

Nickel Coated Graphite Microparticle Based Electrodes for Carbon Dioxide Reduction in Monoethanolamine Medium

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Abstract: A composite electrode that contains home-made nickel coated carbon micro-particles as active materials and epoxy binder has been prepared. The surface morphology, elemental composition and size distribution of microparticles were investigated using SEM, EDS, AAS, micro Raman spectroscopy and appropriate seizer apparatus. The prepared micro-particles appeared monodispers with 33 μm most numerous particle size diameter and with 10.1 w/w % Ni content. Conventional electrochemical methods like impedance

spectroscopy and voltammetry as well as scanning electrochemical microscopy (SECM) were used for investigation the properties of the composite electrodes. It has been proved that the electrode can be well used for electrocatalytic reduction of CO_2 directly in aqueous monoethanol amine (MEA) solution that frequently are applied for capturing it from power plant flue gases. SECM measurements showed that presence of dissolved CO_2 hinders the hydrogen evolution in aqueous MEA solution.

Keywords: Carbon dioxide reduction • Electrochemical conversion • Monoethanol amine • SECM • Voltammetry

1 Introduction

Carbon dioxide is major, non-wanted byproduct of energy production from fossil energy sources. It is generally accepted that slowing down or avoiding increase of its concentration in the atmosphere is essential for avoiding climatic changes and for saving viability of the planet. According to the importance very extensive research work has been carried out to find safe and economic ways for separating CO_2 content of flue gases and for using it or just getting rid of it.

Zero exhaust power plants capture the CO_2 from flue gases and deposit it in geological reservoirs like depleted oil and gas reservoirs, un-mineable coal seams or deep saline aquifers. Safer and more attractive way would be making useful product from CO_2 [1] instead of deposition. Along this line intensive research are in progress in different laboratories aiming to work out feasible technology for converting CO_2 to some kind of useful material.

In ideal cases solar power or excess electric energy driven electrochemical reduction would be used, and some kind of fuel, like CO or methanol [2] would be resulted [3]. Methanol can be produced reacting CO_2 with electrochemical produced hydrogen [4]. Economic ways of direct electro-reduction of CO_2 to some kind of fuel that is storable, easily and safely transportable and reusable in present day power plants is in the focus of interest. Experiments with Cu [5–7], Ni [8], and different carbon electrodes [9] gave promising results in this field. Very numerous papers have been published about application of different electro-catalysts confined on electrode surfaces or dissolved in background electrolyte for improving Faradaic efficiency or for directing the reduction to resulting in advantageous end product [10].

Specially selected or treated metal or alloy layers, nanoparticles, metal oxides, complexes with redox or hydrogen transferring character [11,12] have been found advantageous electro-catalysts for reducing CO_2 .

Important task is to work out cost effective technology for capturing CO_2 from flue gases of conventional power plants and for supplying it for industrial scale fuel producing process. Absorption in different solvents for capturing and desorption for regeneration is a well-studied and often applied solution. Aqueous solution of ammonia [13], different amines [14] like piperazine [15], have been applied as absorptive solvent. Monoethanol-

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amine (MEA) is one of the most favored amine component used in aqueous post combustion CO₂ capture solutions [16–19]. It would be advantageous if the new fuel producing reduction of CO₂ were performed directly in the same media that was used for capturing it. If it were feasible then energy needed for desorption or other steps could be saved. Therefore, the investigation of electrochemical CO₂ reduction process straight in aqueous, MEA containing capture solution has been an obvious step [20].

In our laboratory Scanning Electrochemical Microscopy (SECM), atom absorption spectroscopy, standard electrochemical methods and gas chromatography was employed for getting information about electrode processes taking place on polarized copper and nickel electrode surfaces in CO₂ containing aqueous MEA solutions [21]. The experiments proved that copper electrode that well applicable in aqueous solutions cannot be used in MEA containing media. It suffers intensive corrosion and loss of its electrocatalytic surface film. The presence of Cu also enhances the oxidative degradation of MEA [22]. Nickel electrode however, has not suffered from corrosion, fouling or reducing activity change. In the electrode process taking place at Ni electrode considerable amount of methanol could be detected.

Vast number of papers report on achieving improved electrochemical performance of different electrodes by confining highly dispersed different particles on surfaces of them. Among them carbon electrodes with catalytic Ni particles [23–25] were proposed. Recently we deposited micro size nickel particles on fine carbon powder and mixing it with epoxy binding matter a kind of graph-epoxy electrodes with catalytic nickel particles were prepared. Experiments proved the applicability of these electrodes for CO₂ reduction in in aqueous MEA solutions. This paper is about preparation procedure, about the property and the electrochemical behavior of the composite and the catalytic electrode.

