



# On the electrografting of stainless steel from para-substituted aryldiazonium salts and the thermal stability of the grafted layer

Mogens Hinge\*, Elsa Silva Gonçalves, Steen Uttrup Pedersen, Kim Daasbjerg

Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000, Aarhus C, Denmark

## ARTICLE INFO

### Article history:

Received 17 June 2010

Accepted in revised form 31 July 2010

Available online 10 August 2010

### Keywords:

Stainless steel

Aryldiazonium salts

Electrografting

Thermal stability

## ABSTRACT

In this study we explore the thermal stability of an organic layer electrografted onto stainless steel (ASTM 316) from four different aryldiazonium salts  $R-C_6H_4N_2^+$  ( $R = NO_2, F, H, \text{ or } OCH_3$ ). The coverage of the surfaces was analysed electrochemically by employing redox probes and cyclic voltammetry. The results obtained clearly show that the steel surface after grafting is electrochemically passivated by the presence of a surface coating. Polarization modulated infrared reflection absorption spectroscopy (PM-IRRAS) was used to characterize the organic films on the surfaces and to monitor the thermal stability of these films from ambient temperature to 400 °C with 50 °C intervals. The PM-IRRAS spectra show a decrease in band intensities at 250 °C for nitrophenyl, independent of layer thickness and atmosphere (air or argon), 300 °C for methoxyphenyl, and 350 °C for phenyl and fluorophenyl films. All the characteristic IR bands were simultaneously and completely lost at 300, 350, 350, 400 and 400 °C for thin-layer nitrophenyl, thick-layer nitrophenyl, methoxyphenyl, fluorophenyl, and phenyl, respectively, which strongly indicates that the entire organic film is lost at these temperatures. The results show that it is mainly the substituent and the layer thickness that are responsible for the difference in thermal stability of the organic films and that all films withstood temperatures up to 200 °C.

This study shows that electrochemical grafting from aryldiazonium salts is simple, fast, and has a low energy consumption which makes the procedure suitable for industrial applications.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Surface modification is an important topic due to the wide range of industrial applications, e.g., increase of adhesion between materials, creation of surfaces with different wettabilities, biocompatibility, protection, and/or decoration of materials. One of the most versatile methods for modifying conducting surfaces discovered almost two decades ago by Pinson et al. [1] uses aryldiazonium salt chemistry. Upon immersion of a conducting surface in a solution of an aryldiazonium salt and by applying an electrochemical potential, the diazonium salt is electroreduced to reactive aryl radicals which will form covalent bonds with the conducting surface.

Various carbon materials such as glassy carbon, graphite, carbon black, highly ordered pyrolytic graphite (HOPG) [2] and carbon nanotubes (CNTs) [3–5] along with metals such as Fe [6], Ni, Zn, Co, Cu, Pt [7], and Au [7,8] have already been grafted successfully in this manner. Recently, we have shown that even Cr can be grafted, despite that its surface is covered with a stable chromium oxide layer [9].

Additional processing of the modified material may easily involve various thermal impacts which can delaminate the surface film. It is

therefore important to know the thermal stability of the organic surface modification. Only a few studies have addressed the thermal stability of the organic films grafted via the aryldiazonium method and they focus mainly on carbon-based materials like glassy carbon [10], carbon black [10], CNTs [3–5], and HOPG [2].

In the pioneering work from 1997 Pinson et al. used Auger Spectroscopy to study the thermal stability under vacuum of grafted film of 4-nitrobenzenediazonium on HOPG and found that bands of O and N remained intact upon heating at 700 K and disappeared only if the temperature was raised to 1400 K [2]. Other studies have taken advantage of the large surface-to-weight ratio of carbon black and CNTs to study the weight loss of the grafted film by thermogravimetric analysis (TGA). In this manner a weight loss of 25% was found by heating 4-nitrophenyl-functionalized single-walled CNTs to 500 °C under argon atmosphere [3–5].

