

**FULL PAPER**

# Electrocatalytic hydrogenation of azobenzene and nitrocyclohexane with dispersed copper microparticles into poly(pyrrole-alkylammonium) films

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This paper presents the results of the electrocatalytic hydrogenation of azobenzene and nitrocyclohexane on carbon felt cathodes modified by poly(pyrrole-alkylammonium) films and containing dispersed metallic copper microparticles in a hydroorganic medium at neutral and basic pH. The effect of the polymers' structures, the cathode nature, and the effect of synthesis methods on the electrocatalytic activity of the electrodes have been examined, as well. The obtained products were identified by gas chromatography in comparison with authentic ones. It is found that azobenzene leads to aniline, while nitrocyclohexane to cyclohexanone oxime. Indeed, these cathodes allow the hydrogenation of the substrates at potentials between -1 and -1.2 V/SCE in basic medium and between -0.65 and 0.85 V/SCE in neutral medium, lower as compared with their reduction potentials. It is indicated that the best chemical and electrical yields are obtained in a basic medium and the chemical yields of the formed products increase with the amount of copper inserted, while the length of the alkylammonium chain has no remarkable influence on yields. It has been demonstrated that these cathodes have a good electrocatalytic activity despite the very small amount of copper inserted into the polymer film.

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**KEYWORDS**

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**Introduction**

The initial investigation on electrocatalytic hydrogenation goes back at the beginning of the 20<sup>th</sup> century [1-3]. This was forgotten for sometimes due to the low activity of the utilized cathodes, often made of bulk transition metals. Electrocatalytic hydrogenation can be likened to the conventional catalytic hydrogenation. However, this method has important advantages:

- The use of hydrogen generated in situ rather than from an external source; its

production can therefore be controlled by adjusting the potential or the current density;

- The electrocatalytic hydrogenation can take place at lower pressures and temperatures because hydrogen is generated in an already activated form;

- In comparison with the conventional electroreduction techniques, electrocatalytic hydrogenation makes it possible to achieve reductions at less negative potentials, which makes it possible to orient the reduction differently, to decline energy consumption, and to avoid the formation of by-products [4].

Due to its low cost, catalytic activity and interesting selectivity, nickel has been widely used in the electrocatalytic hydrogenation of organic compounds, either in the form of electrodeposited nickel on various conductive substrates or in the form of Raney nickel [5-8]. On the other hand, the use of copper in electrocatalytic hydrogenation remains limited to a few experiments carried out with electrodes based on Devarda copper [9-10] or polycrystalline copper [11-12]. In the meanwhile, nitrobenzene, phenylhydroxylamine, azoxybenzene, azobenzene, and hydrazobenzene have been reduced to aniline. In addition, the Devarda copper cathode allows to reduce nitro aliphatic compounds, such as nitrocyclohexane into cyclohexylamine [9]. Other electrodes have further been used for the electrocatalytic reduction of nitroarenes and nitrocyclohexane [13-18]. Recently, cyclohexanone oxime has been synthesized by liquid phase hydrogenation of nitrocyclohexane using a bimetallic catalyst [19]. Likewise, the recent development of electrodes for the degradation of dyes [20-22], the reduction of CO<sub>2</sub> [23], as an electrochemical sensor [24-25] and photoacoustic response of organic compounds is of high significance [26-27].

The dispersion of microparticles in conductive polymer films provides effective cathodes for the electrocatalytic hydrogenation of organic compounds due to the formation of chemisorbed (active) hydrogen on the surface of the electrode. The initial electrodes modified by polymer films containing noble metal particles for the electrocatalytic hydrogenation of organic compounds were developed in France at the laboratory of organic electrochemistry and redox photochemistry [28]. It has been shown that the incorporation of particles of noble metals and transition metals in films of poly (pyrrole-viologen) and polypyrrole alkylammonium, makes it possible to manufacture modified electrodes effective for

the electrocatalytic hydrogenation of a number of organic functions in hydroorganic medium (water-alcohol) [28-32].

