

# Electrochemical Pretreatments of Carbon Paper and Their Effect on the Electrodeposition of Metallic Nanostructures

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Gas diffusion electrodes (GDEs) represent a fundamental element for the development of gaseous electrochemical cells like water electrolysis reactors and fuel cells.

Various technologies and materials are employed in order to obtain a conductive, stable and gas permeable structure. Among them, carbon-based structures such as carbon paper are widely used: their composition allows the diffusion of gaseous reagents and products and simultaneously does not permit the flooding of the gas-diffusion structure by aqueous electrolytes. However, the hydrophobicity of this material may represent a drawback to water-based electrode synthesis like galvanic deposition, and various chemical or thermal pretreatments were developed in the last decades.

A new kind of pre-treatment based on electrical oxidation of the carbon paper surface is here described and evaluated. The electro-oxidative method allows a rapid and localized pre-treatment of the carbon paper, avoiding the use of highly reactive chemicals or long thermal treatments, reducing treatment wastes, time loss and electrical consumption.

Surface wettability of the carbon paper before and after pretreatment was compared by contact angle analysis.

Pre-treated and virgin carbon paper were subsequently electroplated from a copper deposition bath and deposition morphologies were compared, in order to establish the effect of the pre-treatment. Electroplated supports were analyzed by scanning electron microscopy (SEM) in order to analyze both micro and nanomorphology of the metallic structure.

## 1. Introduction

Carbon paper is a carbon-based material widely used in the production of electrochemical cells such as fuel cells, redox flow batteries or water splitting cell (Dicks & Rand, 2018). Being a light, conductive and porous material, it is currently employed both as electrode support and as electrode, according to the specific process requirement. Its main technical property consists in its gas permeability, associated with an almost complete impermeability to aqueous fluids. These characteristics are a consequence of the carbon paper structure and composition. The paper is composed of two different layers: a carbon fiber-based film and a thinner film of carbon nanoparticles, called gas diffusion layer (GDL). A fluorinated polymer, usually PTFE, is dispersed in both structures acting as ligand and anti-wetting agent.

Carbon paper-based electrodes may allow the input of gaseous reactants or the extraction of gaseous reaction products. Such electrodes are known gas diffusion electrodes (GDEs).

Various techniques were designed for the production of electrodes using carbon papers as support: chemical functionalization of the carbon paper, obtained by the introduction of functional groups or single atoms in the carbon structure (Singh et al., 2019), or deposition of active species on the support structure (Lisi et al., 2011). Among deposition strategies, the galvanic electrodeposition represents a promising synthesis method (Dhiman & Ivey, 2020). This technique may be used to obtain a morphological controlled deposition of metals or metal derivatives onto a conductive support. It is easily scalable and requires a simple technical equipment. Nevertheless, carbon paper specific proprieties represent a possible obstacle to the galvanic synthesis: being the support hydrophobic, the contact with the electrodeposition bath is partially hindered, leading to

uncomplete and inhomogeneous coverage of the deposition support. In order to exploit the advantages of the galvanic synthesis, wetting proprieties of the carbon paper need to be modified and various pretreatment were adopted to such an aim.

Chemical pretreatments are the most common kind of modifications adopted (Hu et al., 2017). Carbon paper is submerged in either concentrated mineral acids, inorganic oxidants or a mixture of them. The target is the partial oxidation of the carbon structure, leading to the formation of hydroxyl or carboxyl groups. Those treatments may affect the whole structure of the carbon paper, and a partial disintegration of the support may happen.

Thermal pre-treatments have been previously evaluated for modification in carbon-based electrodes for applications on redox flow batteries both applying thermal oxidation (Greco et al., 2018) or thermal-induced modifications of the structure (Liu et al., 2017). Modifications in the carbon paper structures were observed: enhanced porosity, a deeper wetting degree and a deterioration in the mechanical resistance of the whole paper structure. While a wetting increase is a remarkable target, the induced fragility and the treatment duration (from several hours to more than a day) represent a strong drawback in the application of thermal operations as pretreatments for the galvanic deposition on carbon paper.

In order to ease the application of galvanic techniques in the GDE nanosynthesis, it is required the development of an efficient and fast carbon paper pretreatment whose application does not requires toxic, corrosive or environmentally hazardous reagents or long, energy consuming thermal operations. In this context, electrical treatments could be suitable, being already applied in the alteration of the interaction between liquids and solid surfaces, e.g. by electrowetting (Mugele & Baret, 2005) and electro-oxidation.

