Electrocatalytic oxidation of methanol on CoNi electrodeposited materials

X. Tarrús, M. Montiel*, E. Vallés, E. Gómez

Departament de Química Física and Institut de Nanociència i Nanotecnologia (IN^{2}UB), Universitat de Barcelona, Martí i Franquès 1, E-08028 Barcelona, Spain.

*Author to whom correspondence should be addressed

e-mail: manuel.montiel@ub.edu

Phone: +34 934 039 241

Fax: +34 934 021 231

Abstract

Cobalt-nickel bimetallic materials electrodeposited on Si/Ti/Ni substrates were evaluated for the oxidation of methanol in alkaline media. CoNi samples were prepared potentiostatically selecting the adequate conditions to achieve the desired Co/Ni ratio. All samples were characterized by X-ray fluorescence and cyclic voltammetry to determine their composition and electrochemical behavior. The electrocatalytical performance of prepared samples was evaluated also by cyclic voltammetry using methanol solutions in alkaline media. Material composition, methanol and NaOH concentration, and temperature were the variables studied. The results indicate that excessive amount of cobalt inhibits the methanol oxidation reaction. In the same way, significant enhancement of the oxidation current is observed increasing the NaOH concentration up to 0.5 M, but from this value the electrocatalytic performance of these materials decreases. With regard to the increase of MeOH concentration or temperature, both variables are related to an improvement of the electrocatalytic performance. Finally, the effect of platinum skin on the CoNi deposits was evaluated, concluding that it favours MeOH oxidation but does not protect from the damage exerted by excessive NaOH concentration over the substrate surface.

Keywords

1. Introduction

In recent years, direct methanol fuel cells (DMFC) have gained interest as possible power devices, especially for portable electronic devices and electric vehicles. Among different possible alcohols, methanol is one of the most promising fuels because holds the advantages of high energy density, low operating temperatures, usage in aqueous electrolytes, low cost and easy fuel delivery and storage [1–6]. Methanol is usually produced using the synthesis gas route ($CO + H_2$) from fossil reserves such as natural gas or coal. Along with it, synthesis gas and therefore methanol can be produced in large quantities from biomass, maintaining unchanged the balance of carbon dioxide in the atmosphere [7–9].

Platinum group metals and alloys are the most effective electrocatalysts for the methanol oxidation in acid media, but they have two important disadvantages besides the high cost of metals: kinetic constraints and catalyst poisoning by CO [10,11]. Nevertheless in an alkaline electrolyte, the kinetics would significantly improve as compared with the acid counterpart. But, the issue of the cost of the electrocatalytic material deserves be resolved. Alkaline medium, additionally, allows the use of platinum free electrocatalysts, eliminating the problem of the catalysts poisoning by CO. So, a great deal of interest has been focused on the search of alternative transition materials cheaper than platinum.

Nickel is considered as a suitable electrocatalyst for the conversion of small organic molecules in basic media, due to its surface oxidation properties connected with the proposed formation of nickel hydroxides [12–15], that along with its relatively low cost and abundance in nature make it and its alloys some of the best candidates as electrocatalysts in the DMFC. Likewise, parallel studies have been found that the presence of certain metal cations such as cobalt, zinc or cadmium can affect the electrocatalytical behavior of nickel. Addition of $Co(OH)_2$ to nickel electrodes may increase the oxygen evolution potential and the charge acceptance of Ni electrodes [16–21].

In the present work CoNi deposits have been tested as a less-expensive way to allow effective methanol electrocatalyst. CoNi alloy is a versatile material used in many applications due to its wide range of properties. CoNi electrochemical preparation is well established [22–25]. It allows obtaining different composition ratios with little efforts. As well, the possible enhancing of the electrocatalytic performance of CoNi modified by skin Pt surface was investigated. Platinum skin was obtained by means galvanic displacement reaction. Studies about the possibilities of the prepared CoNi materials as electrocatalyst have been performed mainly by cyclic voltammetry.

2. Experimental

A conventional three-electrode cell and a potentiostat/galvanostat Autolab with GPES software were used. Preparation of CoNi deposits was performed from solutions freshly prepared, containing $NiCl_2$, $CoCl_2$, H_3BO_3 and saccharin at pH=3 and T=55ºC. The pH of the solutions was carefully controlled in order to minimize the hydrogen reaction evolution during the preparation. The pH was measured before and after operating CoNi plating, and

did not deviate from the initial value. The Ni(II)/Co(II) ratio in solution was varied between 10 and 5.

The reference electrode was Ag/AgCl mounted in a Luggin capillary containing 3 M KCl. The counter electrode was a platinum spiral. Vitreous carbon was the selected working electrode to establish the adequate electrodeposition conditions. Previous to each experiment the substrate was polished using alumina (1.75 and 3.75 µm) conveniently rinsed for 2 minutes in Millipore Milli Q water in an ultrasonic bath. Deposits were prepared on test samples of Si/Ti (100nm)/Ni (50nm). The Ti/Ni seed layer was obtained by sputtering, and supply the good electrical connection required by the electrochemical experiments.

The deposits composition was evaluated using X-Ray Fluorescence (XRF) (Fisherscope X-Ray DAL) and EDX analysis of JEOL JSM-840. X-Ray diffraction (XRD) phase analysis was performed on a PAnanalytical X'Pert-PRO MRD diffractometer. The Cu Kα radiation (λ=0.15418 nm) was selected by a means of a diffracted beam flat graphite crystal. $2\theta/\theta$ diffractograms were obtained in the 5-120º 2θ range with a step of 0.035º and a measuring time of 5 s per step. X-ray photoelectron spectroscopy (XPS) measurements of the binding energies (BE) were performed with a PHI 5600 multitechnique system.

Electrochemical study focused on methanol oxidation was made using a conventional cell of three electrodes, using NaOH and MeOH solutions from reactants of analytical grade, the same counter and reference electrodes than under preparation experiments and as working electrodes the different CoNi samples prepared.

3. Results

3.1. Electrochemical preparation of substrata

The preparation of the CoNi coatings was performed at from $NiCl_2$ 1M + $CoCl_2$ x M + H_3BO_3 0.5M + saccharin 3.8 10^{-3}M solutions varying x between 0.1 and 0.2. A previous voltammetric study was made using vitreous carbon as substrate in order to establish the electrochemical behaviour and the potential range at which CoNi deposition takes place (Figure 1A, curve a). Scanning at first to negative values, typical features for a nucleation and growth process were recorded after reversing the scan, followed by an oxidation peak during the positive scan, corresponding to the alloy oxidation [25,26]. Similar voltammetric

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behaviour was obtained using Si/Ti/Ni as working electrode, although the reduction current appearance occurs before (Figure 1A, curves b and c).