In this work, the electrocatalytic activity of carbon felt cathodes were studied which were modified by a film of polypyrrole alkylammonium containing dispersed copper microparticles for the hydrogenation of azobenzene and nitrocyclohexane in an environment of water-ethanol at neutral and basic pH. The length of the carbon chain of polypyrrole substituted by alkylammonium with 3 carbons (poly1) and 12 carbons (poly2) and the method of copper insertion by exchange-reduction as well as the direct reduction were investigated.

### *Experimental*

#### *Instrumentation*

The electrochemical equipment consisted of an EGG PAR 273 potentiostat/galvanostat. The reference electrode was either the system Ag/Ag<sup>+</sup> 10<sup>-2</sup> M consisting of a silver wire immersed in a solution of 10<sup>-2</sup> M AgNO<sub>3</sub> in 0.1 M acetonitrile in TEAP for the study in acetonitrile, or a saturated calomel electrode with KCl (SCE), Tacussel C10, equipped with an electrolytic bridge.

#### *Chemicals*

The used reagents, electrolytes, and solvents were commercial products used without prior purification. The monomers (3-pyrrol-1-ylpropyl) triethylammonium [33], denoted as **1**, and (11-pyrrol-1-yl-dodecyl) triethylammonium [34-35], denoted as **2**, were synthesized at the Department of Molecular Chemistry, University Joseph Fourier Grenoble (France).

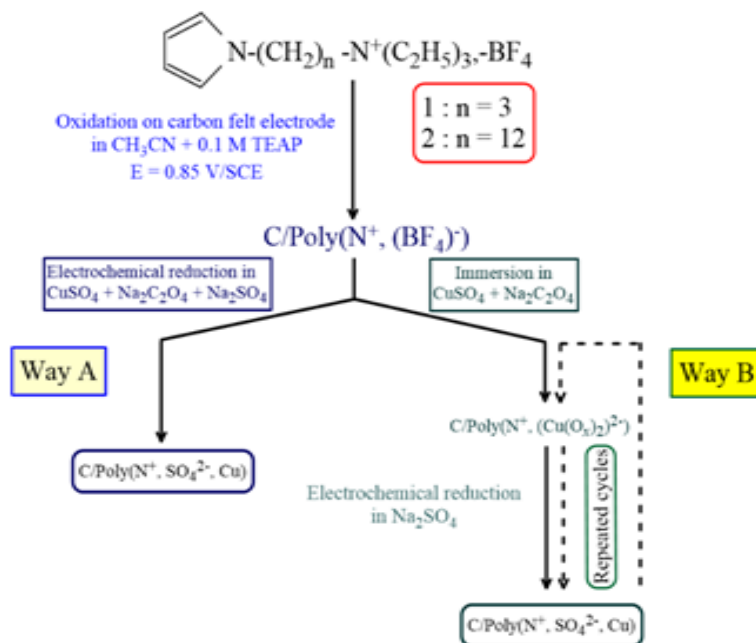
#### *Electrodes elaboration*

The preparation of the modified electrodes for the preparative electrolysis is carried out in a Metrohm cell of 50 ml volume without

barriers, where the auxiliary electrode is a cylindrical platinum grid placed around the working electrode. The latter having the dimension  $25 \times 20 \times 4 \text{ mm}^3$  were carbon felts (RVC 2000,  $65 \text{ mg cm}^{-3}$ , Le Carbone, Lorraine) with an active electrochemical surface area of  $42.5 \text{ cm}^2$  per  $\text{cm}^3$  of felt [36]. These were modified by polymer films containing copper microparticles.

After depositing the polymer film by electrochemical oxidation of the monomer at  $0.9 \text{ V}$  in  $0.1 \text{ M}$  acetonitrile medium in TEAP on the carbon electrode, the incorporation of metallic copper particles into poly1 and poly2 films was carried out according to two

manners, as given in the schematic diagram of Figure 1. The first manner consists of a simple immersion of the modified electrode in an aqueous solution of  $\text{CuSO}_4$  and  $\text{Na}_2\text{C}_2\text{O}_4$ . Then, the anions  $(\text{Cu}(\text{O}_x)_2)^{2-}$  exchange with the counter ions  $\text{Cl}^-$  initially present in the film, and thus an electrochemical reduction at the potential of  $-0.5 \text{ V/SCE}$  in an aqueous medium makes it possible to precipitate the metallic copper in the polymer film (Way A). The second manner consists of a direct electrochemical reduction of the modified electrode in an aqueous solution of  $\text{CuSO}_4$  and  $\text{Na}_2\text{C}_2\text{O}_4$ , without going through an independent ion exchange step (Way B).



