deviation from ideal capacitive behavior ($\alpha$ = 1). $C_{dl}$ values from CPE were calculated with equation proposed by Hsu and Mansfeld [31]:

$$C_{dl} = Y_0 (\omega_{max})^{\alpha - 1}$$

where $Y_0$ is the parameter related to the electrode capacitance and $\omega_{max}$ is the angular frequency ($\omega_{max} = 2\pi f_{max}$). $f_{max}$ corresponds to the maximum of the imaginary impedance $Z''$ i.e. maximum of the semicircle in a Nyquist plot. If semicircle was not observed in the impedance plot (in case of blank PBS measurements), $f_{max}$ was obtained from the maximum of the semicircle in admittance plot ($Y''$).

As EIS measurements were carried with small deviations from equilibrium, the standard heterogenous constant $k^0$ at formal potential was calculated from the charge transfer resistance [32]:

$$R_{ct} = RT \cdot (F i_0)^{-1}$$

where $R$ is the gas constant, $T$ the temperature, $F$ the Faraday constant and $i_0$ is the exchange current density at equilibrium. $i_0$ is given by:

$$i_0 = F A k^0 (c_b^{1/\alpha} (c_k^{1-\alpha})$$

where $c_b$ and $c_k$ are the surface concentration of oxidized and reduced species of Ru(NH$_3$)$_6^{3+}$. $\alpha$ is the transfer coefficient. At equilibrium the bulk concentrations $c_b^0$ can be found from the surface. Therefore, it can be expected that $c_b^0 = c_b$ and $c_k^0 = c_k$. With this assumption $k^0$ can be obtained by combining Eqs. (4) and (5):

$$k^0 = R_{ct} \cdot (F^2 A R_{ct} (c_b^{1/\alpha} (c_k^{1-\alpha})$$

Initially, only oxidized species Ru$^{3+}$ is present. However, as redox reactions for Ru(NH$_3$)$_6^{3+}$ is reversible, it was assumed that at formal potential $c_b^0 = c_b^k = 2.5$ mM and $\alpha = 0.5$. Fitting of EIS data was carried out with both ZView and Gamry Echem Analyst software.

### 3. Physicochemical properties of carbon nanomaterials

In this work, we investigate four types of catalyst free carbon nanomaterials (a-C, ta-C, GC, PyC) and three types where Fe metal catalysts are present (CNF, MWCNT, SWCNT). All materials are fabricated in-house, except for GC that was purchased from a commercial provider. Structurally a-C and SWCNT exemplify the extreme ends as the former is “completely” amorphous and the latter one exhibits a high degree of long-range order. The synthesis parameters and properties of carbon nanomaterials are summarized in Table 1, whereas SEM images from the structures are presented in Fig. 2. Structural and chemical properties in Table 1 are collected from our earlier work [17], where detailed characterization of carbon nanomaterials was carried out with soft X-ray absorption spectroscopy (XAS).

a-C and ta-C are both amorphous structures and only ones that contain sp$^3$ bonded carbon in their bulk regime. Even though both films have been fabricated with identical processes, the thinner film (7 nm) is classified here as a-C and thicker (15 nm) as ta-C. This is because only ta-C is observed to have a significant volume fraction of sp$^3$ bonded carbon as shown in Table 1. The difference arises from the fact that the surfaces of both a-C and ta-C are sp$^2$ rich regardless of the film thickness [10,12] and the sp$^3$/sp$^2$ ratio shown in Table 1 is arising from the whole film volume including both bulk as well as surface region. Thus, the overall content of sp$^2$ is higher in the thinner (7 nm) film where the surface and interface contributions (both rich in sp$^2$ rich) is higher. Major functional group for both films is carboxyl. However, amount of oxygen at the

### Table 1: Synthetic parameters for carbon nanomaterials and their structure - surface properties. Majority of the results are collected from work of Solisio et al. [17].

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Substrate</th>
<th>Carbon source</th>
<th>pressure/ \text{atm}</th>
<th>growth atmosphere</th>
<th>Catalyst</th>
<th>Relative amount of O</th>
<th>Functional groups</th>
<th>Roughness/Geometry</th>
<th>Growth rate</th>
<th>Crystallinity of carbon phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-C</td>
<td>p-CVD</td>
<td>N$_2$</td>
<td>C/30 min</td>
<td>Vacuum</td>
<td>C/30 min</td>
<td>Vac</td>
<td>Low</td>
<td>amorphous</td>
<td>rough, wide, 10 \text{ nm}</td>
<td>600 \text{ C}</td>
<td>C/H$\Delta$H$^\text{pr}$</td>
</tr>
<tr>
<td>ta-C</td>
<td>p-CVD</td>
<td>N$_2$</td>
<td>C/30 min</td>
<td>Vacuum</td>
<td>C/30 min</td>
<td>Vac</td>
<td>Very low</td>
<td>amorphous</td>
<td>smooth, surface roughness 0.17 nm</td>
<td>600 \text{ C}</td>
<td>C/H$\Delta$H$^\text{pr}$</td>
</tr>
<tr>
<td>GC</td>
<td>CVD</td>
<td>N$_2$</td>
<td>CVD</td>
<td>Vacuum</td>
<td>C/30 min</td>
<td>Vac</td>
<td>Low</td>
<td>amorphous</td>
<td>smooth, surface roughness 0.17 nm</td>
<td>600 \text{ C}</td>
<td>C/H$\Delta$H$^\text{pr}$</td>
</tr>
<tr>
<td>PyC</td>
<td>PECVD</td>
<td>N$_2$</td>
<td>CVD</td>
<td>Vacuum</td>
<td>C/30 min</td>
<td>Vac</td>
<td>Low</td>
<td>amorphous</td>
<td>smooth, surface roughness 0.17 nm</td>
<td>600 \text{ C}</td>
<td>C/H$\Delta$H$^\text{pr}$</td>
</tr>
<tr>
<td>CNF</td>
<td>CVD</td>
<td>N$_2$</td>
<td>CVD</td>
<td>Vacuum</td>
<td>C/30 min</td>
<td>Vac</td>
<td>Low</td>
<td>amorphous</td>
<td>smooth, surface roughness 0.17 nm</td>
<td>600 \text{ C}</td>
<td>C/H$\Delta$H$^\text{pr}$</td>
</tr>
<tr>
<td>MWCNT</td>
<td>PECVD</td>
<td>N$_2$</td>
<td>CVD</td>
<td>Vacuum</td>
<td>C/30 min</td>
<td>Vac</td>
<td>Low</td>
<td>amorphous</td>
<td>smooth, surface roughness 0.17 nm</td>
<td>600 \text{ C}</td>
<td>C/H$\Delta$H$^\text{pr}$</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Floating</td>
<td>N$_2$</td>
<td>CVD</td>
<td>Vacuum</td>
<td>C/30 min</td>
<td>Vac</td>
<td>Low</td>
<td>amorphous</td>
<td>smooth, surface roughness 0.17 nm</td>
<td>600 \text{ C}</td>
<td>C/H$\Delta$H$^\text{pr}$</td>
</tr>
</tbody>
</table>