Selected the potential range, potentiostatic study revealed that at first the j-t transients show progressive increase in current with time, which evolves into a steady value, greater as more negative was the applied potential (Figure 1B). The compositional characterization of the prepared samples makes in evidence that anomalous deposition occurs [27]. Decreasing applied potential, the nickel percentage increases to attain a quasi steady value, as the manner that to increment cobalt percentage it was necessary to decrease Ni(II)/Co(II) in solution (Table 1). Gentle stirring of the solution prevents composition variation thorough the deposit thickness and favours the cobalt incorporation in the deposit. For all applied potentials, deposits were smooth and fine grained (Figure 2A), although those prepared at the more negative potentials show some holes due to hydrogen codeposition. The structural characterization of these deposits confirms fcc-CoNi solid solution formation accompanied by low presence of hydroxides for the deposits obtained at the lowest potentials. As deposits are nickel-rich, the diffraction peaks of the alloy were near the position of the pure fcc-Ni peaks (Figure 2B).

Considering these results, deposits were prepared potentiostatically under gentle agitation selecting the bath solution according to the CoNi percentage desired (75, 60 and 50 Ni wt. %) at potentials at which interference of hydrogen coevolution was minimized. The solution with 0.2 M of Co(II) was chosen in the preparation of the Co richer deposits, because allowed less negative applied potentials.

It is worth noting that this study has been carried out using Si/Ti/Ni test samples as support for CoNi catalyst. Employment of this substratum is owing to the ease to perform the measurement in half-cell. This electrodeposition method can be used to prepare samples over other conductive supports as metals, glassy carbon, or porous carbon.

3.2. Electrochemical behaviour of the CoNi coatings in NaOH solutions

Previous to study the methanol oxidation in alkaline medium, it was considered to analyze the electrochemical response of a 75 wt. % Ni substrate in the blank solution. At first, it was selected a 0.1 M NaOH solution. Voltammetric curves were recorded by cycling the potential between 0.1 and 0.65 V at 20 mV s^{-1}. During the positive scan, prior to oxygen evolution a wide oxidation peak appeared which maximum was located around 0.47 V (Figure 3A). This peak is related to the Ni(OH)$_2$/NiOOH oxidation process [28]. Likewise, in the negative scan

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the corresponding reduction peak was centred around 0.39V. Consecutive scans gave an increase of the involved charge, as the manner that the voltammogram attains steady profile and subsequent curves are reproducible. Increasing the NaOH concentration similar electrochemical behaviours were observed, although a shift to lower potential values of the oxidation peak occurs.

3.2. Methanol oxidation on CoNi

Adding methanol to the 0.1 M NaOH solution just attain 0.1 M MeOH, voltammograms were recorded at 20 mV s^{-1} using CoNi 75 wt. % as electrode. In the positive sweep beyond the oxide formation, a new current feature associated to methanol oxidation was recorded previous to oxygen evolution (Figure 3B). In the backward scan, also positive current was observed previous to the oxide reduction. As the interest of these materials is the continuous work, the effect of consecutive cycles on the voltammetric response was considered. The electrode was cycled consecutively for 60 cycles. As previously observed in the blank solution, current slightly increased with cycling, up to a constant value get at cycle 30, number of cycles from now will consider in order comparison of results.

Voltammetric experiments using substrata of the compositions prepared, (50, 60 wt. % Ni) show similar profiles that those obtained using CoNi substratum of 75 wt. % Ni, revealing that independently of the cobalt percentage in the alloy, all tested CoNi compositions result electrocatalytic to methanol oxidation. However, as the cobalt content in the deposit increases the recorded methanol oxidation current diminishes and their appearance delayed slightly to more positive potentials (Figure 3B). According to this result, it was decided pursue the characterization study of the materials in the methanol oxidation reaction using exclusively CoNi with 75 wt. % Ni as substrate.

Prior the analysis of the influence of different parameters over the recorded methanol oxidation current, it was considered to test the influence of activation step involving previous cycling of the electrode in the alkaline solution. The selected protocol consisted in applying continuous voltammetric scans at 50 mV s^{-1} between 0.1 and 0.65 V just during 40 cycles in the blank solution [16]. The observed behaviour of the electrode was similar to the previous one analysed at lower scan rate, and the current progressively increases just to reach a maximum. Afterwards, the electrode was immersed in the methanol solution. The consecutive voltammograms recorded show that increasing the cycle number continuous decrease in the

current associated to methanol oxidation just attains a stationary value, whereas the associated to the charge/discharge of electrode remains constant independently of the cycle number.

The comparison at fixed conditions of the voltammograms recorded using electrodes with and without previous activation evidenced that, in the first sweeps at equal number of scans, the recorded current was greater using activated electrode. But, increasing the cycle number, the difference between currents narrows. Although the stationary current value attained with activation it is always slightly higher, it was considered that this difference was not significant to justify the time consuming in the activation process.

The influence on the overall process of both reactants was also considered. At first the influence of the alkaline medium maintaining MeOH concentration at 0.1 M was analysed. The NaOH concentration was progressively increased in the solution in order to evaluate the effect of the hydroxyl concentration on methanol oxidation current. For all NaOH concentrations studied, the general profile of voltammetric curves was similar, but an advancement of the processes, both charge/discharge electrode and methanol oxidation was observed increasing NaOH concentration. The comparison of the voltammetric current recorded after stabilization evidences that, the increase of NaOH concentration up to 0.5M gave a significant enhancement of the oxidation current recorded, but from this value, the NaOH concentration increase in solution causes a clear diminution of current related to methanol oxidation (Figure 4). The current recorded at 1M NaOH was smaller than that recorded at 0.1M. It appears that the chemical hydroxylated species presumably formed on the substrate at the highest NaOH concentrations perturb the surface, as the manner that the species formed lose part of their catalytic activity.

