

Blocking Properties of Nickel Electrodes Modified with Aryldiazonium Compounds

Marek Mooste¹, Elo Kibena¹, Leonard Matisen², Kaido Tammeveski^{1,*}

¹Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia

²Institute of Physics, University of Tartu, Ravila 14c, 50411 Tartu, Estonia

*E-mail: kaido.tammeveski@ut.ee

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In this work, various diazonium compounds including azobenzene (AB), Fast Garnet GBC (GBC), Fast Black K (FBK), 4-bromobenzene (PhBr) and 4-nitrophenyl (NP) were used to modify nickel electrodes *via* electrochemical reduction of the corresponding diazonium salts in acetonitrile in order to study the blocking properties of aryl-modified Ni electrodes towards the ferricyanide redox probe. For the first time, an attempt has been made to modify Ni with NP groups by redox grafting. The attachment of different aryl groups to Ni surface was confirmed by X-ray photoelectron spectroscopy (XPS). The blocking behaviour of aryl-modified Ni electrodes in the presence of $\text{Fe}(\text{CN})_6^{3-}$ ions was studied using cyclic voltammetry and the rotating disk electrode (RDE) method. The results revealed that the blocking properties greatly depended on the diazonium salt as well as the modification procedure used. In more specific, the best blocking action for the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox system was observed in case of NP-modified Ni electrodes (using redox grafting during the modification), whereas PhBr-modified Ni electrodes showed the lowest blocking effect compared with the other modifiers.

Keywords: Nickel; Blocking properties; Redox grafting; Diazonium salts; Ferricyanide probe

1. INTRODUCTION

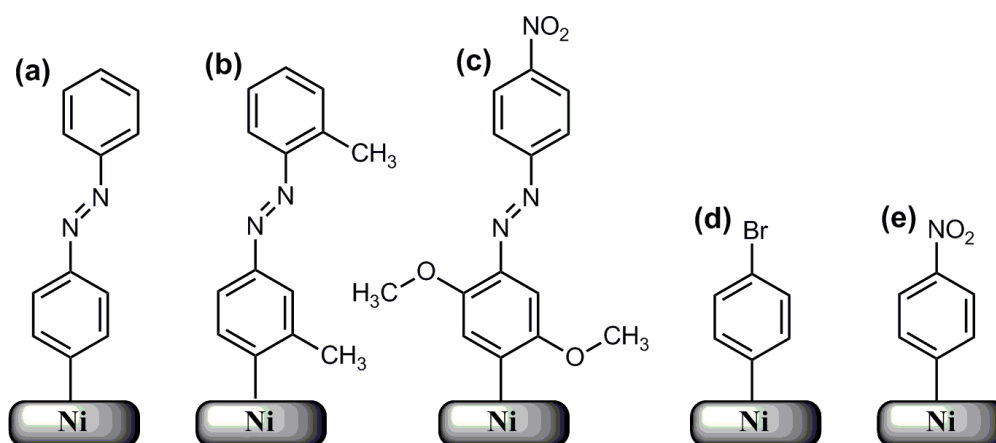
The modification of conductive surfaces with aryl groups has been widely studied since the aryl-modified substrates have shown promising applications including molecular electronics, corrosion protection and (bio)sensor fabrication [1-4]. For the functionalisation of electrodes, the reduction of diazonium salts has been extensively investigated since the first introduction of the method by Pinson and Savéant workgroup [5]. In a simplified way, this method is based on a two-step pathway which consists of (a) the reduction of aryldiazonium cation (Ar-N_2^+) to an aryl radical (Ar^\bullet) and (b) the attachment of aryl radical to the substrate forming a strong (covalent) bond between the aryl group and

the electrode surface [6]. It is possible to carry out the surface modification by diazonium chemistry either in aprotic (for example, in acetonitrile) or acidic aqueous solutions [7], however, for more easily oxidisable materials, like nickel, acetonitrile is preferable [8]. In general, the surface grafting by diazonium chemistry could be divided into two groups: spontaneous and electrochemical approach [1,7,9,10]. In case of the spontaneous modification method the reduction process occurs without applied potential and is easier to conduct, but the growth of an organic layer and the quantity of the attached modifier cannot be controlled as precisely as in case of the electrochemical method. However, using the electrochemical method the amount of aryl modifier on the surface can be relatively well-controlled for example with the number of potential cycles, the applied potential range and the time the electrode is held at a certain potential [6]. Therefore for a comparative study of different aryl layers the electrochemical method seems to be more suitable.

For the functionalisation of electrodes, the diazonium chemistry is attractive since it is easy to carry out and various functional groups (4-nitrophenyl (NP), 4-bromophenyl (PhBr), aminophenyl, azobenzene (AB), 9,10-anthraquinone, etc.) can be strongly attached to the underlying substrate. This method has been applied to carbon materials (e.g. glassy carbon (GC), highly oriented pyrolytic graphite, carbon powder, carbon nanotubes, graphene [11-25]) as well as metal substrates (e.g. gold, iron, steel, copper, nitinol, nickel [26-46]). The strong attachment of aryl layers to metals (like Ni) is particularly important in order to protect the metal from the environment, but also to provide particular properties to the surface [47]. Although different aryl groups (e.g. NP, 4-methoxyphenyl, 1,4-carboxyphenyl, 4-diethylaminophenyl, 9,10-anthraquinone) have already been successfully grafted on the Ni or Ni-containing substrates (e.g. nitinol) by the spontaneous or electrochemical reduction of aryldiazonium salts and the presence of corresponding aryl films has been confirmed by different spectroscopic techniques (e.g. atomic force microscopy, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy) [8,40,41,43,47-51], only a few groups have reported on the blocking properties of aryl-modified Ni electrodes [40, 48]. In contrast, the electrochemical behaviour of bare Ni electrodes in the presence of ferricyanide in KOH solution has been well studied [40,52,53]. First, it has been shown that while performing the experiments in KOH solution containing ferricyanide ions, the contamination of the Ni surface with oxides grows with the time meaning that the Ni surface requires regular cleaning (polishing) and in addition, the solution should be freshly made because of the decay of ferricyanide ion to cyanide ions over time [52,53]. However, in case of aryl-modified Ni electrodes, Kullapere *et al.* [40] and Jacques *et al.* [48] have studied the blocking behaviour of Ni substrates modified with NP and 4-pyrrolylphenyldiazonium compounds, respectively. Both studies revealed that the aryl-modified Ni electrodes suppressed the rate of the electron transfer of the ferri/ferrocyanide redox couple, however the blocking effect depended on the diazonium salt as well as the modification procedure used [40,48].