(a) Relative amount of functional groups and sp$^3$/sp$^2$ ratio was obtained from 30 nm ta-C (see Fig. S2 in supplementary). XAS C1s spectrum was fitted with same procedure presented in Ref. [17]. (b) Obtained from commercial vendor and thus synthesis parameters are unknown. Material properties are tabulated based on results published elsewhere.
surfaces is relatively low as stated also in Ref. [17]. This is especially true for ta-C film as seen from Table 1. GC is non-graphitizing carbon fabricated at elevated temperatures from certain polymers, mainly phenol-formaldehyde resins [33]. The detailed microstructure of GC is still under debate as it is known to be complex with a variety of coexisting phases, symmetries and defects. Several models have been suggested throughout the years, including but not limited to models from Franklin [34], Jenkins [35] and Harris [36]. General understanding is that GC contains microporous structure with sp² hybridized carbon and randomly intertwined graphitic-type of planes as reviewed recently in Ref. [37]. Surface is expected to be rich with reactive edge-plain sites. Although it contains a graphitic type of planes there is no long-range order in GC and thus it is often categorized as amorphous carbon. Nevertheless, it has been shown that at least some of the commercial GCs can contain fullerene-type of motifs [38]. In addition, it is noteworthy to mention that GC electrochemical properties are extremely dependent on the electrode preparation. In general, the polishing and cleaning step is carried out before the measurements. These steps can differ considerably from lab-to-lab and thus a variety of surface morphologies as well as chemistries can exist at GC surface after reacting with air and water [39].

PyC is often referred to as nanographic in its structure. However, in this study PyC fabricated from SU-8 is mainly amorphous in its structure as shown in Ref. [13]. Some degree of order was however observed with XAS and DFT simulations. Pyrolytic carbon exhibits different types of surface chemistry in comparison to other carbon nanomaterials, which have carboxyl as the major surface group, whereas PyC tends to have equal amounts of ketone, ether and hydroxyl at its surface (Table 1).

From Fe containing materials CNF and MWCNT are predominately crystalline, whereas SWCNT is completely crystalline. It should be noticed that even though the metal catalyst is the same in all cases, the distribution and size of the Fe particles is very different [14,30]. Especially in CNFs the size of the Fe particles is much larger in comparison to MWCNT and SWCNT, which will affect the surface chemistry and reactivity. Based on our earlier results one can also expect that more metal(oxide) surface is exposed in CNF structures in comparison to CNTs [14]. CNF appears to exhibit similar surface chemistry as MWCNT and SWCNT, which will affect the surface chemistry and reactivity. In addition, CNF contains the highest amount of oxygen. However, as it also has the highest amount of Fe and thus it is likely that the majority of the difference is due to the large amount of oxidized Fe (Fe₃O₄) particles. CNFs and MWCNTs have carboxyl as their major surface group whereas SWCNT has about equal abundance of C–H and carboxylic groups (Table 1).

Materials fabricated from Fe have very different macroscopic geometries as seen from Fig. 2. Carbon nanofibers are aligned vertically with Fe particles at the tip of every fiber, whereas MWCNT and SWCNT are tangled structures with smaller Fe particles distributed all over the network. It should be noted that tubes in SWCNT network used here are mainly in bundles i.e. there are hardly any individual tubes in the structure. This means that the common discussion, especially in the case of SWCNTs, about the relative reactivity of the tip and the sidewalls of the tubes is not really relevant here. In the case of CNF, the structure is most likely platelet type as seen with Ni grown CNFs [14] that were fabricated with identical substrate and fabrication parameters. From these different macroscopic geometries, only MWCNT with porous structure tentatively promotes formation of ‘true’ thin liquid layer, which will be shown in the upcoming sections of this study. With cyclic voltammetry the effect is very dependent on the applied scan rate as it affects the thickness of the diffusion layer. With a certain range of scan rates, diffusion layer thickness can be matched with the thickness of porous MWCNT layer.

More extensive description of carbon nanomaterials physico-chemical properties has been reviewed in Ref. [5].