Electro-oxidation, induced by placing the carbon paper support into an electrolytic cell and imposing to the material a suitable electrical potential, possesses various appealing features.

This process requires as reagent only a conductive fluid, the electrolytic solution. Various kind of electrolytic solutions may be used. The choice of an aqueous solutions of non-toxic, highly dissociated salts may lead to a good electrical conductivity, a simplification in the wastewater's management and a reduction in the cost of the reagents.

In second instance, electrochemical oxidations are surface-linked processes, and their action is localized on the electrode-electrolyte interface. By using an electro-oxidative process instead of a chemical or a thermal process, the only affected area would be the surface of the electrode in direct contact with the electrolyte. This allows a modification of the external electrodeposition sites with scarce alteration in the overall structure of the bulk material, without modifications in its global hydrophobicity and its mechanical properties. Furthermore, the process is completely driven by electricity, so the required power may be obtained from renewable sources.

An electro-oxidation process was already tested on nanowire-coated carbon paper, obtaining modifications in wettability and superficial properties, using nitric acid as electrolyte (Bordjiba et al., 2007).

In this work, an oxidative treatment was developed and analyzed in order to verify the feasibility of an electrical pretreatment to the galvanic electrodeposition on carbon paper.

An aqueous solution of sodium acetate was utilized as electrolyte, being this substance a cheap, non-toxic bulk chemical whose degradation does not produce dangerous byproducts.

The effects of the pretreatment were at first evaluated by analysis of the carbon paper behavior pre and post oxidation. Subsequently, electrodeposition tests were performed to observe eventual effects of the pretreatment on deposition yield, distribution and morphology.

## 2. Materials and methods

### 2.1 Pretreatment

The carbon paper support (Sigracet, GDL 39 BC) was purchased in foils and cut in smaller samples with a geometrical surface of 1 cm<sup>2</sup>.

In order to test the pretreatment effect on a specific side of the carbon paper, both GDL-exposed and fiber-exposed samples were prepared.

The electrolytic solution was prepared by an aqueous 1 M sodium acetate solution (Sigma, 99 %).

A three-electrode setup was used for the oxidative pretreatment. Carbon paper samples were placed as working electrodes, while a graphite foil (Alfa Aesar, 99.8 %) was used as counter-electrode. A silver-silver chloride electrode (Amel Instruments, R1/AG-AGCL/4MMSKT) working with 3.0 M potassium chloride solution was used as reference.

The electrolytic cell was thermostated at 25 °C and stirred by a magnetic stirrer.

The pretreatment was carried on in potentiostatic mode, imposing -3.0 V vs Ag/AgCl 3 M KCl to the working electrode for a fixed period of time. The same pretreatment conditions were applied for 1, 5 or 10 minutes. Electrical parameters were controlled by a digital potentiostat (Ivium, Nstat), used for all the electrochemical procedures.

After the pretreatment, carbon paper samples were washed with distilled water, rinsed with ethanol (Carlo Erba Reagents, 96 %) and then dried at room temperature.

## 2.2 Contact angle observations and Electronic Impedance Spectroscopy

Qualitative contact angle observations were performed in order to evaluate the superficial wetting degree of the carbon paper before and after the pretreatment. 100  $\mu$ L of an aqueous solution of 0.001 % w/w methylene blue (Alfa Aesar) were placed on a plain carbon paper sample and the wetting angle was observed by photographing the droplet profile against a white background. Observation was performed 1 min after the droplet releasing on the surface.

Treated and untreated carbon paper samples were characterized by electronic impedance spectroscopy (EIS). EIS scans were performed using a three-electrodes setup, having platinum wire as counter electrode and the Ag/AgCl electrode as reference.

EIS were performed in an aqueous electrolyte of 1 M sodium chloride (Sigma Aldrich), thermostated at 25 °C. The impedance analysis was carried on in the range 100 kHz – 10 mHz, with an amplitude of 10 mV from the open cell circuit measured for each electrode.

A flat graphite foil electrode with a geometrical area of 1 cm<sup>2</sup> was analyzed with the same setup and in the same conditions.