Recently, Daasbjerg's workgroup has extensively studied the formation of thick aryl films on different substrates (for example GC, Au, stainless steel) by the method called redox grafting [54-56]. This method is based on the diazonium chemistry, but instead of using narrow potential range in surface modification where only the reduction peak(s) of diazonium cation is observed, a wider potential range is chosen where the redox wave of the formation of radical anion occurs [54-56]. As mentioned above then in the previous work conducted by our workgroup the blocking behaviour of

NP-modified Ni electrode towards the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple was investigated, however the electrografting of Ni substrate with NP moieties was performed in a narrow potential range [40]. Yet to be explored is the probability to form thicker NP film on Ni surface using redox grafting and to investigate the barrier properties of the prepared aryl film. Also, to the best of our knowledge, the electrografting of Ni with AB, Fast Garnet GBC (GBC), Fast Black K (FBK) and PhBr diazonium compounds and the investigation of blocking behaviour of the aryl-modified Ni electrodes obtained has not been reported as yet. Therefore, the aim of this work was to modify Ni electrodes with various aryl groups using five different diazonium salts in order to get new insights into the metal modification area by diazonium chemistry (including electrografting and redox grafting) and to explore the barrier properties of these aryl films. The five modifiers used in this study are depicted in Scheme 1.



Scheme 1. Structures of surface modifiers attached to nickel by electrochemical reduction of: a) azobenzene diazonium salt; b) Fast Garnet GBC sulphate salt; c) Fast Black K salt; d) 4-bromobenzenediazonium salt and e) 4-nitrobenzenediazonium salt.

Furthermore, all aryl-modified Ni electrodes were characterised by XPS and the blocking behaviour towards the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple of these electrodes was studied using cyclic voltammetry and the rotating disk electrode (RDE) method.

2. EXPERIMENTAL

2.1. Preparation of Ni electrodes

Nickel electrodes with geometric area (A) of 0.196 cm^2 were prepared by mounting the Ni disks (99.995%, Alfa Aesar) into Teflon holders. Before modification, the Ni electrodes were polished with silicon carbide grinding paper P4000 (Buehler) and alumina slurries (1.0 and $0.3 \mu\text{m}$, Buehler) to a mirror finish. In order to remove the alumina residue, the Ni electrodes were cleaned by sonication in Milli-Q water (Millipore, Inc.) for 5 min.

2.2. Modification procedures

The attachment of azobenzene (AB), Fast Garnet GBC (GBC), Fast Black K (FBK), 4-bromophenyl (PhBr) and 4-nitrophenyl (NP) diazonium compounds onto Ni electrodes was performed by the electrochemical reduction of azobenzenediazonium tetrafluoroborate, Fast Garnet GBC sulphate salt (Sigma-Aldrich), Fast Black K salt (Sigma), 4-bromobenzenediazonium tetrafluoroborate (96%, Aldrich) and 4-nitrobenzenediazonium tetrafluoroborate (97%, Aldrich). Azobenzenediazonium tetrafluoroborate was pre-synthesised from the 4-aminoazobenzene hydrochloride (97%, TCI) according to the procedures described in the literature [23,57,58]. The rest of the diazonium salts used were commercially available.

The electrografting of Ni electrodes with AB, GBC, FBK, PhBr and NP groups was performed in acetonitrile (ACN, HPLC grade, Sigma-Aldrich) containing 3 mM of the corresponding diazonium salt and 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄, Fluka) as a base electrolyte. In the same order as aryl groups subscribed above, the modified Ni electrodes are denoted as Ni/AB, Ni/GBC, Ni/FBK, Ni/PhBr and Ni/NP1. Pt-foil served as a counter electrode and saturated calomel electrode (SCE) was used as a reference electrode. All the potentials in this paper are referred to the latter electrode. For the electrochemical grafting, 10 potential cycles between 0.3 and -0.4 V were used. After potential cycling, the electrode was held at -0.2 V for 10 min. It should be noted that in case of Ni/NP, the electrode was held for 10 min at -0.4 V instead of -0.2 V. Similarly to Ceccato *et al.* [56], Ni electrodes were also modified by redox grafting in order to obtain thicker NP films on Ni surface. For that purpose, 10 potential cycles between 0.3 to -1.8 V were carried out. This electrode is designated as Ni/NP2. In all cases, the potential cycling was performed with a sweep rate (ν) of 100 mV s⁻¹ and after surface grafting the aryl-modified Ni electrodes were sonicated in ACN for 5 min.

2.3. Characterisation of aryl-modified Ni electrodes by X-ray photoelectron spectroscopy

The elemental composition of aryl-modified Ni electrodes was studied by the X-ray photoelectron spectroscopy (XPS). The 1.1×1.1 cm Ni plates were prepared and modified according to the same procedures as described above. The XPS measurements were carried out with a SCIENTA SES-100 spectrometer by an unmonochromated Al K _{α} X-ray source (incident energy = 1486.6 eV), a take-off angle 90°, source power of 300 W. The pressure in the analysis chamber was under 10⁻⁹ Torr. At the time the survey scan was collected, the energy range was from 0 to 900 eV, pass energy 200 eV and step size 0.5 eV. For high-resolution scans the pass energy was 200 eV and step size 0.1 eV.

2.4. Electrochemical characterisation of aryl-modified Ni electrodes

The electrochemical measurements with bare and aryl-modified Ni electrodes were performed in Ar-saturated (99.999%, AGA) 0.1 M KOH (p.a. quality, Merck) solution containing 1 mM K₃Fe(CN)₆ (Aldrich). Cyclic voltammetry (CV) experiments were carried out in the potential range from 0.35 to 0 V (ν = 100 mV s⁻¹). In addition, the rotating disk electrode (RDE) method was employed in the potential range between 0.3 and -0.7 V and the electrode rotation rate (ω) was varied

from 360 to 4600 rpm ($v = 20 \text{ mV s}^{-1}$). The CTV101 speed control unit (Radiometer) and an EDI101 rotator were used for the RDE measurements. The potential was applied with an Autolab potentiostat/galvanostat PGSTAT30 (Eco Chemie B.V., The Netherlands) and the experiments were controlled with General Purpose Electrochemical System (GPES) software. All experiments were carried out at room temperature ($23 \pm 1^\circ \text{C}$).