Toupin and Bélanger [10] used TGA-MS and XPS to study in detail the thermal degradation of 4-nitrophenyl-modified carbon black in air and nitrogen. The results show that degradation takes place essentially in three steps in both air and nitrogen. At low temperature between 100 and 200 °C the physisorbed film is lost followed at temperatures between 300 and 450 °C by the decomposition and cleavage of parts of the covalently attached film. However, two-third of the initial weight of the film is still present on the surface at 450 °C, although XPS clearly shows that all nitro groups have already been

\* Corresponding author. Tel.: +45 8942 3782; fax: +45 8619 6199.  
E-mail address: [hinge@chem.au.dk](mailto:hinge@chem.au.dk) (M. Hinge).

lost at this temperature. The remaining film is not lost until the temperature is raised to 1000 °C.

The thermal stability of diazonium grafted films has also been studied on two metals. For gold Paulik et al. showed that the surface gold atoms are mobile and rearrange substantially during sonication in water or petroleum ether [8]. The mobility is increased by elevating the temperature to 45 °C compared to 0 °C in air. It is not known if the diazonium grafted film stabilizes the gold surface and to which extent the organisation of the highly porous surface film is affected by the Au mobility. No measurements were conducted at higher temperatures in air.

While many different pure metal surfaces have been electrochemically grafted via the aryldiazonium route only a few reports on more common engineering alloys like stainless steel have been published. A study on polymerization of vinylic monomers initiated by diazonium salts has shown that by electrochemically reduction of the diazonium group at a stainless steel electrode it is possible to generate a polymer attached to the stainless steel surface [11,12]. Surface modifications of stents made of stainless steel have also been reported [13–16]. In one study the authors grafted stents with five different diazonium salts<sup>1</sup> with increasing lipophilicities, thus, generating a lipophilic surface that was loaded with a variety of lipophilic drugs for controlled drug delivery aimed at treatment of vascular diseases [13]. In a recent study the authors grafted stents with 4-(2-bromoethyl)benzenediazonium and in this way a surface-attached initiator could be formed for atom transfer radical polymerization (ATRP) of methyl methacrylate, hence forming surfaces of biocompatible poly(methyl methacrylate) brushes [16]. In another recent study 4-dodecyloxybenzenediazonium was employed to graft an adhesive promoter (base coat) for a polymeric topcoating on the metallic stents [14,15]. The quality and stability of the coatings (base coat plus drug/polymer coat) were examined after days under physiological conditions either at 37 °C or in accelerated tests at 60 °C. It was shown that the base coat improved the quality of the stents and no deterioration of the surface quality was observed even after 30 days of incubation at 60 °C. To our knowledge no other thermal studies have been reported in literature for more common engineering materials such as stainless steel grafted via the aryldiazonium method.

In this work we report on the thermal stability of electrografted organic layers on stainless steel plates using four different aryldiazonium salts. The diazonium salts have the general structure of 4-R-C<sub>6</sub>H<sub>4</sub>N<sub>2</sub><sup>+</sup> where R = NO<sub>2</sub>, F, H, or OCH<sub>3</sub>. The stability of the grafted films was studied by heating the sample to temperatures ranging from room temperature to 400 °C. The modified surfaces were analyzed using polarization modulated infrared reflection absorption spectroscopy (PM-IRRAS), scanning electron microscopy (SEM) and electrochemical measurements.

## 2. Materials and methods

### 2.1. Chemicals and solvents

4-nitrobenzene-, 4-methoxybenzene-, 4-fluorobenzene- and benzenediazonium tetrafluoroborates were synthesised by diazotation of the corresponding aniline by NaNO<sub>2</sub> in HBF<sub>4</sub>(aq) following the general procedure described elsewhere [17]. Further purification consisted of dissolving the diazonium salt in acetonitrile, precipitation by addition of diethyl ether and after filtration and vacuum drying, storing it at –18 °C for no longer than two weeks before recrystallization was repeated. 2,4,6-Triphenylthiopyrylium tetrafluoroborate was prepared according to the method outlined in literature [18]. Acetonitrile (anhydrous, 99.9%) was purchased from Lab-Scan and used as received for all grafting experiments. For CV analysis of

surfaces grafted with 4-nitrobenzenediazonium, acetonitrile was dried by passing through an Al<sub>2</sub>O<sub>3</sub> column (Sigma Aldrich, 99.99%). Al<sub>2</sub>O<sub>3</sub> had prior to this been activated by heating in a vacuum oven at 450 °C. Tetrabutylammonium tetrafluoroborate (Bu<sub>4</sub>NBF<sub>4</sub>) was prepared using standard procedures. All other compounds were commercial and used in the highest grade available. For all electrochemical experiments Bu<sub>4</sub>NBF<sub>4</sub> was added as supporting electrolyte in 0.1 M concentration to acetonitrile.