## 2.3 Electrodeposition

Carbon paper supports were electroplated using an additivated deposition bath, obtained by an aqueous solution of 0.1 M CuSO<sub>4</sub> (VWR Chemicals, 99.7 %) and 0.01 M 3,5-diamino-1,2,4-triazole (DAT, Alfa Aesar, 98 %). Bath pH was regulated at 2.0 by addition of sulfuric acid.

The same three-electrodes setup described for the pretreatment was used.

Electrodeposition was carried on in a galvanostatic mode, imposing a deposition current density of -2 mA/cm<sup>2</sup> and a deposition charge of 4 C/cm<sup>2</sup>. The deposition cell was thermostated at 25 °C and the deposition bath was stirred.

Electroplated samples were washed with distilled water, rinsed with ethanol 96 % and then dried at room temperature.

## 2.4 Deposition characterization

Deposition abundance, i.e. the actual amount of copper electroplated on the support, was quantified by acidic leaching of the electrode and subsequent atomic absorption spectrometry (AAS) analysis.

Each electroplated sample was placed in 10 mL of aqua regia and leached in a static setup for 2 h. After that, the leaching solution was normalized at 100 mL with water and then adequately diluted for the AAS analysis.

The atomic absorption spectrometer was calibrated by external standards (1, 2, 3 and 5 mg/L of copper nitrate in nitric acid aqueous solution).

Electrode micro and nanomorphology was observed by scanning electronic microscopy (SEM). SEM measurements were performed using a Zeiss AURIGA FESEM with an electron energy in the range 10 -15 keV. Being the electroplated support a dry, conductive material, samples required no pretreatment besides the mechanical removing of the PVC film prior of being analyzed.

# 3. Results and discussion

## 3.1 Pretreatment direct effects

PTFE-treated carbon paper exhibits some classical behavior of high hydrophobicity. The material does not show any sign of macroscopic wetting even when submerged for several hours in water and water drops show no sign of maintaining contact with the carbon paper structure, both on the fibrous side or the GDL side. The presence of an air film adherent to the carbon paper surface may be observed in submerged carbon paper as a mirror-like film. This behavior of total internal reflection is a common feature of hydrophobic structures (Jiang et al., 2015) and may be observed both in synthetic or natural materials.

Contact angle observations were made in order to give an approximated but clear vision of the modification occurred in the carbon paper structure after the pretreatment. Being this observation purely qualitative, a manual procedure was utilized. Instead of pure water, a diluted methylene blue aqueous solution was used. This choice was made in order to achieve the best visualization of the droplet's contact border without the necessity of complex instruments and experimental setups.

Droplet of this reference solution placed on the surface behaved differently according to the nature of the substrate.

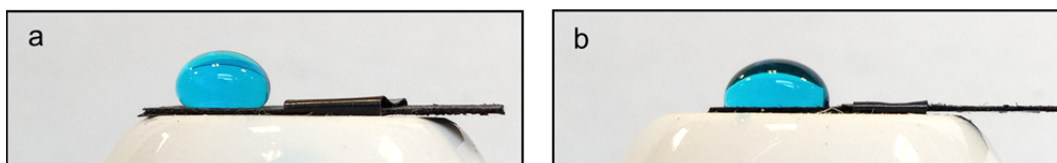


Figure 1: Contact angle observation of dyed water droplets on the surface of a carbon paper support, fibrous side. (a) untreated support; (b) 10 min-treated support.

As shown in Figure 1, untreated carbon paper samples present clear signs of hydrophobicity, showing a pronounced contact angle. When the droplets were removed by cleaning the surface with distilled water, the support showed no macroscopic appearance of wetting. This is due to the simultaneous presence of hydrophobic polymers and hydrophobic graphitic micro and nanostructures on the surface of the carbon paper. Treated carbon paper showed a decreasing in the wetting degree and macroscopic signs of wetting. EIS were performed in order to analyze the behavior of the carbon paper as electrode in an aqueous electrolyte.

A concentrated sodium chloride solution was used to achieve the adequate conductivity needed. The impedance scan, conducted at the open cell voltage specific for each electrode, was conducted both on carbon paper samples and graphite foil samples as a mean of comparison between the carbon paper itself and a hydrophilic carbon-based structure.