3. RESULTS AND DISCUSSION

3.1. Electrochemical grafting of Ni electrodes with aryl groups

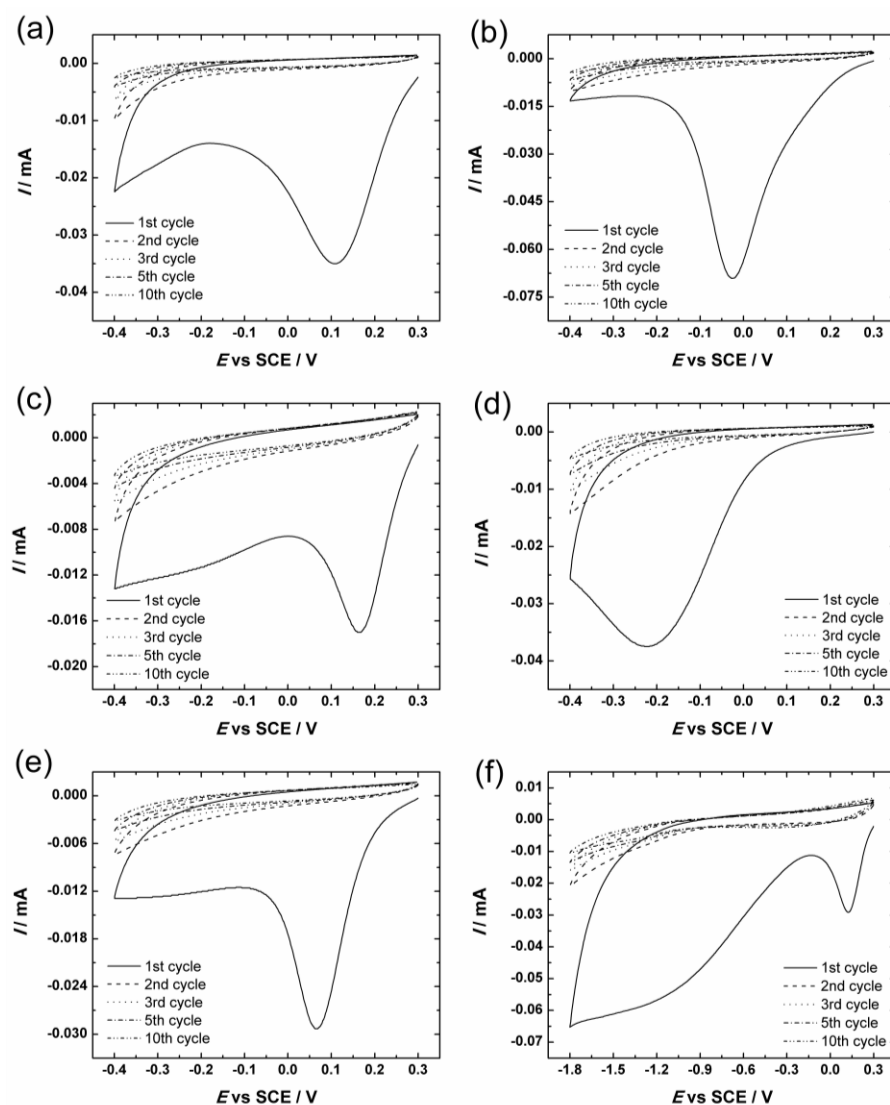


Figure 1. Electrografting (a-e) or redox grafting (f) of Ni electrodes using 3 mM diazonium salts: (a) azobenzenediazonium tetrafluoroborate; (b) Fast Garnet GBC sulphate salt; (c) Fast Black K salt; (d) 4-bromobenzenediazonium tetrafluoroborate and (e,f) 4-nitrobenzenediazonium tetrafluoroborate in Ar-saturated ACN containing 0.1 M TBABF₄ as a base electrolyte ($v = 100 \text{ mV s}^{-1}$).

Figure 1 presents the cyclic voltammograms (CVs) registered during electrografting of Ni electrodes in various aryldiazonium salt solutions. As can be seen from Figures 1a-e, during the first potential cycle a clear cathodic peak is observed in the potential range between 0.3 and -0.4 V in case of all diazonium salts used. Based on the literature data, this peak corresponds to the reduction of the aryldiazonium cation and to the formation of the radical, which binds to the Ni surface [44]. On the subsequent potential cycles, these reduction peaks disappear (see Figures 1a-e), which presumably refers to the blocking of the Ni surface with the corresponding aryl layer. This kind of electrochemical behaviour is rather common for electrografting of different electrode materials by the electrochemical reduction of diazonium salts [6]. Although the electrochemical behaviour during electrografting is very similar in case of all diazonium salts used, the values of peak potential (E_p) which appeared on the first electrografting cycle are different. In more specific, the E_p values are as follows: E_p (Ni/AB) = 0.07 V, E_p (Ni/GBC) = -0.02 V, E_p (Ni/FBK) = 0.16 V, E_p (Ni/PhBr) = -0.22 V and E_p (Ni/NP1) = 0.11 V. To the best of our knowledge, this is the first attempt to modify the surface of Ni electrodes with AB, GBC, FBK and PhBr diazonium compounds and therefore, the direct comparison with literature data is rather complicated. However, the AB, GBC and FBK groups have been electrografted on the GC substrates in our earlier report [23]. In the latter paper, the first cyclic voltammogram showed two cathodic peaks (the pre-peak and the reduction peak) during the electrografting of GC with AB, GBC and FBK diazonium moieties. Interestingly, the position of the reduction peaks was rather the same while using Ni as an underlying substrate in this study. Also, while electrografting gold and chemical vapour deposition (CVD) grown graphene on Ni foil with AB groups [38,59], the reduction peak potentials were similar with the one obtained in case of Ni substrate. In contrast, the location of the reduction peak for the GBC and FBK was rather different while using Au and CVD-grown graphene as an underlying substrate [38,59] compared with the Ni electrode. In addition, the PhBr groups have been electrografted to the Au and CVD-grown graphene electrodes and the value of E_p was ca 0.15 V and 0.04 V, respectively [35,59]. As can be seen, these values are more positive than the value of E_p obtained in case of Ni electrode in this study ($E_p = -0.22$ V). From these findings, we may conclude that the values of the diazonium reduction potential depend on the modifier as well as on the underlying substrate used.