4. Results and discussion

4.1. Electrochemical performance in phosphate-buffered saline

Measurement of potential of zero total charge is quite difficult for such reactive electrodes as here because adsorption from the electrolyte is very hard to avoid. The most reproducible data was obtained by using HClO₄ as expected, because of the very low adsorption tendency of its components on even as reactive surface as our carbonaceous nanomaterials. It turned out that it was also possible (although not easy) to measure the pztc in undiluted PBS at different pHs, the only exception being CNFs. The results from the pztc measurements are shown in Fig. 3 and the values collected in Table 2. For clarity each curve is plotted separately in Fig. 3. The overlaid plots are shown in Fig. S3. It should be noted that all the capacitance minimums shown are very broad, because of the heterogeneous nature of the surfaces. In principle, we can assume that we have an ensemble of local pztc values originating from local chemistries on the surface that contribute to the measured sum curve. Isoelectric point or open circuit potential can in general be taken to be about the same as pztc, if there is no specific adsorption on the electrode surface using dilute electrolytes. These different variables can be correlated (approximately) using the linear relationship between the surface charge and the surface potential by linearizing the Poisson–Boltzmann equation at zero distance i.e. at the surface of the electrode.
under small potential conditions and assuming no specific adsorption, (approximate validity of Gouy-Chapman model must thus be assumed) [42]. Based on the results the OCP and ptzc are quite close, especially in HClO$_4$ as expected, but not always equal, indicating presence of some adsorption in most cases. We can, however, see a trend that pztc is often close, but slightly positive with respect to OCP. A notable exception is SWCNTs where the location of OCP and pztc are reversed. Also, the pztc of SWCNT is negative already at pH 7.4, whereas for the other carbonaceous materials it becomes negative only at higher pH. Typically, Fe and its oxidation products exhibit more negative pztc (or capacitive minimum) in comparison to carbonaceous materials [43]. Thus, in the case of SWCNT the presence of FeOx with larger overall volume ratio to

![Image of capacitance graphs for various carbon nanomaterials](image-url)
carbon matrix than in any other carbon nanomaterial in this set may explain this behavior as the measured values are then a mixture of contributions from significant amount of FeOx in addition to carbon phase. By volume ratio we mean the total amounts of carbon and iron (sub)oxides in the sample and it does not take into account the distribution of these species in the system (for instance surface fraction). In all other cases carbon appears to dominate both the pzc and OCP values. At high pH they appear to be more or less the same - most likely all surfaces are practically similar owing to strong OH-adsorption. It is to be noted that the pzc and OCP characterization carried out here is far from complete and thus the values should be taken more like giving indications of what kind of surfaces different redox probes under specific pH conditions would encounter. Likewise, the information should be useful in rationalizing the results from protein adsorption studies carried out under different potential-pH conditions, for instance.

The potential windows in PBS with pH 2.5, 7.4 and 12 are shown in Fig. 4. From the presented data both solvent and analytical potential windows are defined and tabulated in Table 3. Former is defined by decomposition of water, where hydrogen is produced at the cathodic (hydrogen evolution reaction, HER) end and oxygen at the anodic end (oxygen evolution reaction, OER), respectively. These reactions are seen as the exponential increase in the current. However, from the electroanalytical point of view, it is more practical to define a potential window where analyte signal can still be measured i.e. analyte oxidation/reduction is not yet overrun by HER and OER, even though the Table 2
Point of total zero charge and open circuit potential of carbon nanomaterials in PBS and HClO4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH 2.5</th>
<th>pH 7.4</th>
<th>pH 12</th>
<th>pzc/OCP in PBS (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>pH 2.5</td>
<td>pH 7.4</td>
<td>pH 12</td>
<td>pzc/OCP in PBS (V)</td>
</tr>
<tr>
<td>a-C</td>
<td>0.33/0.25</td>
<td>0.11/-0.05</td>
<td>0.05/-0.08</td>
<td>0.31/0.11</td>
</tr>
<tr>
<td>ta-C</td>
<td>0.35/0.21</td>
<td>0.06/0.01</td>
<td>0.00/-0.15</td>
<td>0.31/0.16</td>
</tr>
<tr>
<td>GC</td>
<td>0.38/0.28</td>
<td>0.13/0.17</td>
<td>-0.05/-0.04</td>
<td>0.38/0.32</td>
</tr>
<tr>
<td>PyC</td>
<td>0.55/0.40</td>
<td>0.30/0.17</td>
<td>0.05/0.13</td>
<td>0.60/0.41</td>
</tr>
<tr>
<td>CNF</td>
<td>NA/0.38</td>
<td>NA/0.03</td>
<td>NA/-0.10</td>
<td>NA/0.36</td>
</tr>
<tr>
<td>MWCNT</td>
<td>0.55/0.30</td>
<td>0.30/0.11</td>
<td>0.05/-0.03</td>
<td>0.60/0.26</td>
</tr>
<tr>
<td>SWCNT</td>
<td>-0.12/-0.29</td>
<td>0.00/0.05</td>
<td>-0.21/-0.07</td>
<td>-0.15/0.3</td>
</tr>
</tbody>
</table>

Fig. 4. Carbon nanomaterials cyclic voltammograms in PBS with pH 2.5, 7.5 and 12. Black dotted line defines the analytical potential window limit with a threshold current limit of ±10 μA. For all measurements v = 100 mV/s. (A colour version of this figure can be viewed online.)
ever, as PyC is catalyst free material, it is challenging to rationalize what particles catalyze hydrogen evolution reaction to some degree. How

\( \text{(b)} \)

\( \text{pH } 2.5, 7.4 \) and \( 12. \)

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analytical potential window (V) (^{\text{a}})/Solvent potential window (V) (^{\text{b}}) in PBS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 2.5</td>
</tr>
<tr>
<td>a-C</td>
<td>2.43 ± 0.02/2.58</td>
</tr>
<tr>
<td>tc-C</td>
<td>2.42 ± 0.03/2.97</td>
</tr>
<tr>
<td>GC</td>
<td>2.21 ± 0.01/2.45</td>
</tr>
<tr>
<td>PyC</td>
<td>1.04 ± 0.04/1.42</td>
</tr>
<tr>
<td>CNF</td>
<td>1.12 ± 0.02/1.93</td>
</tr>
<tr>
<td>MWCNT</td>
<td>1.34 ± 0.02/1.50</td>
</tr>
<tr>
<td>SWCNT</td>
<td>1.94 ± 0.02/2.16</td>
</tr>
</tbody>
</table>

\( \text{(a)} \) Analytical potential windows are defined with the threshold current limits of ±10 \( \mu \text{A} \) i.e. ±140 \( \mu \text{A/cm}^2, N = 3. \)

\( \text{(b)} \) Solvent potential windows are estimated at area where current starts to increase exponentially owing to massive solvent decomposition.