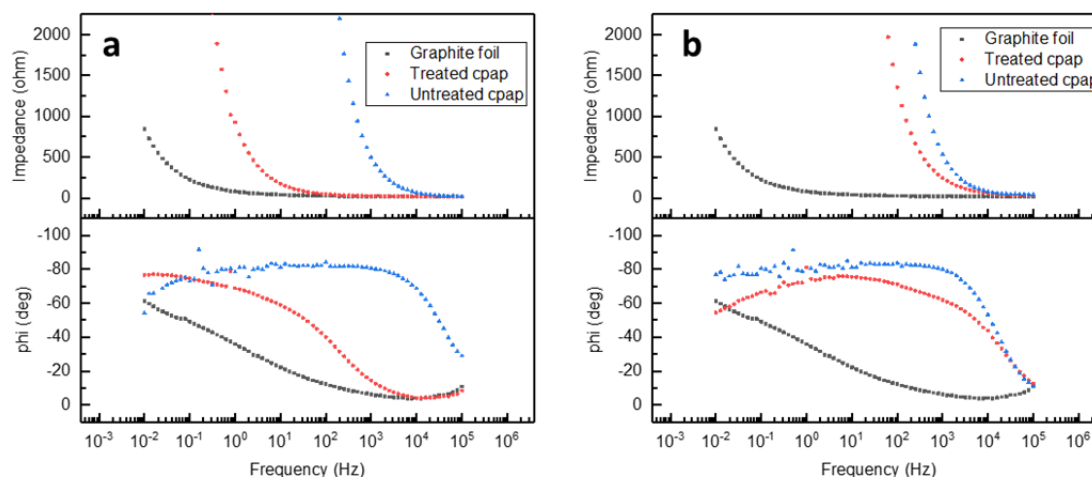


Figure 2: Electronic impedance spectra of untreated carbon paper (blue), 10 min-treated carbon paper (red) and graphite foil (black). Spectra are represented as Bode plots: impedance absolute value and phase response of the system is analysed as a function the applied frequency. (a) GDL side (b) fibrous side.

Bode diagrams obtained from the EIS are shown in Figure 2. Considering the GDL side, the electrode behavior of the untreated support differs strictly from a sample pretreated for 10 min. The latter is closer, both in impedance and in phase displacement, to the graphite foil response to alternated current. This underlines a possible modification of the carbon paper structure towards a more hydrophilic structure.

It is important to notice that this modification is only slightly observed on the pretreated fibrous side of the carbon paper, as shown in the Bode diagram. This observation denotes a difference in the response of the carbon paper to the pretreatment: the GDL structure seems to be more sensible to the imposed oxidation.

### 3.2 Electrodeposition

Electroplating test were performed using a galvanic bath combined with deposition condition already known for their nanostructuring effect. Hoang et al. (2017) observed the formation of tangled copper nanowires while performing galvanostatic electrodeposition at  $-2 \text{ mA/cm}^2$  from a DAT additivated plating bath. The same deposition conditions were chosen in order to enlighten how the pretreatment could affect both macroscopic aspects of the deposition, namely yield and distribution, and microscopical aspects, i.e. micro and nanostructures on the deposition.

Electrodeposition morphology has been investigated by SEM imaging, a system both capable of metal identification on the carbon-based structure and of a deep field analysis of micro and nanostructures.

Low enlargement images (magnification factor 250 X) give a good overview of the deposition macroscopic distribution on the support, and treatment effects may be analyzed. Figure 3a and Figure 3b show, respectively, a copper deposition on an untreated carbon paper sample and on a treated sample (treatment duration of 10 min); both depositions were done on the GDL side of the carbon paper.

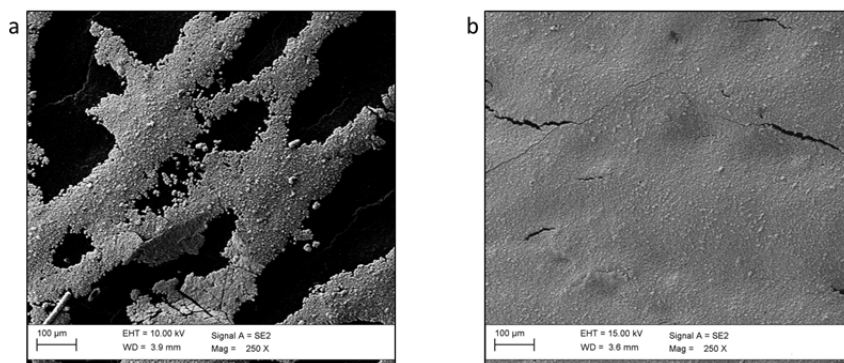


Figure 3: Copper depositions on the GDL of a carbon paper sample. (a) Deposition on an untreated support; (b) Deposition on a 10 min-treated support.