In the literature, there are numerous studies about the electrografting of Ni electrodes with NP groups by the diazonium reduction method using shorter potential range where only the reduction peak of diazonium cation appears. Therefore, it is easy to compare the results obtained in this study. In general, both the electrochemical behaviour as well as the value of E_p is in a good accordance with the previously reported data [40,47,60]. However, an attempt has been made to modify Ni electrodes with thicker NP films by redox grafting for the first time. Recently, several papers have been published by Daasbjerg's as well as by our workgroup about the redox grafting of different conducting materials including GC, Au, stainless steel, highly oriented pyrolytic graphite and CVD-grown graphene (on Ni or Cu foil) with different aryl layers of high thickness [25,54-56,61]. Moreover, in our recent study [59], the formation of thick NP layers on CVD-grown graphene on Ni foil by redox grafting was thoroughly investigated. Based on the foregoing papers [25,54-56,59,61], thick organic layers can be accomplished by reducing the functional group (e.g. $-\text{NO}_2$) of an aryl-modifier to an anion radical under more negative potential which should promote the growth of an aryl layer. In general, the CVs

registered during the redox grafting in a wider potential range have shown that the reduction peak of the diazonium moiety which appears at more positive potentials diminishes with the following potential cycles, whereby the redox wave which appears at more negative potentials grows during subsequent cycles [25,54-56,59,61]. Herein, interesting electrochemical behaviour during redox grafting of Ni substrate with NP groups using wider potential range (from 0.3 to -1.8 V) was observed. First, as can be seen from Figure 1f, the second reduction peak occurs at ca -1.0 V which may refer to the reduction of nitrophenyl group to its radical anion and which is in a good accordance with previous studies [56,59]. In contrast, a reproducible redox wave did not appear during the first or following cycles (see Figure 1f) as was seen by Ceccato *et al.* [56] and Mooste *et al.* [59] in case of redox grafting of GC and CVD-grown graphene on Ni foil with NP groups, respectively. Interestingly, the results obtained here reveal that the disappearance of the reduction peak(s) during subsequent potential cycling is rather comparable with the electrochemical behaviour observed during electrografting in narrow potential range (see Figure 1e) and does not follow the tendency reported earlier [25,4-56,59,61].

3.2. XPS study of bare and aryl-modified Ni electrodes

The AB-, GBC-, FBK-, PhBr- and NP-modified Ni electrodes were characterised through the XPS analysis in order to confirm the presence of the corresponding aryl films on Ni surface. In all cases, the XPS measurements revealed that the electrografting with all diazonium compounds was in evidence since all the XPS spectra showed photoelectron peaks (e.g. N1s and Br3p) characteristic of the diazonium salts used (see Figure 2). It should be noted that these peaks were absent on the bare Ni surface (data not shown). As can be seen from Figures 2a-c, the survey spectra exhibited N1s region in case of Ni electrodes electrografted with AB, GBC and FBK diazonium moieties. The peak at 400 eV corresponds to the azo groups [23,38,59] indicating the attachment of AB, GBC and FBK groups on the Ni surface. However, this peak may also be characteristic of an azo linkage ($-N=N-$) which may occur within the formation of multilayers on the Ni surface. Saby *et al.* [13] were the first who reported about the determination of azo groups in the aryl layers on aryl-modified carbon surface by this peak (400 eV) in the XPS spectra and later, the same was proposed by Hurley and McCreery [62] where Cu and Al alloy 2024 T3 were electrografted with different diazonium compounds. Similar conclusion was made by other workgroups using different metal substrates as an underlying material [8,30,49,63] or the same diazonium salts as applied in this study [23,38,59]. In addition, the N1s core level spectra of Ni/FBK electrodes exhibited another peak about 406 eV (see Figure 2c inset) which is attributed to the nitro ($-NO_2$) group. This is another proof that the Ni surface is covered with FBK groups since FBK contains nitro functionality (see Scheme 1). Next, the presence of PhBr film on the Ni surface was verified by the presence of Br3d and Br3p peaks at 190 eV and 183 eV, which is characteristic to bromide (see Figure 2d inset). The appearance of the characteristic peaks of Br3d and Br3p on Ni, Fe and Zn surface after spontaneous grafting with PhBr diazonium moieties has been reported by Combellas *et al.* [64] and Adenier *et al.* [50]. Similarly to FBK-modified Ni electrodes, the

presence of NP film on Ni substrate was confirmed via $-\text{NO}_2$ group at 406 eV in the N1s spectra as shown in Figures 2e,f insets. Additionally, the peak at 400 eV was also present (Figures 2e,f insets).