In the same way, the influence of MeOH concentration was investigated. The progressive increase of MeOH concentration in the solution leads to a subsequent increase of the recorded current, although the relative increase was softened with the increase of methanol content in the solution. Similar behaviour was observed independently of NaOH concentration in solution, although, evidently, the recorded currents depend of the NaOH concentration. Figure 5 collects the stationary currents recorded at different NaOH concentrations, and makes in evidence the prevalence of 0.5 M, condition at which the greater currents were obtained for all MeOH concentrations analysed. It is noteworthy that the increase of MeOH concentration does not carry significant advancement of the oxidation process in none of the NaOH concentrations studied.

Established that the best conditions correspond to the 0.5 M NaOH solution, was also considered the voltammetric analysis of the temperature influence on the methanol oxidation

reaction at these conditions. The selected solution was that containing 0.1 M MeOH. An increase of the recorded current associated to methanol oxidation was observed as the temperature rose (Figure 6), accompanied by an important advancement of the oxygen evolution reaction. Similar results were obtained both rising and descending temperature. As a manner of test, experiments from 0.1M NaOH solution were performed, the general behaviour was similar to the observed at the 0.5 M NaOH solution, it is to say, clear increase of current recorded rising temperature, although at these conditions, the effect on the oxygen evolution was moderate.

As the final application of this kind of substrata supposes the continuous use of the material during a long term process, potentiostatic experiments were performed applying potential values corresponding to methanol oxidation. In all conditions the j-t recorded shows a sharp current diminution followed by a smooth one, just to attain a stationary value (Figure 7). Stirring the solution during the experiment, the profile is compatible with the former description although the stabilization was achieved at shorter times. In order to analyze the process related to current diminution, the effect of pulsed signal was investigated. A double step signal was used. The system was carried out alternatively between potentials at which methanol oxidation occurs followed to that at which alcohol oxidation does not occur. Two pairs of potential values were selected. Methanol oxidation potential (E_1) was always selected corresponding to the potential range at which quasi stationary voltammetric oxidation current was observed. In the first pulsed signal investigated, the second potential (E_2) was selected in the potential range at which substratum oxidation occurs. At these conditions the successive potential steps recorded (Figure 7B) show that during the application of E_1 a sharp current increase occurs followed by a continuous decrease of current during the pulse length. At E_2, the current drops to very low positive values. The comparison of the consecutive curves show that the current value recorded at the end of E_1 diminishes as the number of cycles increases.

In the second pulsed signal the E_2 potential corresponds to a potential value previous to the electrode oxidation. Using this kind of values for E_2, the recorded current at the end of the pulse length in E_1 was greater as the cycle number increases (Figure 7C). At these conditions, the influence of the length of the pulse in E_2 was investigated maintaining the length of pulse in E_1 at 150 s. Experiments were performed at different t_2 values. It was observed that it was necessary pulse lengths (t_2) greater than 10 s to improve the recorded current for the methanol oxidation as the number of steps increases, using $t_2=10$ s it was only achieved to keep the current.

These results could be interpreted in line of a poisoning of the electrode during the methanol oxidation, so that a certain potential value must be attained in order to achieve the reduction of poison species, being the "cleaning" a relatively slow process.

3.3. Methanol oxidation on CoNiPt. Skin Pt on CoNi deposits

Known the general behaviour of the methanol oxidation on the prepared CoNi deposits, the substrate modification with Pt was proposed in order to evaluate the capability of the modified material and the effect of the surface Pt presence on the CoNi in the methanol oxidation. Partial platinum skin was incorporated to the substrate by means a displacement reaction, immersing the CoNi substratum in a solution containing 0.4 mM of Pt(IV). This concentration was selected because allows to modify the surface Pt amount varying the immersion duration, in affordable times. The effectiveness of the reduction process was previously tested using long immersion times in which was detected important Pt presence even using these low Pt(IV) concentration.

The interest was focused on the effect of the partial Pt skin presence on the CoNi deposits. Substrata with 75 wt. Ni % were subjected to different immersion times to vary the Pt content on the substratum. The recorded voltammograms show similar features that to those observed using Pt-free CoNi substrata. The comparison between the voltammetric response obtained from Pt-free CoNi and CoNiPt substrata evidences that the Pt presence enhances the current related to methanol oxidation. However, upon increasing the immersion time the relative current change was moderated (Figure 8).

Established that the Pt presence exerts favourable effect, it was noted that, as occurs using Pt-free CoNi, the increase of NaOH concentration advances and favours also the oxidation processes, but the enhancing of methanol oxidation current occurs until the NaOH concentration rose to 0.5 M, concentration from which the recorded current begins to decrease, as occurs over the Pt-free CoNi substrata. The Pt presence is unable to overcome the damage effect that the excessive OH^- concentration exerts over the substrate surface.

3.4. XPS characterization of substrata before and after methanol oxidation

XPS characterization was performed in order to confirm the state of the elements present in both freshly prepared deposits and on the surface after having service as electrocatalyst for methanol. At first, a superficial analysis of freshly prepared samples was performed before

and after surface cleaning with argon ions during short time in order to remove physiadsorbed carbon and superficial oxygen. The corresponding spectra in the 2p spectra region of both components confirm the metallic nature of the alloy prepared. The features corresponding to both nickel and cobalt in metallic state appear, with the main peaks centered at 852.8 eV for nickel and at 778.2 eV for cobalt respectively (Figure 9A and B). These results are coincident with those obtained after consecutive runs, confirming that the CoNi coating prepared maintain composition and nature throughout the deposit.

XPS analysis will attempt to elucidate also the superficial oxidation state of the deposits after experimental voltammetric cycling in different alkaline media. The selected samples were two CoNi substrata with nickel percentage of 75 wt. % that had been previously cycled in NaOH 0.5 or 0.7 M solutions containing MeOH. Significant changes were observed in the spectra respect to those recorded in the freshly prepared sample. In the nickel energy range, a wide peak was recorded centred at 856 eV (Figure 9C, curves a and b), as corresponds to the presence of oxide/hydroxides of Ni(III). In the energy range of cobalt, a band peak between 779.5 and 780.2 eV was recorded (Figure 9D, curves a and b), related to the possible existence of Co_3O_4, Co_2O_3 or/and CoOOH. Although these results are not conclusive about the species present on the surface, confirm the existence of oxides or hydroxylated forms of both Ni (III) and Co (III) formed during the voltammetric cycling. The XPS analysis of these samples after sputtering with argon ions during certain time was also performed to analyze the composition in depth, after removing the formed superficial layer, the XPS spectra (Figures 9C and 9D, curves c) were similar to those obtained from the freshly prepared samples, demonstrating that the formation of oxide/hydroxilated species in the work conditions corresponds to a superficial process.