In the SEM images copper deposition appears as light gray, while the GDL carbon nanopowder appears as pitch black.

It is clearly visible a difference in the deposition distribution. Untreated carbon paper appears to be only partially covered; copper structures are localized on the most external parts of the GDL forming an inhomogeneous network. Treated carbon paper shows a full coverage, interrupted only by rifts already present in the carbon paper before the treatment. There seems to be no difference amongst the deposition obtained at different treatment durations. No differences in the deposition nanomorphology were observed.

The same analysis, conducted on the fibrous side of the carbon paper, does not show a clear difference between the depositions, neither in distribution nor in nanomorphology.

Deposition yields were estimated by measuring the amount of copper deposited on the support and comparing it with the theoretical mass of electroplated metal, calculated by the Faraday's electrolysis law.

A  $4 \text{ C/cm}^2$  deposition is theoretically equivalent to  $1.317 \text{ mg/cm}^2$  of copper. Actual deposited yield is lower than the unity, mostly for the inhibition effect linked with the DAT additive, giving the formation of poly complexes with copper (Aznar et al., 2006). While differences in deposition yields pre and after treatment are low, fibrous faces and GDL faces of carbon paper seems to be affected slightly differently by the treatment. As shown in Figure 4, fibrous side shows a small but significant decreasing in yield, not correlated to the treatment time.

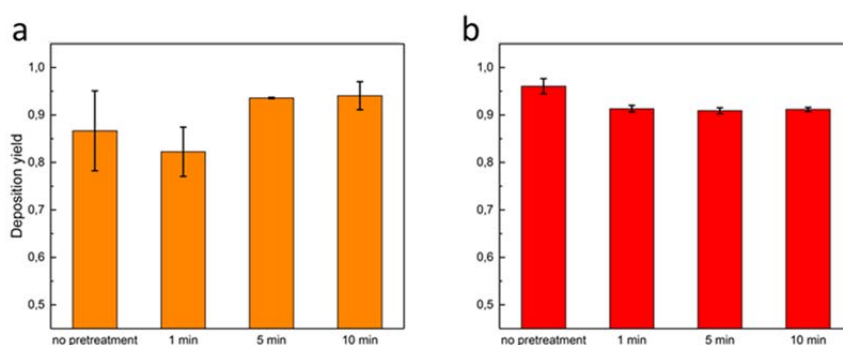


Figure 4: Deposition yields of metallic copper onto the carbon paper support. Support subjected to different pre-treating times are compared with an untreated support. (a) Deposition yields on GDL side; (b) Deposition yields on fibrous side.

Treatment effect on the GDL side seems to be less clear, with low yields associated with short treatment durations. Modifications in the deposition yields may be correlated to various alterations of the carbon paper

structure. The main side reaction observed during electrodeposition in acid aqueous electrolytic baths is the water reduction reaction to hydrogen (Kanani, 2005). This process may be magnified by modifications in the deposition conditions, e.g. electrode structure, and vice versa the process of copper electroplating may be hindered, in favor of the hydrogen evolution (Rosa-Ortiz et al., 2019).

#### 4. Conclusions

Electrodeposition has been successfully used as a nanosynthesis technique to produce gas diffusion electrodes. Carbon paper could represent a suitable support, but its hydrophobicity hinders the success of the deposition.

A new pre-treatment method for carbon paper supports has been developed and evaluated. The process, involving non-toxic reagents and a common electrochemical equipment, modifies the superficial structure of the carbon paper by electric-induced oxidation. This process decreases the superficial hydrophobicity of the material, altering its wetting degree and its macroscopic wetting behaviour. Variations in the electrochemical properties of the carbon paper support were observed, before and after the pre-treatment, by electronic impedance spectroscopy analysis. Electrodeposition tests were performed in order to evaluate the distribution, the yield and the morphology of the deposition. While the nanomorphology of the deposition seems unaffected, micromorphology and distribution of the deposition appears to be more even on the pre-treated supports. Electrodeposition yields appear to be only mildly affected by the treatment.

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