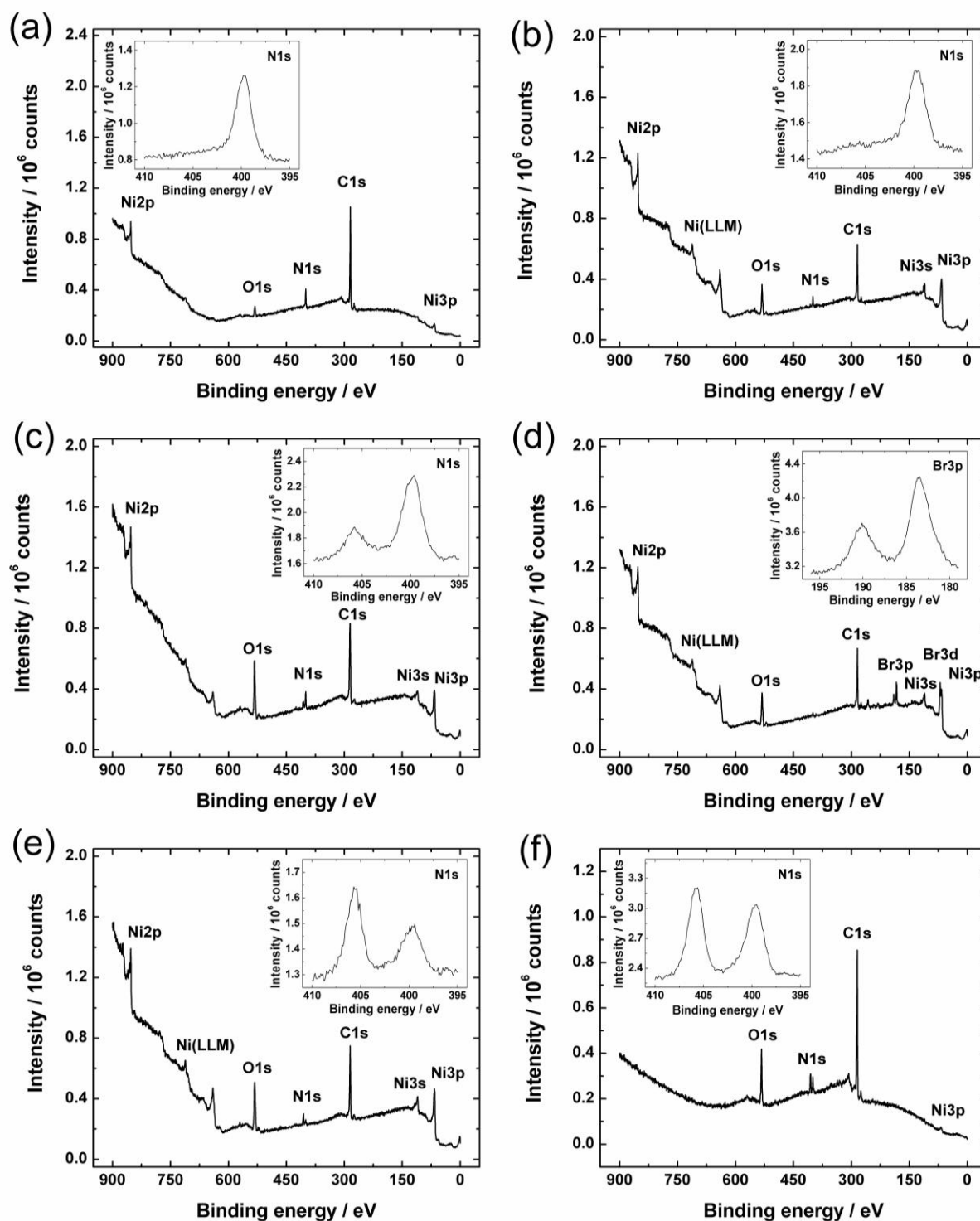


Figure 2. XPS survey spectra of (a) Ni/AB; (b) Ni/GBC; (c) Ni/FBK; (d) Ni/PhBr; (e) Ni/NP1 and (f) Ni/NP2 electrodes. The insets show the XPS spectrum of N1s region (a-c,e,f) and Br3p region (d) for aryl-modified Ni electrodes.

This peak has been attributed to inherent atmospheric nitrogen or amine groups which may form when the $-\text{NO}_2$ groups are reduced under the X-ray beam during XPS measurements [40,50]. These results are in good accordance with earlier reports about the XPS data of NP-modified Ni [40,60]. Also, it cannot be ruled out that the $-\text{N}=\text{N}-$ linkages inside the aryl film during the multilayer formation may occur and therefore the peak at ca 400 eV is seen in both cases (see Figures 2e,f insets).

It is also important to point out that the survey spectrum of all aryl-modified Ni samples showed a decrease in the characteristic Ni peaks (e.g. $\text{Ni}2\text{p}$, $\text{Ni}(\text{LLM})$, $\text{Ni}3\text{s}$, $\text{Ni}3\text{p}$) in comparison with the Ni peaks in the XPS spectrum of bare Ni (data not shown). Still, after the electrochemical grafting these peaks are more or less visible (see Figures 2a-e). This result may indicate that the aryl film is partially incomplete or thinner on Ni surface and also this kind of trend has been seen in earlier reports [40,50]. Furthermore, the $\text{Ni}(\text{LLM})$ peaks of AB- and FBK-modified Ni electrodes (see Figures 2a,c) are more suppressed compared with GBC- and PhBr-modified Ni substrates (see Figures 2b,d). This would imply that the AB and FBK films are thicker than GBC and PhBr films on Ni. Interestingly, it can be noticed that the XPS spectra of Ni/NP2 electrodes (Figure 2f) in comparison with the XPS data of Ni/NP1 samples (Figure 2e) shows that the peaks inherent to Ni ($\text{Ni}2\text{p}$, $\text{Ni}(\text{LLM})$, $\text{Ni}3\text{s}$) are missing, only a very small peak of $\text{Ni}3\text{p}$ was observed (see Figure 2f) when the redox grafting was employed for the Ni electrode modification. From that it can be assumed that the NP film is thicker when the electrode is cycled to a more negative potential. This is further confirmed by the electrochemical measurements in the presence of the ferri/ferrocyanide redox probe (see Section 3.3). Moreover, Combellas *et al.* [65] demonstrated that the stronger the decrease of the signal of an underlying substrate of aryl-modified electrodes in the XPS spectra, the higher the thickness of the grafted layer.

3.3. CV response of aryl-modified Ni electrodes towards the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe

Next, the blocking behaviour of aryl-modified Ni electrodes was studied by electrochemistry in the presence of ferri/ferrocyanide as an electroactive redox probe. Figure 3 shows the CVs of bare and aryl-modified Ni electrodes recorded in Ar-saturated 0.1 M KOH containing 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$.

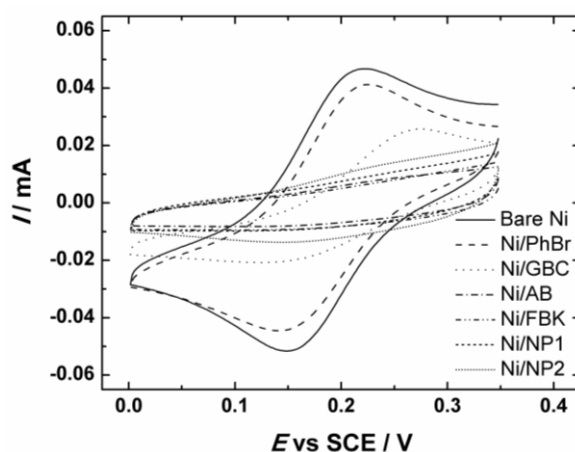


Figure 3. Cyclic voltammograms of bare and aryl-modified Ni electrodes recorded in Ar-saturated 0.1 M KOH solution containing 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$. $\nu = 100 \text{ mV s}^{-1}$.