Table 4

The capacitance values evaluated from CV and EIS measurements carried out in blank PBS. \( C_{\text{pseudo}} \) was calculated with Eq. (1) and \( C_{\text{gb}} \) obtained by fitting EIS data with Randles equivalent circuit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Capacitance (( \mu \text{F/cm}^2 )) in PBS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 2.5</td>
</tr>
<tr>
<td>a-C</td>
<td>109 ± 9</td>
</tr>
<tr>
<td>tc-C</td>
<td>109 ± 9</td>
</tr>
<tr>
<td>GC</td>
<td>179 ± 21</td>
</tr>
<tr>
<td>PyC</td>
<td>408 ± 421</td>
</tr>
<tr>
<td>CNF</td>
<td>709 ± 333</td>
</tr>
<tr>
<td>MWCNT</td>
<td>732 ± 927</td>
</tr>
<tr>
<td>SWCNT</td>
<td>80 ± 52</td>
</tr>
</tbody>
</table>

analytical window as well as smallest pseudocapacitance. Most likely more 'inert' behavior of SWCNT is associated with its highly crystalline structure with less reactive-edge sites as well as the smaller amount of amorphous ‘impurity’ carbon present in the network in comparison to MWCNTs, for instance.

Capacitance values reflect to some degree (i) topology of the electrodes, (ii) cleanliness of the system and (iii) how much of the actual structure is probed with the applied electrochemical method. For example, with EIS, only the surface of the electrode is probed with small high frequency perturbing signals, whereas in CV the entire structure of material is examined. Hence, in general EIS reduces the contribution of the pseudofaradaic reactions to the capacitance (see supporting information, Fig. S5). Therefore, capacitances evaluated with EIS are here referred to as true double layer capacitance \( C_{\text{dl}} \). Values are shown in Table 4, where it can be seen that \( C_{\text{gb}} \) values are considerably smaller when compared to \( C_{\text{pseudo}} \). The most significant change is seen with MWCNT. In this case the reason behind the marked difference is most likely skin effect caused by high frequency signals where the electric field is confined to the very surface of the rather porous and thick MWCNT network, therefore sampling only the immediate interfacial region instead of the whole bulk of the structure as in CV. Otherwise, the ranking of the capacitance values obtained with EIS are consistent with CV. Nyquist, Bode and admittance plots from the measurements can be found from supplementary material (Fig. S6).

When considering biosensing application, a wide analytical potential window is generally preferred as it enables a broader range of analytes to be measured. Also, low capacitance i.e. low background current is beneficial as it enables measuring smaller concentrations of the analyte with a reasonable signal to noise ratio. However, it should be noted that capacitance of the electrode depends also on the applied electrochemical method as discussed above. If high temporal resolution is not needed, there are several methods to reduce the contribution of the capacitive current to the measurements, for example differential pulse voltammetry (DPV).

4.2. Reaction kinetics in outer-sphere redox systems

Outer sphere redox systems are considered to be insensitive to the surface chemistry of the electrode material due to the strong solvation shell around them. Thus, it can be expected that OSR reactions occur without any specific chemical/electrocatalytic interactions with the electrode from a certain fixed distance, typically taken to be located in the outer Helmholtz plane of the electrochemical double layer. Therefore, OSR probes are excellent for characterizing electronic properties of the electrode material.
Here electrode kinetics of carbon nanomaterials was characterized by utilizing two known OSR probes Ru(NH$_3$)$_6^{2+/3+}$ and IrCl$_6^{2-/3-}$ [7, 46]. As a note, Fe(CN)$_6^{4-/3-}$ is more extensively used as an OSR probe than the two mentioned previously. However, it has been shown that ferrocyanide kinetics is sensitive to the sample preparation history [47, 48] and seems to strongly interact with oxygen-based functional groups at the electrode surface [49] and cations in the electrolyte [50, 51]. Thus, Fe(CN)$_6^{4-/3-}$ cannot be considered as an ‘ideal’ OSR system and is therefore omitted here.

CV results for Ru(NH$_3$)$_6^{2+/3+}$ and IrCl$_6^{2-/3-}$ are presented in Figs. 5 and 6 and Table S5 (see also supporting information, Fig. S7). In the case of Ru(NH$_3$)$_6^{2+/3+}$, MWCNT and PyC exhibit truly reversible ($\Delta E_p \leq 59$ mV) behavior with scan rate of 100 mV/s, whereas a-C and GC are just at the limit within the standard deviation. Rest of the electrodes show close to reversible HET, out of which the SWCNT and ta-C have the most sluggish kinetics. The increasing scan rate further demonstrates the quasi-reversible behavior of SWCNT and ta-C as $\Delta E_p$ of these electrode materials are most heavily dependent on the scan rate. On the other hand, opposite phenomenon is seen with MWCNT as $\Delta E_p$ decreases with increasing scan rate. This is expected to be due to a thin film liquid layer effect, where the solution is trapped inside the MWCNT porous structure and exhibits surface confined reaction instead of semi-infinite linear diffusion controlled one [52, 53] since any adsorption related effects should be absent. Increased scan rate further enhances thin film liquid layer effect as it pushes the diffusion layer to be even thinner. The log($i_p$) vs. log($v$) – plot (see supplementary material) supports this observation as slope is > 0.5 for MWCNT. The occurrence of thin film electrochemistry requires that the ratio of the diffusion layer to the surface layer (here MWCNT network) is within certain specific limits [54]. Therefore, the effect seen with MWCNTs is also restricted to a specific range of scan rates where this matching of diffusion layer to surface feature thickness is achieved. The other carbon materials are under conventional semi-infinite linear diffusion control. However, weak adsorption of oxidation product Ru$_3^{3+}$ may take place at the carbon electrodes as reduction current is slightly increased with all materials ($i_{p,a}/i_{p,c} < 1$) [55]. This observation is especially true with porous structures CNFs, MWCNTs and SWCNTs. The lowest peak current ratio is seen with PyC, but it should be noticed that the redox reactions take place at the limit of the analytical potential window (see Fig. 4). Currents are therefore heavily affected by HER, thus it is difficult to evaluate what are the actual peak currents caused by ruthenium reaction.