**FIGURE 1** Schematic diagram of the two ways of preparing the electrode C/PolyN<sup>+</sup>-Cu. Way A: Direct electrochemical reduction; Way B: Reduction after an exchange procedure

The characterization of polymer-metal composites has already been presented in details in previous work. This technique makes it possible to insert the metal in the form of microparticles dispersed uniformly in the polymer film. The amount of metal introduced not exceeding a few micrograms [28-32,37].

### Electrocatalysis

The electrolysis of azobenzene and nitrocyclohexane were carried out according

to the experimental conditions described by Lessard *et al.* [10-11]. These were carried out in a three-compartment H-shaped cell. The modified carbon felt electrodes were placed in the cathode compartment containing  $40 \text{ ml}$  of the electrolyte. The potential was maintained between  $-1.0$  and  $-1.2 \text{ V/SCE}$  in basic solutions, and between  $-0.85$  and  $-0.65 \text{ V/SCE}$  in neutral ones. After  $30$  minutes of electrolysis (hydrogen evolution),  $1 \text{ mM}$  of substrate was introduced into the cathode compartment. The electrolyses were stopped after the

current fell to a few mA. The end products were extracted with diethyl ether. Their identification was based on gas – chromatography (GC) in comparison with authentic samples and confirmed by GC – mass spectrometry experiments.

### Chromatography analysis

The qualitative and quantitative analyzes of the electroreduction products were carried out using a Shimadzu GC-14A chromatograph equipped with a flame ionization detector and connected to a Merck D 2000 recorder-integrator. The doses were thereafter performed by comparison with authentic samples. The column (diameter 2 mm, length 3m) was filled with the phase SE 30 phase at 10% on Chromosorb W washed with acids (45/60 mesh) and sieved at 0.1 mm.

## Results and discussion

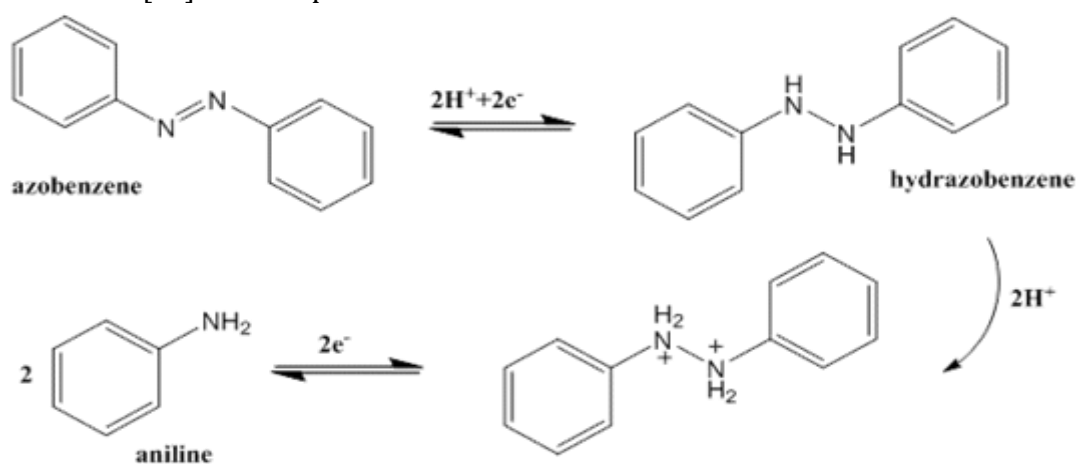
### Electrocatalytic hydrogenation of azobenzene

During the nitrobenzene reduction to aniline, Zouaoui *et al.* [31] have reported that the

formation of azobenzene with variable yields depended on the utilized electrode and the medium pH.

With the electrodes prepared by incorporation of copper microparticles in films of poly1 or poly2, the chemical yields of azobenzene are very low due to the high catalytic activity of these cathodes, which allows the preferential reduction of nitrobenzene to aniline. On the other hand, on the electrodes of felt of bare carbon or modified by the copper deposit, the chemical yields of azobenzene are relatively high.