In addition, to evaluate the inhibition of the aryl-modified Ni substrates towards the $\text{Fe}(\text{CN})_6^{3-}$ probe, two parameters, the relative blocking efficiency (I_{rel}) and peak-to-peak separation (ΔE_p), were used. The parameter of I_{rel} was taken from the study by Baranton and Bélanger [66] and is defined as:

$$I_{\text{rel}}(\%) = \frac{I_{\text{pc}} \text{ with the film}}{I_{\text{pc}} \text{ for bare Ni}} \times 100 \quad (1)$$

where I_{pc} is the value of the cathodic peak current. These values are presented in Table 1.

Table 1. Cyclic voltammetry results of bare, GBC- and PhBr-modified Ni electrodes recorded in Ar-saturated 0.1 M KOH containing 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$. $\nu = 100 \text{ mV s}^{-1}$.

Electrode	$I_{\text{pc}} (\mu\text{A})$	$I_{\text{rel}} (\%)$	$\Delta E_p (\text{mV})$
Bare Ni	52	-	74
Ni/PhBr	45	87	84
Ni/GBC	21	40	151

Since the CVs of Ni/AB, Ni/FBK, Ni/NP1 and Ni/NP2 electrodes showed no clearly defined peaks due to the suppression of the electron transfer process, the parameters of I_{rel} and ΔE_p could not be determined. It has been claimed that a compact aryl film (without defects or pinholes) blocks the electron transfer completely and the redox response of the probe is not observed, whereas thin or porous (containing defects or pinholes) aryl layer slows the electron transfer between the underlying substrate and redox probe, evidenced by a decrease in the I_{rel} value and increase in the ΔE_p values compared with the bare substrate [36,67,68]. As can be seen from Figure 3 and Table 1, the blocking effect of different aryl films compared to bare Ni greatly depends on the modifier used. In more specific, the CV of Ni/PhBr is only slightly affected as further indicated by the values of I_{rel} and ΔE_p (see Table 1). The electrochemical response of Ni/GBC electrodes towards the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple is considerably more inhibited than the one characteristic to the Ni/PhBr electrode (see Figure 3 and Table 1). Also, the value of ΔE_p increased and the value of I_{rel} is more than two times lower compared to the Ni electrode modified with PhBr groups. This gives evidence about the formation of more compact GBC film with greater barrier properties compared with PhBr layer on Ni surface. However, the response of $\text{Fe}(\text{CN})_6^{3-}$ ions is still apparent (see Figure 3) which may indicate the presence of defects or pinholes within the GBC film [44]. In comparison with earlier studies by our workgroup where similar electrografting procedure for the modification of GC and Au electrodes with PhBr and GBC diazonium compounds were used the blocking effect on both, PhBr- and GBC-modified GC and Au substrates towards the ferri/ferrocyanide redox probe was much more intense than that obtained in this study [21,23,35,38]. First, this shows that the nature of the PhBr and GBC film depends on the underlying substrate and secondly, both aryl films formed on Ni surface may be partial or loosely packed since the electron transfer between Ni surface and $\text{Fe}(\text{CN})_6^{3-}$ ions occurs. However, the ferri/ferrocyanide redox signal is almost completely suppressed in CVs recorded at Ni surfaces modified with AB, FBK and NP groups (see Figure 3). This feature provides evidence that these aryl films on Ni surface may be densely packed containing relatively small amount of defects or

pinholes since these aryl layers are impenetrable for the $\text{Fe}(\text{CN})_6^{3-}$ ions. Similar results about strong blocking behaviour have also been obtained with AB-, FBK- and NP-modified GC and Au electrodes [21,23,35,38].

3.4. RDE results of $\text{Fe}(\text{CN})_6^{3-}$ reduction on aryl-modified Ni electrodes

Next, it was of considerable interest to study the blocking effect of aryl films on Ni substrates by the rotating disk electrode (RDE) method in the same solution as in case of CVs to get some further insight to the barrier properties. First, the RDE voltammetry curves of bare Ni were registered using rotation rates from 360 to 4600 rpm (see Figure 4a).

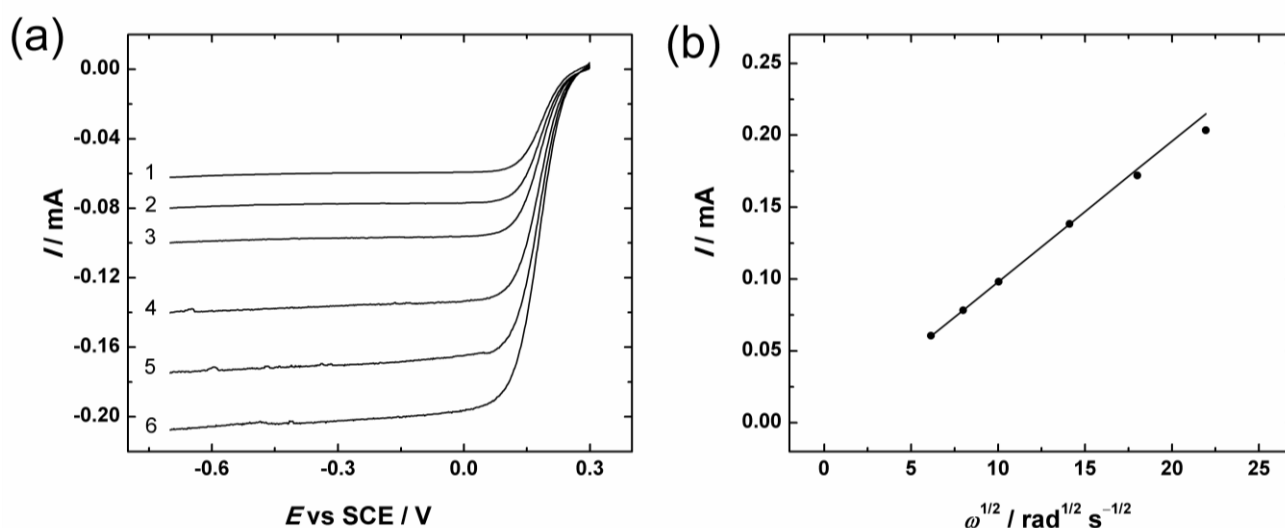


Figure 4. (a) RDE voltammetry curves of ferricyanide reduction on a bare Ni electrode recorded in Ar-saturated 0.1 M KOH solution containing 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ at various rotation rates: (1) 360, (2) 610, (3) 960, (4) 1900, (5) 3100 and (6) 4600 rpm. $\nu = 20 \text{ mV s}^{-1}$. (b) Levich plots of ferricyanide reduction on bare Ni electrode at -0.5 V. The solid and dotted curves correspond to the theoretical and experimental Levich plot, respectively.