In the case of IrCl$_6^{3-/2-}$ MWCNT again exhibits the fastest electrode kinetics, which is enhanced by the increasing scan rate. This is most likely due to the similar reasons as discussed above. With a scan rate of

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**Fig. 5.** Cyclic voltammograms of carbon nanomaterials in A) Ru(NH$_3$)$_6^{2+/3+}$ and B) IrCl$_6^{2-/3-}$ in 1 M KCl with scan rate $v = 100$ mV/s. (A colour version of this figure can be viewed online.)
Fig. 6. Average $\Delta E_p$ values as a function of scan rate are shown for both A) Ru(NH$_3$)$_6^{2+/3+}$ and B) IrCl$_6^{3-/2-}$. (A colour version of this figure can be viewed online.)

Table 5

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta E_p$ (mV)</th>
<th>$i_{p,a}$/$i_{c}$</th>
<th>$k^0$ (cm s$^{-1}$) × 10$^{-2}$</th>
<th>$\Lambda$</th>
<th>$A_{eff}$ (cm$^2$) × 10$^{-2}$</th>
<th>$\Delta E_p$ (mV)</th>
<th>$i_{p,a}$/$i_{c}$</th>
<th>$k^0$ (cm s$^{-1}$) × 10$^{-2}$</th>
<th>$\Lambda$</th>
<th>$A_{eff}$ (cm$^2$) × 10$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-C</td>
<td>59 ± 1</td>
<td>0.93 ± 0.05</td>
<td>22.6 ± 2.9</td>
<td>45 ± 6</td>
<td>5.7 ± 0.0</td>
<td>69 ± 2</td>
<td>0.97 ± 0.02</td>
<td>2.4 ± 0.6</td>
<td>5 ± 1</td>
<td>1.6 ± 0.0</td>
</tr>
<tr>
<td>ta-C</td>
<td>76 ± 2</td>
<td>0.92 ± 0.01</td>
<td>1.3 ± 0.2</td>
<td>3 ± 0</td>
<td>5.6 ± 0.0</td>
<td>120 ± 1</td>
<td>0.96 ± 0.05</td>
<td>0.3 ± 0.0</td>
<td>1 ± 0</td>
<td>0.3 ± 0.0</td>
</tr>
<tr>
<td>GC</td>
<td>59 ± 2</td>
<td>0.95 ± 0.00</td>
<td>23.8 ± 6.1</td>
<td>47 ± 12</td>
<td>5.7 ± 0.0</td>
<td>59 ± 1</td>
<td>1.30 ± 0.22</td>
<td>23.2 ± 3.4</td>
<td>44 ± 6</td>
<td>2.4 ± 0.1</td>
</tr>
<tr>
<td>PyC</td>
<td>51 ± 2</td>
<td>0.29 ± 0.02</td>
<td>44.2 ± 4.9</td>
<td>87 ± 10</td>
<td>12.6 ± 1.2</td>
<td>66 ± 3</td>
<td>1.09 ± 0.7</td>
<td>2.7 ± 0.5</td>
<td>10 ± 8</td>
<td>2.5 ± 0.1</td>
</tr>
<tr>
<td>CNF</td>
<td>61 ± 1</td>
<td>0.82 ± 0.01</td>
<td>16.8 ± 3.3</td>
<td>33 ± 7</td>
<td>5.3 ± 0.1</td>
<td>63 ± 4</td>
<td>1.07 ± 0.02</td>
<td>13.7 ± 11.1</td>
<td>26 ± 21</td>
<td>2.2 ± 0.0</td>
</tr>
<tr>
<td>MWCNT</td>
<td>50 ± 1</td>
<td>0.79 ± 0.06</td>
<td>41.9 ± 4.6</td>
<td>83 ± 9</td>
<td>6.1 ± 0.4</td>
<td>49 ± 2</td>
<td>1.31 ± 0.13</td>
<td>51.7 ± 5.1</td>
<td>98 ± 10</td>
<td>2.1 ± 0.5</td>
</tr>
<tr>
<td>SWCNT</td>
<td>73 ± 1</td>
<td>0.85 ± 0.03</td>
<td>1.6 ± 0.1</td>
<td>3 ± 1</td>
<td>5.7 ± 0.2</td>
<td>69 ± 2</td>
<td>0.98 ± 0.04</td>
<td>5.2 ± 0.4</td>
<td>5 ± 1</td>
<td>2.0 ± 0.1</td>
</tr>
</tbody>
</table>

100 mV/s GC also shows reversible behavior and the rest of the electrodes are close to reversible HET kinetics except for ta-C. When comparing ta-C to a-C it is expected that the reaction kinetics (in both IrCl$_6^{3-/2-}$ and Ru(NH$_3$)$_6^{2+/3+}$) decreases with increasing film thickness [11]. Thicker layer has more bulk region with higher sp$^3$ content, which reduces the overall reaction rate due to slower electron transport inside the film owing to its dielectric properties. Furthermore, increasing scan rate has the highest impact on ta-C. From log-plots slope of 0.37 is seen for ta-C, which suggests that there are additional factors contributing to the overall kinetics than mere semi-infinite linear diffusion, for instance the already mentioned electron transport through the film.