According to the literature, the reduction to 4 electrons of azobenzene should lead to aniline, hydrazobenzene being formed (Figure 2) [38]. The intermediate product of this reduction is hydrazobenzene and a side product is benzidine. We are therefore interested in the reduction of this compound on carbon felt cathodes modified by poly1 or poly2 films and containing copper microparticles and on bare carbon felt electrodes. The results are presented in Table 1.



**FIGURE 2** Schematic diagram of azobenzene reduction

TABLE 1 Azobenzene electrocatalytic hydrogenation

Input	Cathode	Medium	E (V/SCE)	I <sub>0</sub> (mA)	I <sub>f</sub> (mA)	Load (C)	Chemical efficiency <sup>b</sup> (%) PhNH <sub>2</sub>	Electrical efficiency <sup>b</sup> (%) PhNH <sub>2</sub>
1	C/Poly1 (1,5×10 <sup>-5</sup> mol) <sup>c</sup> -Cu (4 exchanges)	Basic	-1	25	1,2	200	36	72
2	C/Poly1 (1,2×10 <sup>-5</sup> mol) <sup>c</sup> -Cu (1 exchange)	Basic	-1	16	4	430	19	17
3	C/Poly2 (1,1×10 <sup>-5</sup> mol) <sup>c</sup> -Cu (4 exchanges)	Basic	-1	100	2,5	245	24	38
4	C/Poly1 (0,6×10 <sup>-5</sup> mol) <sup>c</sup> -Cu (1 exchange)	Neutral	-0.65	13	1,8	210	19	36
5	C/Poly2 (2,2×10 <sup>-5</sup> mol) <sup>c</sup> -Cu (4 exchanges)	Neutral	-0.65	65	3	240	35	58
6	Carbone <sup>d</sup>	Basic	-1	14	5,8	336	e	e
7	Carbone <sup>d</sup>	Neutral	-0.65	25	1	195	21	41

<sup>a</sup>Reduction of 1 mM of azobenzene in 40 ml a mixture of methanol: water (93:7), basic (0.14 M KOH), or neutral (0,37 M CH<sub>3</sub>COONa + 0.54 M CH<sub>3</sub>COOH); <sup>b</sup>detected and doses by CPG; <sup>c</sup>deposited polymer on 25x20x4 mm of carbon felt; <sup>d</sup> carbon felt; <sup>e</sup>non-detected by CPG.

In basic electrolytes (E<sub>app</sub> = - 1 V/SCE) and in neutral electrolytes (E<sub>app</sub> = - 0.65 V/SCE), the electrolysis was stopped after the exchange of about 4 electrons, or after the current dropping to a few mA. Load charges varied between 200 to 430 F, corresponding to approximately 2 to 4 electrons per azobenzene molecule. The only obtained product has been aniline with fairly good chemical and electrical yields (inputs 1 and 5). Hydrazobenzene was never detected at the end of the reactions.

For the same polymer, the amount of incorporated copper had a significant effect on the electrocatalytic activity of the cathodes. In fact, on an electrode prepared with 4 incorporations of copper in poly1, the chemical yield of aniline is clearly greater (36%, input 1) than with a cathode prepared with a single incorporation (19%, input 2).

Furthermore, the amount of deposited polymer on carbon felt had an important influence on the activity of these cathodes. The

comparison between the results of inputs 1 to 5 illustrates that the production of aniline is greater in cases of thicker polymer films. This result is not surprising, since more copper particles are incorporated as the polymer film thickness is increased.