The RDE results presented in Figure 4a show a clear dependence on the electrode rotation rate and well-defined diffusion-limited current plateaux were formed, which is in compliance with the data published earlier [40,53]. As can be seen from Figure 4b, the reduction current is rather equal to the theoretical diffusion-limited current calculated by the Levich equation [68]:

$$I_d = 0.62nFAC^\circ D^{2/3} \nu^{-1/6} \omega^{1/2} \quad (2)$$

where I_d represents the diffusion-limited current, n is the number of electrons involved ($n = 1$), F is the Faraday constant (96485 C mol^{-1}), A is the electrode area, C° is the concentration of ferricyanide in the bulk ($1 \times 10^{-6} \text{ mol cm}^{-3}$), D is the diffusion coefficient of ferricyanide ($7.63 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [69]), ν is the kinematic viscosity of the solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$ [70]) and ω is the electrode rotation rate.

The RDE voltammetry curves of AB-, GBC-, FBK- and NP-modified Ni electrodes at various rotation rates are shown in Figure 5, whereas a comparison of the RDE results of bare and all aryl-modified Ni electrodes at 1900 rpm are presented in Figure 6.

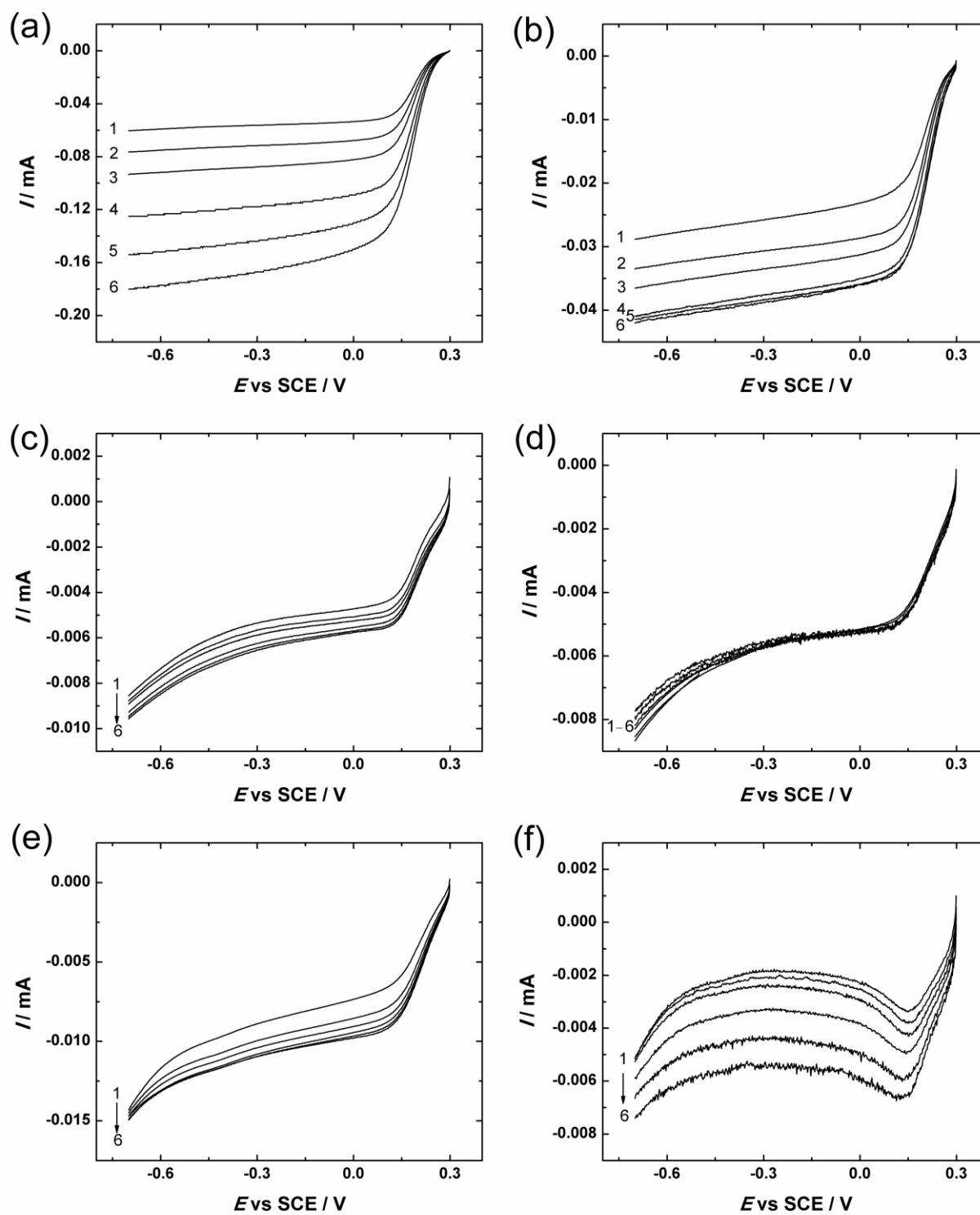


Figure 5. RDE voltammetry curves of ferricyanide reduction on: (a) Ni/PhBr; (b) Ni/GBC; (c) Ni/AB; (d) Ni/FBK; (e) Ni/NP1 and (f) Ni/NP2 electrodes recorded in Ar-saturated 0.1 M KOH solution containing 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ at various rotation rates: (1) 360, (2) 610, (3) 960, (4) 1900, (5) 3100 and (6) 4600 rpm. $\nu = 20 \text{ mV s}^{-1}$.