4. Conclusions

CoNi electrodeposited materials have been tested as catalysts for electrochemical oxidation of methanol in alkaline solution and their electrocatalytical performance and optimal working conditions are showed. Structural characterization of these materials confirms that they are deposited as a CoNi solid solution with low presence of hydroxylated species. Electrocatalytic measurements by cyclic voltammetry indicated that excessive amount of cobalt in the samples (above 25 wt. %) inhibits the methanol oxidation. In the same way, concentration of NaOH greater than 0.5 M perturbs the surface of material and the catalyst performance decreases. The progressive increase of MeOH concentration in the solutions revealed in all cases an

increase of the recorded current up to a quasi-stationary value. Also, the beneficial effect of the temperature increase has been demonstrated. The presence of a partial Pt-skin favours MeOH oxidation but is unable to overcome the damage that the excessive OH$^-$ concentration exerts over the substrate surface.

All results reported in this work indicate the performance of the Ni-rich CoNi coating as good candidate to be implemented as electrocatalyst in the DMFC. This will require CoNi deposit on porous carbon structures increasing both the available surface and accessible passage of fuel. The general ease CoNi electrodeposition on different substrates opens the possibility to obtain these CoNi deposits on the required substrata without much effort obtaining significant economical savings.

Acknowledgements

Figure Captions

Figure 1. From 1.0 M Ni(II) and 0.1 M Co(II) solution: A) Cyclic voltammograms on: a) vitreous carbon, b) Si/Ti/Ni, and c) Si/Ti/Ni at ω=100 r.p.m. Scan rate 50 mV s^{-1}. B) j-t transients at a) -800 mV, b) -850 and c) -880 mV.

Figure 2. A) SEM image of CoNi deposit obtained from 1.0 M Ni(II) and 0.1 M Co(II) solution at -880 mV, B) corresponding XRD pattern.

Figure 3. Cyclic voltammograms from: A) 0.1 M NaOH solution after 10, 20, 30 and 40 consecutive cycles. B) 0.1 M NaOH + 0.1 MeOH solution from different CoNi percentages: a) 75wt. %, b) 60wt. %, and c) 50wt. %. Scan rate 20 mV s^{-1} and cycle n=30.

Figure 4. A) Cyclic voltammograms from x M NaOH + 0.1 MeOH solutions: x=0.1, x=0.5, x=0.7, and x=1. Scan rate 20 mV s^{-1} and cycle n=30. B) Dependence of the voltammetric methanol oxidation current with the NaOH concentration.

Figure 5. Dependence of the voltammetric methanol oxidation current with the MeOH concentrations at different NaOH concentrations: 0.1 M, 0.5 M, 0.7 M and 1M. Cycle 30 and scan rate 20 mV s^{-1}.

Figure 6. Dependence of the voltammetric methanol oxidation current with temperature from 0.5 M NaOH + 0.1 MeOH solution, cycle 30 and scan rate 20 mV s^{-1}.

Figure 7. Chronoamperograms from CoNi electrode in the 0.5 M NaOH 0.1 M MeOH solution: A) at constant oxidation potential E_1=0.58 V, and using pulsed signal B) E_1=0.58 V and E_2=0.35 V and C) E_1=0.58 V and E_2=0.1 V using pulse lengths of t_1=150 s and t_2=50 s.

Figure 8. Cyclic voltammograms from 0.1 M NaOH + 0.1 MeOH solutions from CoNi electrodes after immersion in a 0.4 mM solution of sodium hexachloroplatinate (IV) during: 0 s, 30 s, 60 s and 90 s.

Figure 9. XPS spectra recorded for CoNi depostit freshly prepared: A) Ni 2p and B) Co 2p, and CoNi deposit after service in 0.5 M NaOH 0.1 M MeOH solution: C) Ni 2p3 and D) Co 2p. Curves a, b, and c correspond to consecutive runs with argon.

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Table 1

Table 1. Composition of CoNi samples and experimental conditions

Solution	-E (V)[a]	Ni (wt. %)		
		0 rpm	100 rpm	300 rpm
1M Ni(II) + 0.1M Co(II)	0.75		59	
	0.80[b]	70	62	
	0.85	72	63	
	0.90	75		
	0.91	75		61
	0.93[b]	75		62
	0.95			63
1M Ni(II) + 0.2M Co(II)	0.80	49		
	0.83	50		
	0.85	51		

[a] Total charge deposited at the indicated potential: 5 C cm^{-2}
[b] This samples were also prepared with a total charge of 3 C cm^{-2} and the Ni content was similar to that obtained with 5 C cm^{-2}