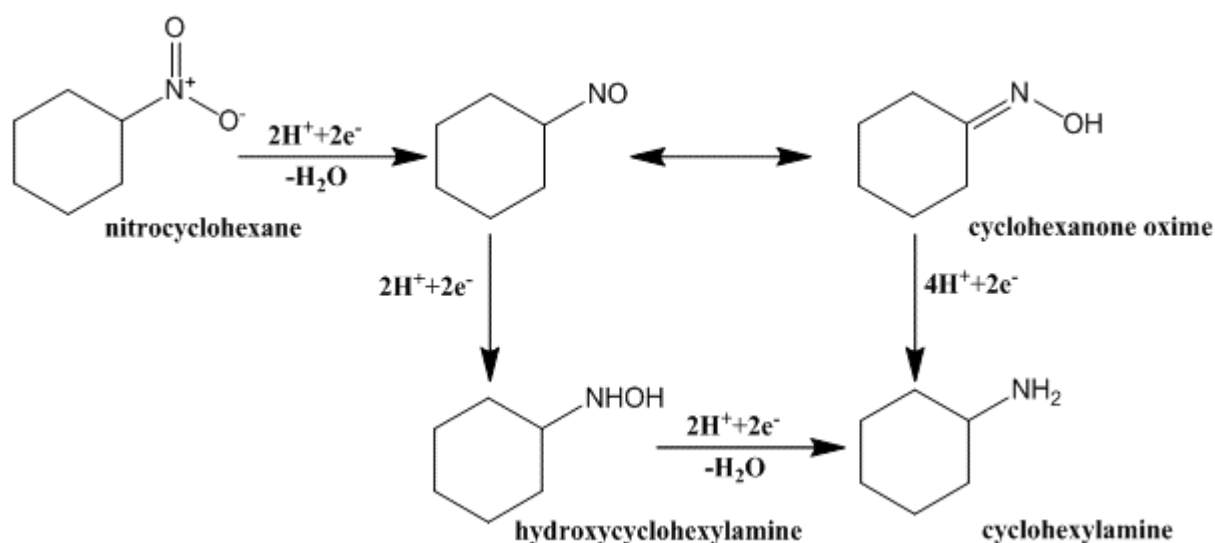
It is worth noting that the reduction of azobenzene on bare carbon felt does not take place at -1 V/SCE in a basic medium (input 6). On the other hand, in a neutral medium and at E<sub>app</sub> = - 0.65 V/SCE, aniline is formed, with a chemical yield (21%, input 7), which markedly lower than that obtained with carbon/polymer-copper cathodes under the best conditions (35%, input 5). Finally, it had been indicated that the reduction of azobenzene on a polycrystalline copper electrode leads only to hydrazobenzene [11]. All of these results once again illustrate the good electrocatalytic activity of these cathodes prepared by the dispersion of copper microparticles in polymer films.

### Electrocatalytic hydrogenation of nitrocyclohexane

In comparison with that of nitroaromatic compounds, the electrochemical reduction of nitroaliphatics to their corresponding amines is more difficult. The intermediate reactions formed during the reduction process such as oxime and hydroxylamine are more stable. The reaction mechanisms of their

electrochemical reduction, taking nitrocyclohexane as an example, is depicted in Figure 3 [9, 39]. It should be noted that the cyclohexanone oxime is obtained by tautomerization of nitrocyclohexane.

The most significant results obtained on the reduction of nitrocyclohexane on carbon felt cathodes modified by poly1 and poly2 films containing copper microparticles and on copper plates are presented in Table 2.



**FIGURE 3** Schematic diagram of nitrocyclohexane reduction

The reduction current of nitrocyclohexane is lower than that of nitrobenzene, even at more negative potentials (- 1.1 V/SCE in basic medium and - 0.9 V/SCE in neutral one). The oxime has been the product essentially which was formed, with often quantitative chemical yields (100%, input 1). In some cases, small amounts of amine were formed (inputs 2 to 6). The non-identified by-products were further detected by gas - chromatography (inputs 5 and 6), nevertheless, hydroxylamine was not detected.

In view of the reported results in Table 2, there is no significant difference in the catalytic activity between the different electrodes, whatever the polymer (poly1 or poly2) and the incorporation manner (ion exchange-reduction or direct reduction). It is worth noting that the highest reduction

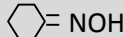
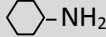
currents were obtained, in the basic medium (input 3) and in the neutral one (input 5), with the electrodes prepared by direct electroprecipitation of a large quantity of copper (4 Coulombs). However, the largest amounts of cyclohexylamine (11% and 13%; inputs 2 and 4) were obtained with electrodes prepared by the ion-reduction exchange procedure. This result reveals that this manner leads to electrodes whose catalytic activity is significantly better, probably due to a more homogeneous dispersion of copper microparticles in the polymer.