Moreover, in order to study the differences between the aryl-modified Ni electrodes the currents of ferricyanide reduction at -0.3 V were taken for comparison with that of bare Ni. The respective current values are given in Table 2. Similarly to CV experiments (see Figure 3), the slightest change in the electrochemical behaviour revealed a PhBr-modified Ni electrode (see Figures 5a, 6 and Table 2). The dependence on the rotation rate is clearly visible (see Figure 5a) and the current of the Ni/PhBr electrode decreased only about 13% compared to bare Ni (see Figure 6 and Table 2). In case of Ni/GBC electrode, the current is significantly suppressed (about 72% compared to bare Ni, see Table 2), however, the electron transfer between Ni surface and redox probe still occurs as was also seen by the CV experiments (see Figure 3). This kind of electrochemical behaviour of both electrodes (Ni/PhBr and Ni/GBC electrodes) suggests that these aryl films (PhBr or GBC) are rather thin containing defects or pinholes. This was also evidenced by XPS where the peaks of the underlying substrate were visible after electrografting of Ni with PhBr and GBC diazonium compounds (see Section 3.2). In addition, the RDE voltammetry curves of Ni/GBC (see Figure 5b) reveal that the current values depend on the rotation rate up to 1900 rpm but the polarisation curves at higher rotation rates closely coincide with the one at 1900 rpm. This may imply that at higher rotation rates the transfer of $\text{Fe}(\text{CN})_6^{3-}$ ions is limited by the permeability of the GBC layer. The AB- and FBK-modified Ni electrodes showed strong blocking effect towards the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe (see Figures 5c,d, 6 and Table 2) as was also observed in the CV measurements (see Figure 3).

In addition, the electrochemical behaviour of Ni/AB and Ni/FBK electrodes is very similar: in both cases the current values are almost independent of the rotation rate indicating relatively small defects or pinholes within the aryl film at which the reaction proceeds and moreover, the current was about 96% lower than that of bare Ni (see Table 2). This indicates that both AB and FBK layers on Ni surface are rather compact containing small amount of defects or pinholes and this is accordance with the XPS data where the characteristic peaks of Ni (for example Ni(LLM)) in the XPS spectrum were greatly inhibited (see Section 3.2). Similar results were achieved with Ni electrodes modified with NP groups and these are in accordance with the CV data (see Figure 3).

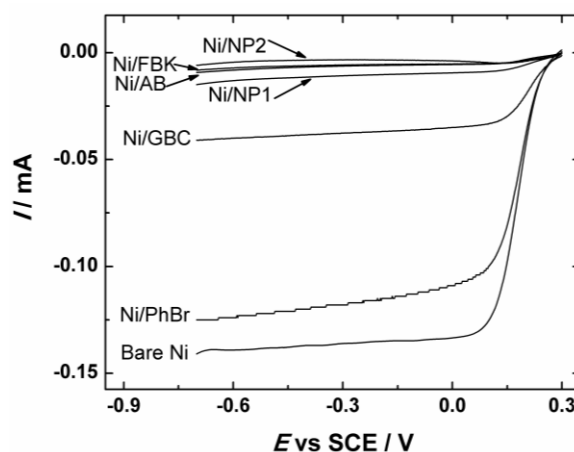


Figure 6. Comparative RDE voltammetry curves of ferricyanide reduction on bare and aryl-modified Ni electrodes recorded in Ar-saturated 0.1 M KOH solution containing 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$. $\nu = 20 \text{ mV s}^{-1}$, $\omega = 1900 \text{ rpm}$.

Although the RDE response of this redox couple was strongly suppressed on both, Ni/NP1 and Ni/NP2 electrodes, one can observe a subtle difference between these two (see Figures 5e,f, 6 and Table 2).

Table 2. Comparison of current values (I , mA) of ferricyanide reduction at -0.3 V for a bare and aryl-modified Ni electrodes obtained by the RDE method in Ar-saturated 0.1 M KOH solution containing 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$. $\omega = 1900$ rpm, $\nu = 20$ mV s $^{-1}$.

	bare Ni	Ni/PhBr	Ni/GBC	Ni/AB	Ni/FBK	Ni/NP1	Ni/NP2
I , mA	0.136	0.118	0.038	0.006	0.006	0.011	0.003

More specifically, after electrografting of Ni electrodes with NP groups the current decreased by 92% (Ni/NP1), meanwhile modifying Ni with NP moieties by redox grafting the current was suppressed almost totally (98%) (see Figure 6 and Table 2). Additionally, the RDE voltammetry curves of Ni/NP1 reveal only a slight dependence on the rotation rate between 360 and 610 rpm, whereas at higher rotation rates the reduction current is almost unchanged indicating effective blocking action towards the ferri/ferrocyanide redox couple (see Figure 5e). Even though compared to bare Ni (see Figure 4) a slight dependence between the current values and rotation rates is observed in case of Ni/NP2 electrodes (see Figure 5f), the dependence is rather negligible. Furthermore, the efficient passivation data obtained with Ni/NP2 electrodes towards the ferri/ferrocyanide redox probe is in compliance with the XPS analysis conducted above (see Section 3.2), where the characteristic Ni peaks in the XPS spectra (Ni2p, Ni(LLM) and Ni3s) were suppressed implying the formation of compact and thick NP layer on Ni surface during the redox grafting.

All these findings are important for the practical application of aryl-modified Ni electrodes in various fields. For example if protective barriers are necessary then thick and compact aryl films (e.g. thick NP layers) are preferable. In contrast, if very compact coverage of the surface is not necessary, then these surfaces (e.g. PhBr or GBC films) may be further used for the development of (bio)sensors.

4. CONCLUSIONS

In this study, nickel electrodes were electrografted with various diazonium compounds (e.g. AB, GBC, FBK, PhBr and NP) and for the first time, special modification procedure called redox grafting was applied in order to obtain thick NP films on the Ni surface. After modification, the attachment of AB, GBC, FBK, PhBr and NP groups on the Ni electrodes was in evidence since the corresponding aryl groups were visible in the XPS spectra. In addition, the multilayer formation was possible while the peak at 400 eV in the XPS N1s spectra was seen in case of AB-, GBC-, FBK- and NP-modified Ni electrodes. However, the main aim was to investigate the barrier properties of the prepared aryl layers on Ni substrates using the ferri/ferrocyanide redox probe. Based on the results obtained by cyclic voltammetry and the rotating disk electrode method, one can conclude that the

partial blocking of the electrochemical response of the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox system by GBC- and even less by PhBr-modified Ni electrodes can be indicative of the presence of rather thin or porous (consisting pinholes or defects) aryl film where the electron transfer between the underlying substrate material and redox probe takes place. In contrast, the Ni electrodes electrografted with AB, FBK and NP diazonium moieties strongly suppressed the signal of the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple referring to the fact that these aryl layers are rather compact consisting only small amount of defects or pinholes. It is also important to point out that the largest blocking effect was observed in case of the NP-modified Ni electrodes when the redox grafting during the surface modification was employed. This leads to the formation of thick NP films which possess strong barrier properties towards the $\text{Fe}(\text{CN})_6^{3-}$ probe.

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