Figure 1
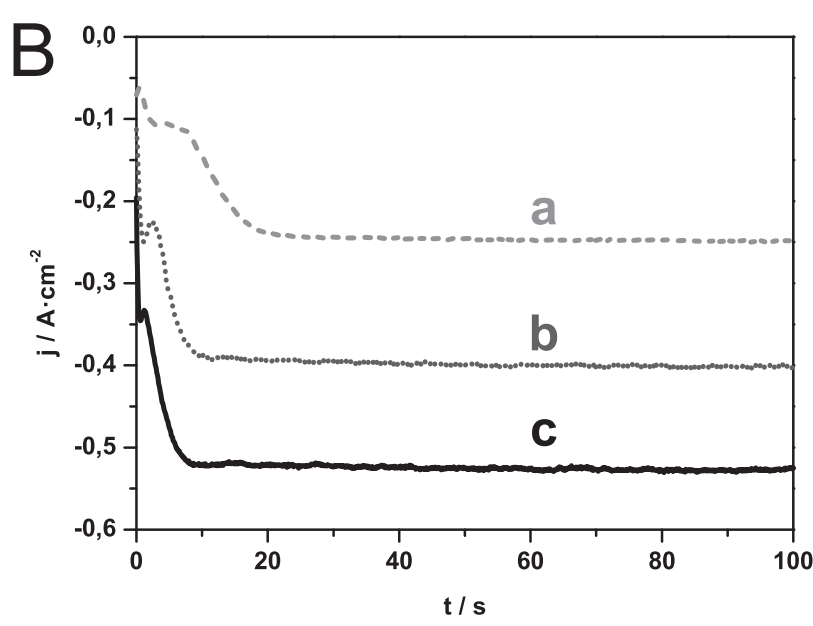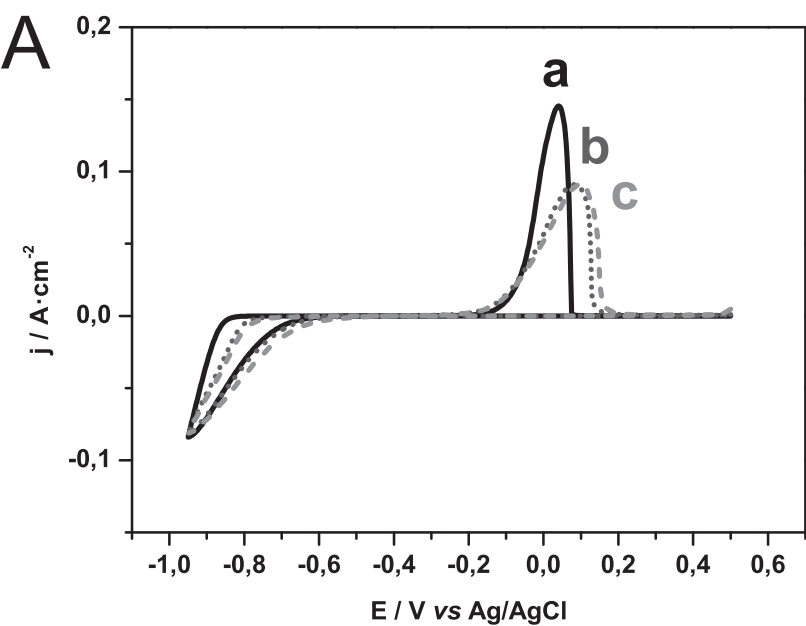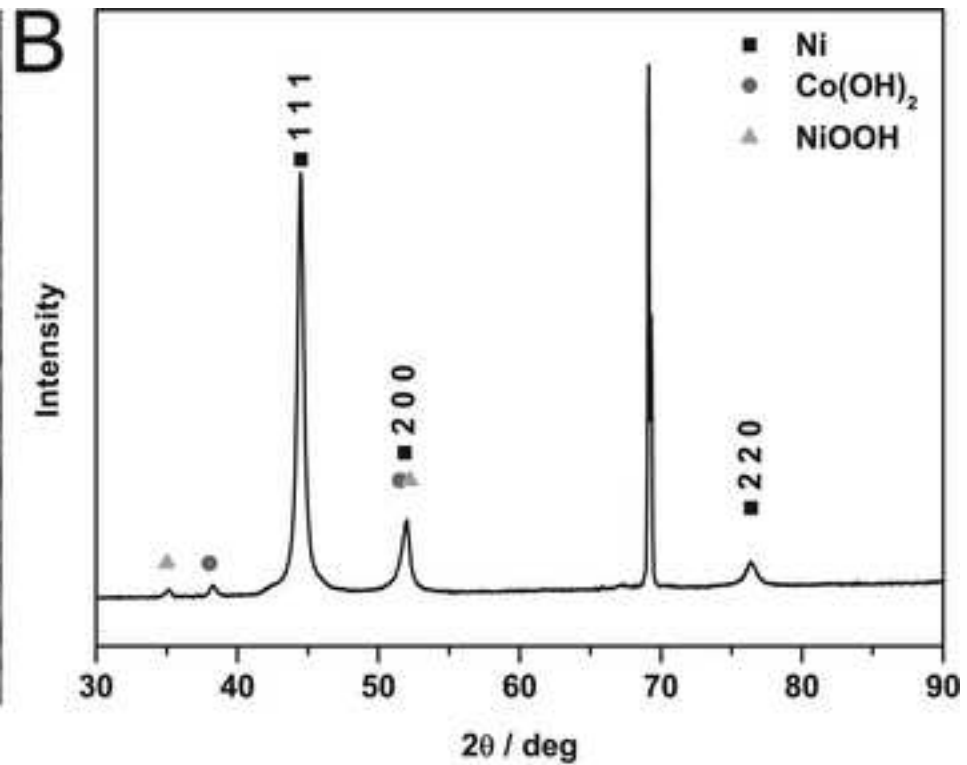