When comparing Ru(NH$_3$)$_6^{2+/3+}$ and IrCl$_6^{3-/2-}$ results, very different redox peak currents are seen for the two OSR probes. With IrCl$_6^{3-/2-}$ the observed currents are approximately half or less of that of the Ru (NH$_3$)$_6^{2+/3+}$ redox currents, as seen from Table 5, where electrochemically effective area $A_{eff}$ evaluated based on anodic peak currents are reported (see also Fig. S9). What might be the cause of this marked difference? One contributing factor is that redox probes are seeing very differently charged electrode surfaces in the case of Ru (NH$_3$)$_6^{2+/3+}$ and IrCl$_6^{3-/2-}$. In pH of 7.4 the pzc is around 0–0.1 V vs. Ag/AgCl for the carbon based electrodes. The formal potentials of the Ru (NH$_3$)$_6^{2+/3+}$ and IrCl$_6^{3-/2-}$ redox probes are about −165 mV and 790 mV vs. Ag/AgCl, respectively. This translates into the fact that during the former reaction surface will be mildly negatively charged (as we are quite close to the pzc) whereas during the latter reaction the surface will be strongly positively charged. It is known that cations in the supporting electrolyte will not adsorb specifically very easily owing to their strong solvation sheet. On the other hand, anions are much more easily specifically adsorbed even in the case of unfavorable electrostatic interactions and thus it is likely that at the potential range of IrCl$_6^{3-/2-}$ reaction there are a lot of specifically adsorbed co-anions as well as strongly bound solvent molecules on the electrode surfaces that can decrease the overall kinetics of the reaction, by affecting the distance of closest approach of the OSR probe. Another interesting outcome observed from evaluating $A_{eff}$ is that no significant changes are seen in the effective electrochemical area between different carbon materials. Generally, it is expected that current response enhancements with increased surface area, for example with MWCNTs and CNFs. However, in the case of OSR probes higher surface area does not appear to have that of a high impact.

Carbon nanomaterials were further characterized with EIS. The Nyquist plots obtained from the measurements in Fig. 7 were fitted with Randles circuit model together with Warburg diffusion element and CPE as the double layer capacitance. Bode plots are presented in supplementary material. The obtained parameters from the fitting are presented in Table 6. It is to be noted that in the case of ta-C a modified Randles circuit as presented in Ref. [11] would be more appropriate, but here the same equivalent circuit has been used for all electrode materials to have a consistent data set.

The $Q_0$ values obtained from the fitting are very low (varying from 0.5 to 3.5 μF cm$^{-1}$) for most of the electrodes as already discussed above. Only GC and CNF had higher capacitances with values of 72 and 43 μF cm$^{-1}$, respectively. Interestingly, obtained parameter μ indicates that MWCNTs constant phase element behaves like an ideal capacitor, whereas with GC the CPE is close to the Warburg diffusion element. With other carbon nanomaterials the constant phase exponent μ varies between 0.7 and 0.85. Observed value for MWCNT most likely arises as only the immediate surface is probed with EIS. The charge resistance values are also considerably low for these electrodes, especially for PyC, MWCNT and CNF with $R_p$ around 5–7 Ω. $R_p$ obtained for a-C and GC are slightly higher with values of 28 Ω and 32 Ω, respectively. The largest $R_p$ are seen for ta-C and SWCNT, which is consistent with the CV results discussed above. It should be noticed that no clear semi-circle is observed from Nyquist plot for GC as reaction is mainly under diffusion control. To verify that observed electrode kinetics for GC and other carbon nanomaterials in EIS is consistent with the results from CV we calculated theoretical $\Delta E_p$ with the heterogeneous electron transfer rate $k^0$ fitted from the Nyquist plot (see Table 6). Calculations show that...
using the heterogeneous rate constant from the EIS fitting for these systems provides very similar peak-to-peak separation as actually observed in CV measurements. We highly recommend that CV would be used together with EIS to make a sanity check for the obtained kinetic parameters from the fitting.

Here heterogeneous rate constants are obtained with both EIS and CV. It can be seen that \( k^0 \) does not significantly variate between the methods (comparison illustrated in Fig. S11). While the values for few samples differ a bit, it should be noticed that (i) Nicholson method is most accurate at quasi-reversible region and (ii) even small changes in peak-to-peak separation have drastic effect on \( k^0 \), especially when near the reversible limit. For example, with CV the peak separation for a-C is \( \Delta E_p = 59 \text{ mV} \) and \( k^0 = 0.226 \text{ cm s}^{-1} \) for Ru(NH\(_4\))\(_2\)(I\(_3\))\(_2^2-\), whereas with EIS a decade smaller \( k^0 = 0.054 \text{ cm s}^{-1} \) produces \( \Delta E_p \) of 64 mV. Additionally, millivolt changes in peak-to-peak separation around reversible area are also seen as larger standard deviations in \( k^0 \) and Matsuda-Ayabe parameter \( \Lambda \) evaluated from the CV data (see Table S5).

EIS characterization of carbon nanomaterials is typically carried out in Fe(CN)\(_6\)^{3-/4-} [58,59]. Thus, it is challenging to find a comprehensive set of publications to compare results presented here. To our knowledge, EIS characterization in IrCl\(_6\)^{2-/3-} hasn’t been done with materials investigated here. Most likely due to low solubility of IrCl\(_6\)^{2-/3-} in aqueous solutions i.e. high enough concentrations cannot be prepared to clearly distinct the kinetic and mass transfer contributions. Thus, in this case in particular and also more generally, cross checking the kinetic data from CV and EIS is a very good idea.

4.3. Reaction kinetics in inner-sphere redox system

Here DA was used as a benchmark inner-sphere probe for comparing carbon electrodes. DA was chosen due to its relevance for biosensing applications and wide use as a proof-of-concept ISR probe for new electrode materials providing us with a solid basis for placing our results into a wider context. Inner-sphere redox reactions are strongly affected by the specific chemical interactions between the electrode surface and the redox species [46]. Process that generally takes place is adsorption by the specific chemical interactions between the electrode surface and the redox species. Process that generally takes place is adsorption that can either lead to enhanced (electrocatalytic) or inhibited redox process. ISR systems are well known to be sensitive to electrode surface chemistry, but as discussed in the introduction, several other factors can also affect the interactions between the electrode material and ISR probe.