### 2.2. Electrodes and instrumentation

A standard 3-electrode electrochemical setup was employed. Two different ASTM 316 stainless steel geometries were used as working electrode according to the specific purpose of the measurements. For electroanalytical measurements the working electrode was made from stainless steel rods (diameter = 2.73 mm) embedded in epoxy resin. For spectroscopical analysis the working electrode consisted of a stainless steel sheet (width = 11 mm) which was dipped ~1 cm in the electrochemical cell's solution. Both kinds of electrodes were sanded (down to grid 4000) and polished with diamond suspensions down to 0.25 μm followed by rinsing with water and ethanol and finally 10 min ultrasonic cleansing in acetone. For both kinds of working electrodes a Ag/AgI electrode (silver wire immersed in a Pyrex tube containing 0.01 M Bu<sub>4</sub>NI in electrolyte) separated from the main solution by a ceramic frit served as a pseudo-reference electrode. At the end of each experiment the standard potential of the ferrocenium/ferrocene couple, E<sub>FC<sup>+</sup>/FC</sub><sup>0</sup>, was measured and all potentials were referenced against SCE using a previous determination of E<sub>FC<sup>+</sup>/FC</sub><sup>0</sup> = 0.41 V vs. SCE in acetonitrile [19]. The auxiliary electrode consisted of a platinum wire. All electrochemical experiments were performed on a CH Instruments 601C electrochemical workstation.

### 2.3. Electrografting

Two different grafting procedures were used. The first approach consisted in grafting by means of three successive voltammetric cycles from 0.15 to –0.85 V vs. SCE using a sweep rate of 0.2 V s<sup>–1</sup> in a 2 mM solution of the given aryldiazonium tetrafluoroborate in the electrolyte solution. The second approach consisted of performing a potentiostatic electrolysis (data given in Table 1, vide infra) for 300 s on a 2 mM of the given diazonium salt in the electrolyte solution. In both cases the grafted surface was thoroughly rinsed and ultrasonicated for 10 min in acetone before further analysis.

### 2.4. Cyclic voltammetry

Cyclic voltammograms were recorded in the standard three electrode setup in a freshly dried electrolyte solution. For a 4-nitrobenzenediazonium grafted electrode the electroactivity of the NO<sub>2</sub> group could be studied directly by sweeping from –0.3 to –1.8 V vs. SCE using a sweep rate of 2 V s<sup>–1</sup>. For all other non-electroactive grafted electrodes, the blocking properties of the modified electrodes were tested toward a 2 mM solution of the 2,4,6-triphenylthiopyrylium redox probe in an electrolyte solution. This redox probe have a first reversible half-wave potential for reduction at –0.21 V vs. SCE [20]

**Table 1**

Peak potential determined from the 1st cyclic voltammogram (E<sub>p</sub>), applied grafting potential (E<sub>g</sub>) and charge consumed during grafting of the four different aryldiazonium salts. Values in brackets are the standard deviation. Electrolysis time for all potentiostatic graftings is 300 s.

R	E <sub>p</sub> (V vs. SCE)	E <sub>g</sub> (V vs. SCE)	Charge (10 <sup>–3</sup> C cm <sup>–2</sup> )
–NO <sub>2</sub>	–0.09	–0.87	0.41 (0.26)
–F	–0.34	–0.87	0.37 (0.23)
–H	–0.29	–0.87	0.45 (0.29)
–OCH <sub>3</sub>	–0.66	–0.77	0.85 (0.07)

<sup>1</sup> 3,5-dichlorobenzenediazonium, 2-chloro-4-benzamido-5-methylbenzenediazonium, 4-decyloxybenzenediazonium, 1-pyrenyldiazonium, and 3-ethoxycarbonylnaphthalene-2-diazonium salts.

Download English Version:

<https://daneshyari.com/en/article/1658673>

Download Persian Version:

<https://daneshyari.com/article/1658673>

[Daneshyari.com](https://daneshyari.com)