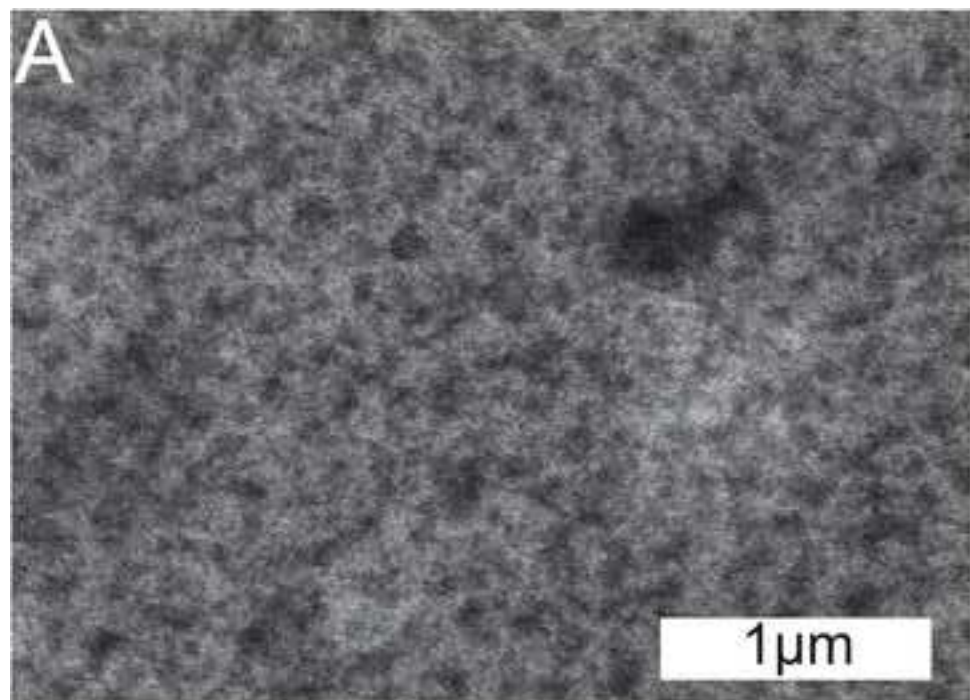
Figure 3
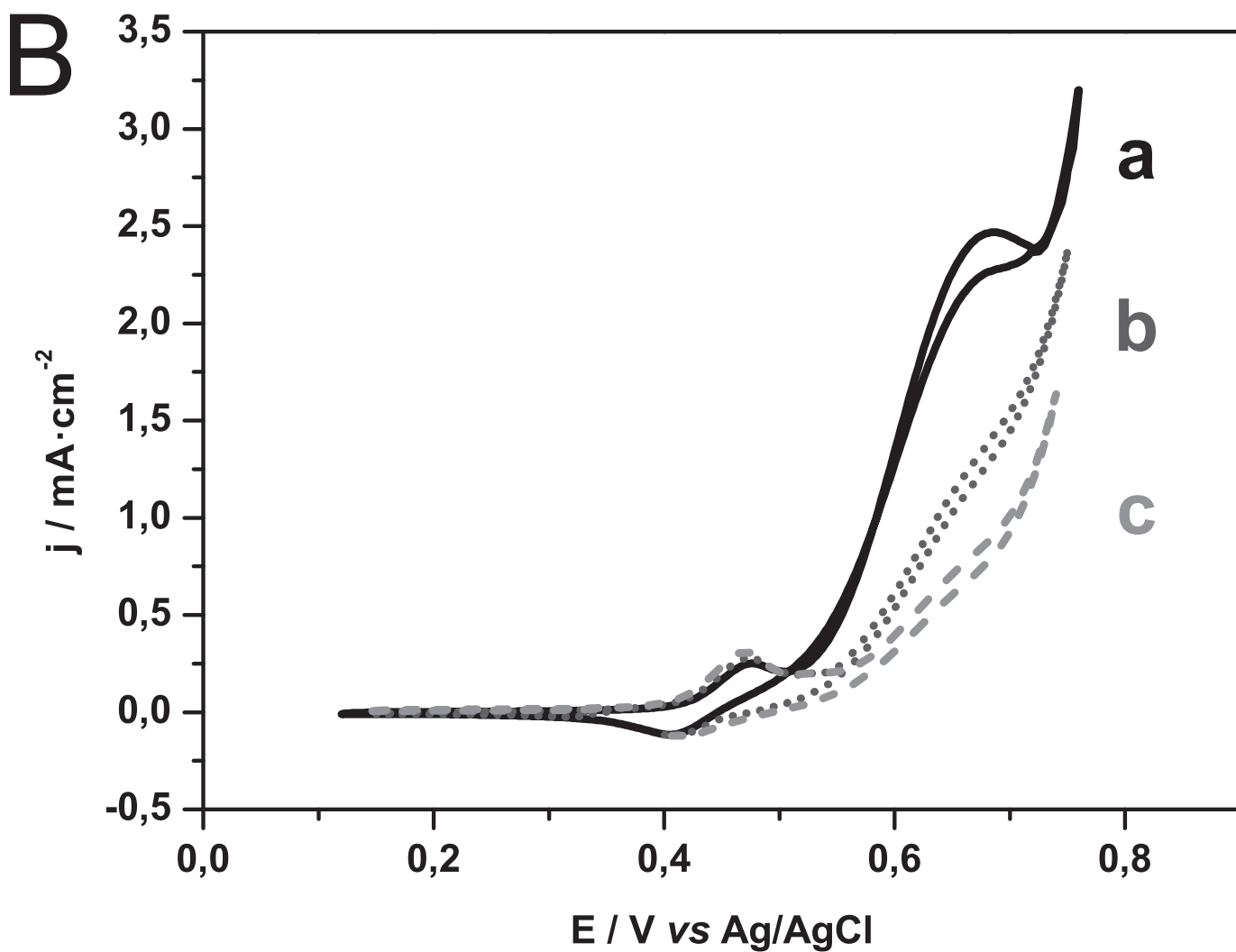