DA measurements with scan rates of 50 mV/s and 1000 mV/s are shown in Fig. 8 and Table 7. In addition, stacked plots from DA measurements are shown in Fig. S12. At slower scan rate both MWCNT and SWCNT show reversible electrode kinetics with \( \Delta E_p \) of 25 ± 1 mV and 28 ± 3 mV, respectively. Symmetrical shape of the redox peaks and slope from log-plot (Fig. S13 in supplementary material) in both cases clearly indicates that additional factors are enhancing the overall kinetics.
Additionally, the peak currents seen with MWCNT are significantly higher than with the other carbon electrodes. With scan rate of 1000 mV/s $\Delta E_p$ increases with GC and specifically with MWCNT i.e. ET is not sufficiently fast to keep up with increased flux although reversible kinetics is observed with 50 mV/s. Generally, more notable increase of $\Delta E_p$ is expected in case of ISR probes as overall electrode kinetics is more complex than with OSR.

The other carbon electrodes are under semi-infinite linear diffusion control as seen from the log-plot and conventional shape of the CV with a clear diffusional tail. Relatively rapid kinetics is also observed with other Fe-containing electrodes (CNF and SWCNT), whereas PyC, a-C and specifically ta-C exhibits show sluggish kinetics. Peak currents are clearly highest with the MWCNT electrode, GC being the second highest. The peak current ratio $i_{p,a}/i_{p,c}$ decreases with increasing scan rate in all cases. With 1000 mV/s $i_{p,a}/i_{p,c}$ becomes close to 1 with almost all the electrodes. Observed behavior is understandable due to ECE reaction mechanism of dopamine [60,61], where the oxidation product dopamine-o-quinone has less time to chemically react to dopamine.

**Fig. 8.** Cyclic voltammograms of carbon nanomaterials in 100 $\mu$M DA, PBS (pH 7.4) with scan rates of A) 50 mV/s and B) 1000 mV/s. (A colour version of this figure can be viewed online.)

**Table 7**
Results of the cyclic voltammetry measurements in 100 $\mu$M DA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$v = 50$ mV/s</th>
<th>$v = 1000$ mV/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta E_p$ (mV)</td>
<td>$E_{p,a}$ (mV)</td>
</tr>
<tr>
<td>a-C</td>
<td>197 ± 11</td>
<td>292 ± 8</td>
</tr>
<tr>
<td>ta-C</td>
<td>371 ± 13</td>
<td>425 ± 11</td>
</tr>
<tr>
<td>GC</td>
<td>29 ± 4</td>
<td>175 ± 2</td>
</tr>
<tr>
<td>PyC</td>
<td>121 ± 18</td>
<td>236 ± 12</td>
</tr>
<tr>
<td>CNF</td>
<td>54 ± 4</td>
<td>191 ± 3</td>
</tr>
<tr>
<td>MWCNT</td>
<td>25 ± 1</td>
<td>186 ± 1</td>
</tr>
<tr>
<td>SWCNT</td>
<td>49 ± 4</td>
<td>186 ± 3</td>
</tr>
</tbody>
</table>
chrome and subsequently electrochemically oxidize to leucodopaminechrome as the scan rate is progressively increased. Thus, there is more and more dopamine-o-quinone available for the reduction reaction subsequently shifting the current ratio towards one.

Detection of DA with a-C and ta-C is consistent with previous studies [40,62], where relatively slow kinetics is seen for these smooth carbon films. Observed oxidation potential for a-C is 292 mV and for ta-C 425 mV, respectively. Thicker film (ta-C) with higher sp² content show increase in $\Delta E_p$ as expected based on the observations with OSR probes owing to increasing charge transport resistance through the film. In addition to the lower sp² content, slightly faster kinetics with a-C is most likely associated with the higher amount of oxygen functional groups on its surface [12]. Oxygen functional groups, especially those that have the ability to form hydrogen bonds, are expected to make the proton tunneling during the DA oxidation reaction strongly adiabatic, subsequently reducing the activation energy for the overall reaction [63].

PyC exhibits slightly faster kinetics ($E_{\text{ox}} = 236$ mV) in comparison to a-C and ta-C. Based on our earlier results [22] DA reaction kinetics on PyC is heavily dependent on the overall amount of oxygen and the nature of the functional groups on the electrode surface. A combination of high total amount of oxygen and the presence of hydroxyl groups was observed to facilitate the fast kinetics of DA on PyC. In Ref. [22], we showed that oxygen plasma treatment of PyC greatly enhanced the overall kinetics on the PyC surface in comparison to untreated sample. Again this may be related to increased adsorption of reaction species as the slope of the log (i) vs. log (v) plot was observed to be $>0.5$ for the high oxygen containing samples [22]. In the present sample set of PyC the overall oxygen content is, however, significantly lower than the amounts that were observed to produce facile kinetics in the previous studies.

From only carbon containing materials investigated here, GC shows very fast electrode kinetics. Oxidation of DA ($E_{\text{ox}} = 175$ mV) occurs close to ptzc of GC. Interestingly, $E_{\text{ox}}$ is also relatively close to Fe-containing carbon nanomaterials. Most probably at least some adsorption takes place at the surface as symmetrical peaks are seen in CV. The edge planes terminated with oxygen functional groups and porous surface structure are favorable for DA redox reactions. However, it is rather challenging to rationalize observed electrochemical response as GC structure is not fully understood and the surface properties strongly depend on the polishing procedure [64]. Thus, it is highly likely that surface chemistry and microstructure of GC can vary widely from lab-to-lab. Also, GC is easily contaminated during electrochemical experiments, especially in case of the surface sensitive ISR probes. Thus, it requires polishing and cleaning between every measurement which makes it very impractical material to use. As a result of polishing, GC surface can contain impurities such as alumina and carbon microparticles [65]. For instance in Ref. [66], it was observed that the presence of alumina on particles dispersed on glassy carbon surfaces would strongly adsorb compounds such as catechols and catalyze their oxidation.