The reduction of nitrocyclohexane in a basic electrolyte to the corresponding oxime on the copper plates is quite effective (input 6), however, this requires the application of a much more negative potential (- 1.5 V/SCE instead of - 1.2 V/SCE) and the resulting

amount of formed amine is low (4%). In this case, the electrocatalytic activity of copper microparticles as dispersed in the films of poly1 and poly2 is further greater than that of copper plates. These cathodes are, however,

less efficient than those based on copper from Devarda, which led to reduce nitrocyclohexane to cyclohexylamine with good chemical and electrical yields [9].

**TABLE 2** Nitrocyclohexane electrocatalytic hydrogenation

Input	Cathode	Medium	E (V/SCE)	I <sub>o</sub> (mA)	I <sub>f</sub> (mA)	Load (C)	Chemical efficiency <sup>b</sup> (%)	
							 =NOH	 -NH <sub>2</sub>
1	C/Poly1 (1,2×10 <sup>-5</sup> mol) <sup>c, d</sup> Cu (1 exchange)	Basic	-1,1	6	1,5	180 <sup>g</sup>	100	-
2	C/Poly2 (2,2×10 <sup>-5</sup> mol) <sup>c, d</sup> Cu (4 exchanges)	Basic	-1,2	9	1,8	320	89	11
3	C/Poly1 (4,2×10 <sup>-5</sup> mol) <sup>c, e</sup> -Cu (2×10 <sup>-5</sup> mol)	Basic	-1,2	12	10	300	95	5
4	C/Poly2 (2,2×10 <sup>-5</sup> mol) <sup>c, d</sup> -Cu (4 exchanges)	Neutral	-0,9	19	1,6	430	87	13
5	C/Poly1 (4,2×10 <sup>-5</sup> mol) <sup>c, d</sup> /Cu (2×10 <sup>-5</sup> mole)	Neutral	-0,85	30	2	430	82	6
6	Copper Plate <sup>f</sup>	Basic	-1,5	25	25	600	90	4

<sup>a</sup>Reduction of 1 mM of nitrocyclohexane in 40 ml of a mixture methanol-eau (93:7), basic medium (0.14 M KOH), or neutral (0.37 M CH<sub>3</sub>COONa + 0.54 M CH<sub>3</sub>COOH); <sup>b</sup>detected products and doses by CPG; <sup>c</sup>deposited polymer on carbon felt; <sup>d</sup>incorporated copper by exchange in a medium of copper-oxalate followed by a reduction in a medium copper-free at E = - 0.5 V/SCE (1 incorporation (input 1), 4 incorporations (inputs 2 and 4)); <sup>e</sup>cuiivre incorporate per direct reduction in a medium copper-oxalate; <sup>f</sup>copper plate; <sup>g</sup>5×10<sup>-4</sup> mol of nitrocyclohexane

## Conclusion

This study allowed us to study the electrocatalytic activity of the modified electrodes (carbon felt/polypyrrole-alkyammonium-copper) vis-à-vis the hydrogenation of azobenzene and nitrocyclohexane in water-ethanol medium at neutral and basic pH. Aniline and oxime were obtained in quantitative yields. It is important to note that, despite the very low amounts of copper contained in the polymer films, these cathodes are effective for the electrocatalytic reduction of nitrates. The amount of the metal incorporated has a great influence on the

electrocatalytic activity of these modified electrodes, as demonstrated by reduction studies of azobenzene. However, we did not observe an influence of the nature of the polymer and of the incorporation manner (ion exchange-reduction or direct reduction of copper complexes) on the activity of these cathodes. Finally, although they are less efficient than the copper-based ones from Devarda, these modified electrodes are more active than the polycrystalline copper electrodes.

To sum up, in the case of nitrocyclohexane, the best result is obtained with the electrode modified with poly1 containing copper

particles inserted by the exchange-reduction method in a basic medium. Electrocatalytic hydrogenation is selective and results only in cyclohexanone oxime with a chemical yield of 100%.

Finally, the results obtained clearly reveal that the electrocatalytic hydrogenation of the studied nitro proves to be selective.

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### Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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