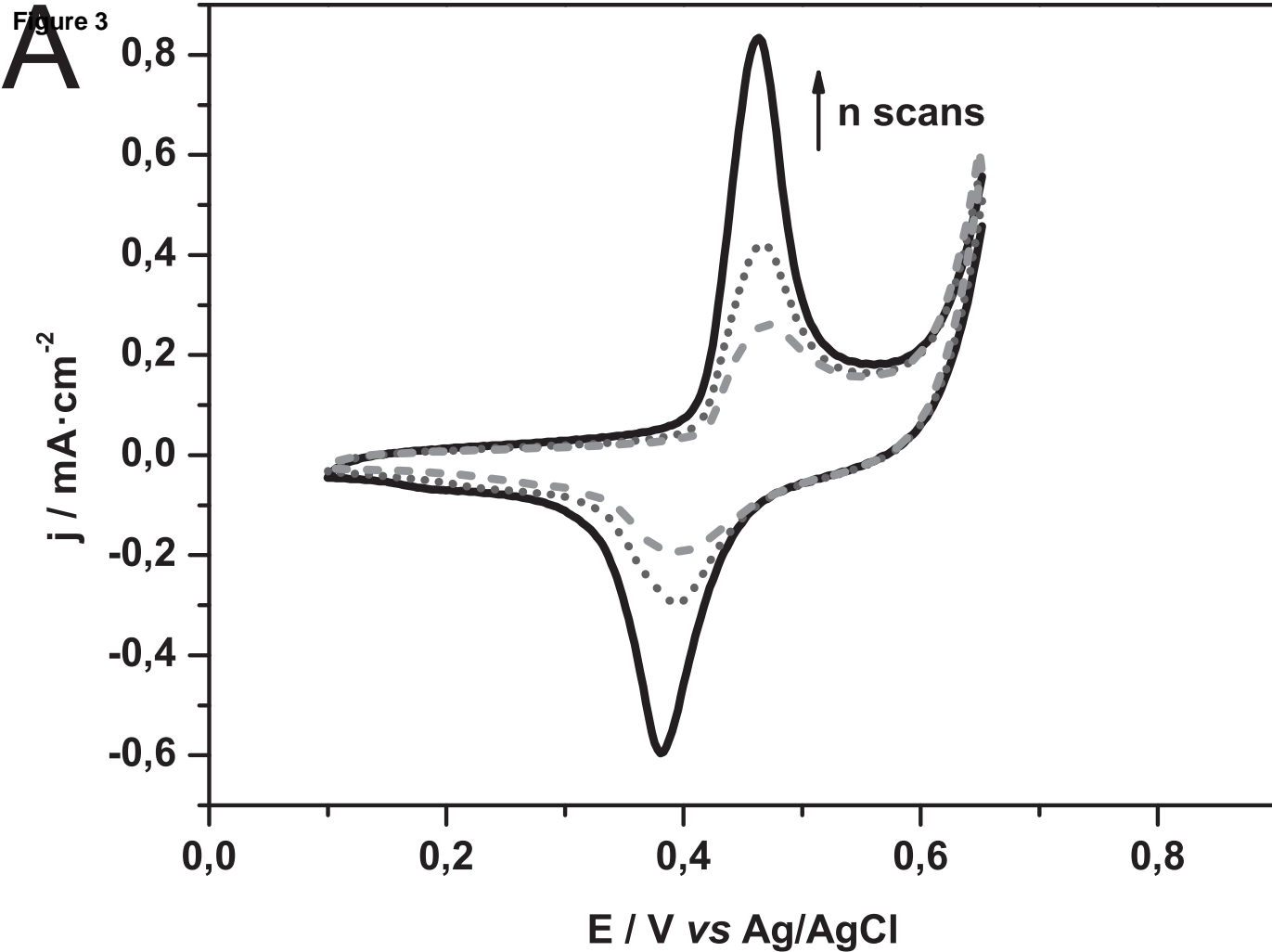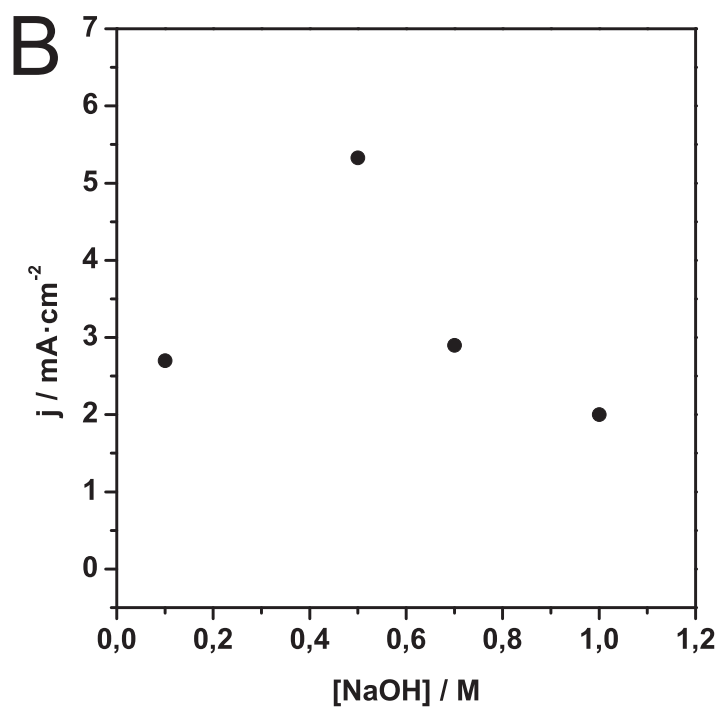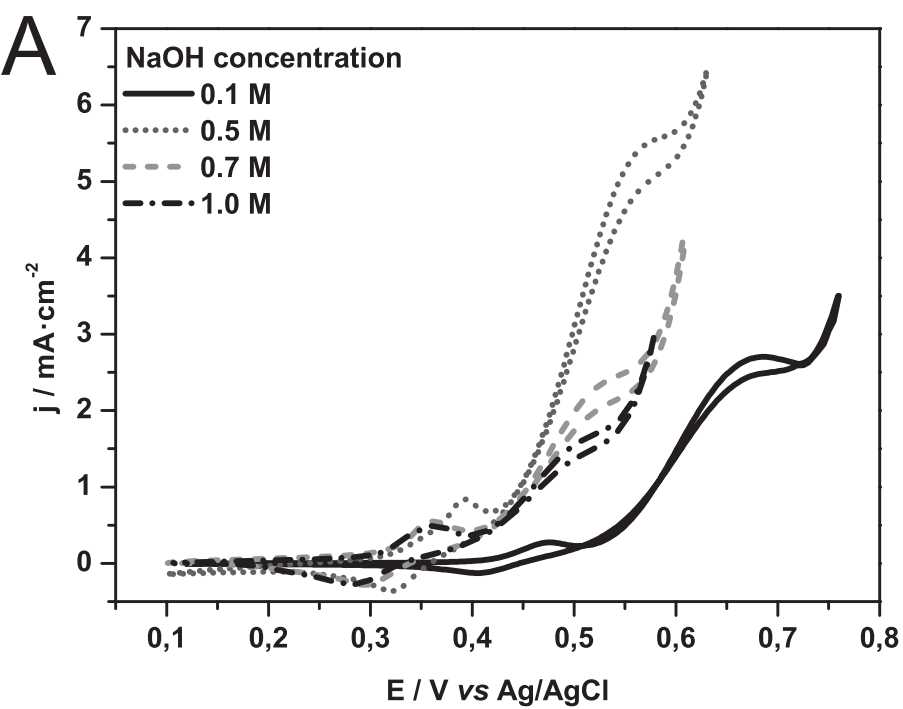
Figure 4