All Fe-containing materials (CNF, MWCNT, SWCNT) show more or less sufficient electrode performance towards DA. In all cases $E_{\text{ox}}$ is close to 190 mV vs. Ag/AgCl. Electrochemical response with MWCNT is strongly affected by a thin film liquid layer effect. This porous ‘forest-type’ of structure easily traps solution inside of the MWCNT network as discussed above in the case of OSR probes. As MWCNT surface charge is negative at $E_{\text{ox}}$ of DA, it is quite likely that electrostatic interaction enhances the thin film liquid layer effect. Also, a high amount of reactive sites on MWCNT interacts with the observed current response. This number can be affected by several factors such as the amount of edge plain sites [46], presence of residual amorphous carbon [67], high internal surface area of MWCNT, and electrocatalytic effect caused by the residual Fe metal(oxide) particles [68].

One would expect that all these factors are somewhat similar to CNF. However, the response is very different from multi-walled CNTs. Overall kinetics is relatively rapid, but evidently limited by diffusion. More ‘open’ structure of CNF does not appear to facilitate formation of a thin film liquid layer at the surface or at least not with the magnitude that would have significant effects on the electrode kinetics. Fe particles at the tip, high content of oxygen functional groups and edge type sites at the sides of the trunk of the CNFs most likely enhance fast kinetics, but current response is still fairly low. In the case of CNF, Fe metal particles are larger and most likely largely oxidized as well as located almost strictly at the tips of the fibers. However, based on these results it is hard to draw any conclusions on how composition of Fe effects on the electrode performance. In our previous study [18] we have shown that higher FeOx content in the SWCNT network can shift oxidation potentials of some of the analogesics, but without a more comprehensive study it is difficult to state what is the case with dopamine, which is outside the scope of this manuscript.

Rather interesting observation is that SWCNT has a relatively similar response as CNF, when background current is not taken into account, although there are clear differences in material properties. The structure of SWCNTs is crystalline and absent of (more or less) amorphous carbon. The amount of edge plane sites is also expected to be significantly smaller than with CNF, which leads to lower content of oxygen functional groups at the surface. Furthermore, the size of Fe particles in SWCNT network is smaller and more unevenly distributed. Regardless of these differences similar responses are seen with DA even with higher scan rates.

The observations done here demonstrate quite well the complexity of reactions occurring via inner-sphere route. It is difficult to rationalize what are the exact properties that favors detection of DA as the relationship between structure-surface chemistry and electrochemical performance is not always that evident. However, based on the observed results, we argue that reaction kinetics of carbon nanomaterial is enhanced when (i) it has porous structure that enables thin film liquid layer effect, (ii) residual metal particles that can catalyze the redox reaction and (iii) favorable surface chemistry facilitating proton tunneling if required in the overall reaction scheme.

To summarize, most of the target molecules relevant for the electroanalytical applications react via inner-sphere route. As the interactions between electrode material and ISR probe (as well as electrolyte) are very much case specific, it is highly important to characterize the physicochemical properties of the electrode materials in as much detail as possible to gain a deeper understanding of the associations between structure and electrochemical performance of the material of choice. Finally, it is important to note that reversible kinetics utilizing OSR probes is not sufficient to expect good electrochemical performance with any kind of ISR probe owing to the drastic differences in nature of the processes, the former being electron and latter ion transfer type of reaction.

5. Conclusion

In this work, we provide the first comprehensive set of electrochemical characterization of carbon nanomaterials with known physicochemical properties including (i) values of ptzc, OCP, double layer capacitance, pseudocapacitance as well as solvent and potential windows in PBS, (ii) heterogeneous electron transfer coefficients and reaction kinetics for a selection of outer- and inner-sphere probes. This study clearly demonstrates the versatile electrochemical properties of different carbon allotropes. It can be concluded that the width of the potential window correlates strongly with capacitance value and morphology. Carbon nanomaterials with non-planar structure exhibit higher capacitances values due to increased reactivity of the surface and thus decreasing the potential window, both solvent and analytical. Although wide potential window and small capacitance are desired in electroanalytical applications, they are often properties of an inert material, which contradicts the requirement for the reactivity towards the target molecules to enhance sensitivity.

In case of OSR no significant differences are seen between the materials studied. The slight differences observed can be rationalized based
on if (i) sp³ is present, as seen decrease of HET with ta-C, or (ii) how far from the ptc (or OCP) of the electrode material the formal potential of the probe molecule is. At this point it is important to note that there is no correlation between HET as determined with MSR probes and the electrode performance in case of ISR probes. This is because the former is purely electron transfer reaction depending mostly on the electronic structure of the electrode material whereas the latter one in an ion transfer reaction influenced heavily by surface chemistry and other complications. For example, in the case of DA, the presence of Fe-catalyst favors reaction kinetics, as does a surface morphology that enables thin film layer effect. In addition, surface chemistry facilitating hydrogen bonding with the DA molecule enhances proton tunneling and thus the kinetics of the reaction. This is of course not transferrable to other ISR reactions as the specific interactions are always case specific.

As in this study, at all stages we strive to find associations between the known structure of these carbonaceous nanomaterials and their electrochemical performance, we feel that these results provide a solid base for future in-depth research of carbon allotropes and can act as an information source for these studies.

CRediT authorship contribution statement

Elli Leppänen: Investigation, Conceptualization, Validation, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. Maedeh Akhhoundian: Investigation, Formal analysis. Sami Sainio: Investigation, Formal analysis. Jarkko Etula: Resources, Writing – original draft. Olli Pitkanen: Resources, Writing – original draft. Tomi Laurila: Supervision, Conceptualization, Writing – original draft, Writing – review & editing.

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.

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Appendix A. Supplementary data

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References