Figure 5
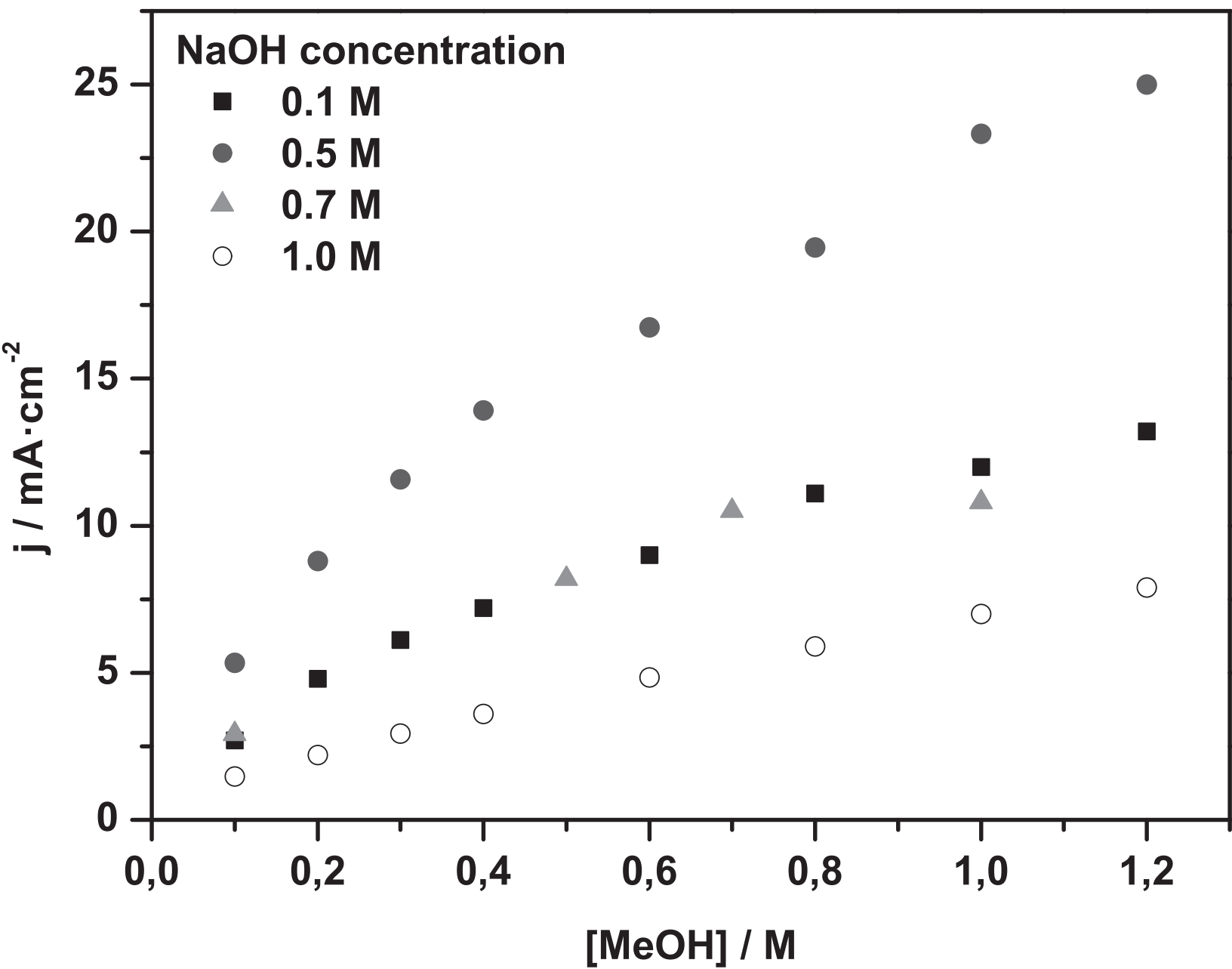
Figure 6
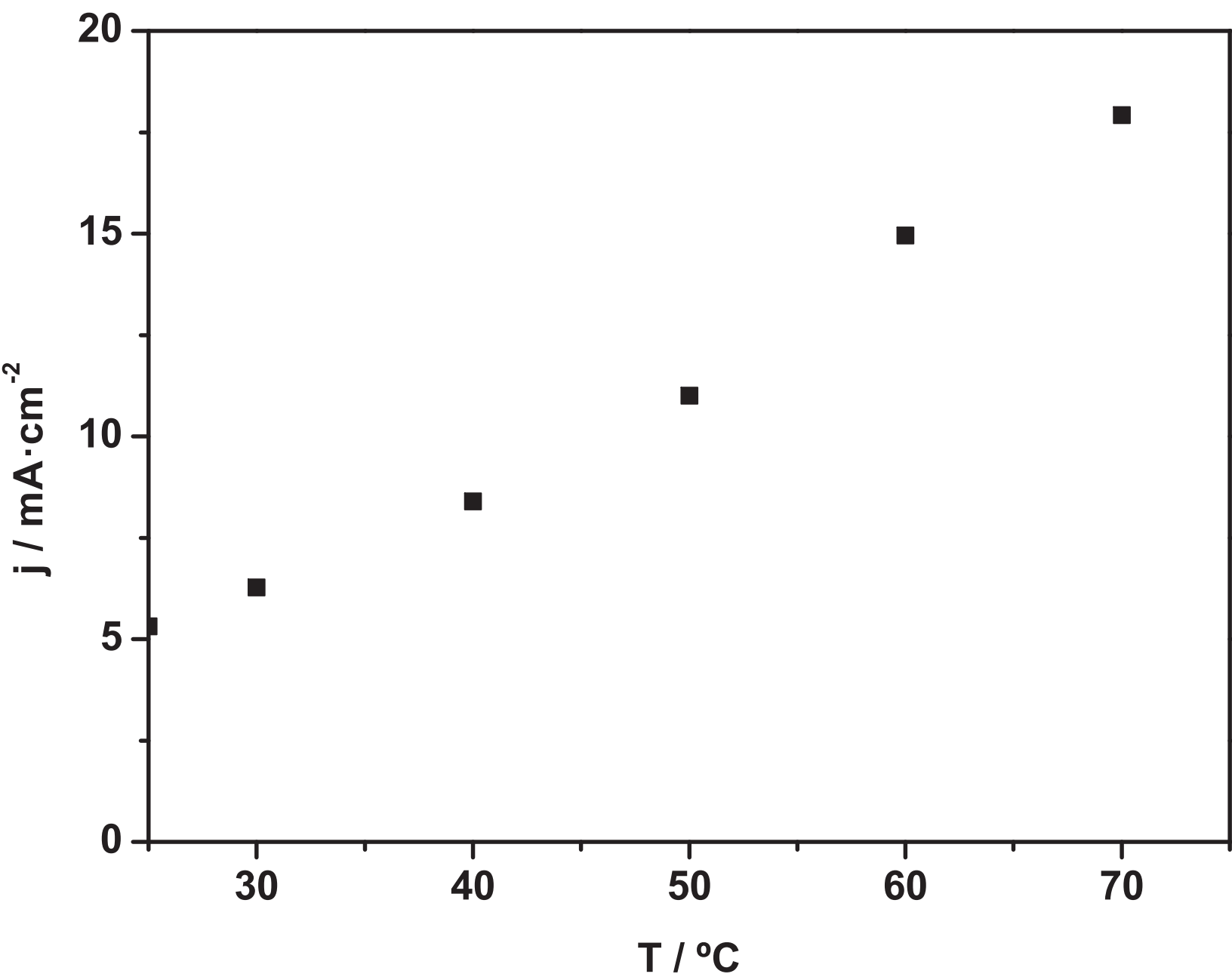
Figure 7

Figure 8

Figure 9