2 Experimental

2.1 Materials and Solutions

Monoethanolamine (>98%) was purchased from Alfa Aesar (Germany). Potassium-chloride, ferrocene-methanol (FcMeOH), nickel chloride and hydrazine sulfate were Sigma-Aldrich products (Germany). Graphite powder (grain size <20 μm) was obtained from Aldrich (Germany). The aqueous testing solution contained 30% MEA and 0.1 M KCl (and in the case of SECM experiments in feedback mode, additional FcMeOH in 0.5 mM concentration). The solutions were prepared with double ion-exchanged water. The samples were embedded in epoxy resin (EpofixKit, Struers, Denmark).

2.2 Preparation of the Nickel Coated Carbon Microparticles (NiC) and the Composite Electrode

The method described and used by Wu et al [26] for preparation of Nickel nanoparticles was modified for attaching Ni micro particles to 20 μm size graphite powder. In brief, 0.1 M NiCl₂ solution in absolute ethanol (solution A; 20 cm³) was mixed with 0.5 M hydrazine sulfate solution dissolved in 0.1 M NaOH (solution B; 20 cm³) solution. 2.0 g carbon powder was added to the solution and the mixture was stirred vigorously with magnetic stirrer at room temperature for 24 h. After, it was decanted, filtered and washed 5 times with water and dried in air.

For the preparation of the electrodes, the mixture of 0.5 g the nickel coated carbon powder and 0.5 g pure graphite powder (Aldrich) was homogenized with 0.95 g binding liquid made of Epofix resin (7:1 ratio of resin: hardener ratio). Between two parafilm coated glass sheets a membrane of about 1.5 mm thickness was made of this dense slurry using slight pressure. After 24 hours a solid membrane was obtained. A rectangular piece of about 5 × 5 mm was cut and copper electric conducting wire was attached to one side of it using silver-epoxy conductive glue. After hardening the silver epoxy the composite piece was placed in the center of a homemade circular mold (diameter 30 mm). Epoxy resin with 7:1 monomer-hardener ratio was poured into the mold and it was left to cure for 12 h at room temperature, as it was mentioned earlier. On the center of the hardened assembly showed up the square shaped composite surface that contained nickel coated carbon particles. Electric connection could be made through the copper wire protruding out in the center of the rear side. The obtained item was appropriate as sample surface for SECM investigation and as working electrodes for CO₂ reduction, as well.

The surface used either for SECM sample or for electrode was abraded gradually using SiC abrasive paper then wet polished using aqueous alumina slurry (1.0, 0.3, 0.05 μm grain size, respectively) on polishing cloth.

The electrochemical cells were created by wrapping the electrode body with Sellotape, so that an about 4–5 ml volume vessel is formed above the electrode with the working electrode at the bottom of the vessel.

2.3 Methods used for Characterization of the Micro Particles Involved

In order to compare the surface morphology of the coated and uncoated graphite the scanning electron microscope (SEM) model EVO MA 10 was used. In addition, the element analysis of the surface was done by energy dispersive X-ray spectroscopy (EDS).

The Particle size distribution of the powder samples were carried out by Mastersizer apparatus, Malvern Instrument (Malvern, United Kingdom).

PerkinElmer type PinAAcle 900T atomic absorption spectrometer controlled by WinLab32™ for AA software

with flame atomization was employed for determination of average Ni percentage of NiC particles prepared.

The Raman spectra were taken by Labram HR 800 Confocal Raman spectrometer (HORIBA JobinYvon S. A.S., Longjumeau, France). Making the micro-Raman measurements a 20 mW He–Ne laser with a wavelength of 632.817 nm was applied. The spatial resolution was $\sim 1.5\text{ }\mu\text{m}$, the spectral resolution $\sim 2.5\text{ cm}^{-1}$ with a magnification of $\times 100$ (Olympus UK Ltd., London, UK). The spectra were attained employing the LabSpec 5.0 software (HORIBA JobinYvon S.A.S., Longjumeau, France).

2.4 Electrochemical Methods and Apparatuses

The electrochemical impedance spectroscopic studies were done using a three-electrode configuration with platinum as counter electrode, Ag/AgCl/KCl (3.5 M) reference electrode, graphite and nickel coated graphite samples as working electrodes connected to Solartron 1287 A potentiostat. Applying a range of frequency between 100 mHz and 100 kHz with 10 mV amplitude. The experiments were performed at the open circuit potential condition.

CH Instruments, Model 600E (Austin, Texas) electrochemical workstation was employed for recording a linear sweep and cyclic voltammograms.

The scanning electrochemical microscopic (SECM) experiments were performed using a homemade scanning electrochemical microscope, it has been described in details in [27]. It consists of the electrochemical cell equipped with Ag/AgCl/KCl (3.5 M) reference electrode, platinum wire counter electrode and with the SECM probe that was a platinum disc microelectrode (25 μm diameter with $R_G \approx 10$). The electrodes were connected to the measuring instrument EF437 type bipotentiostat (Elektroflex Ltd, Szeged, Hungary). The displacement of the microprobe was driven by stepper motors purchased from Newport (Irvine, CA, Type M-MFN25PP) toward generating line scan figures or 2D images on the substrate under study.

3 Results and Discussion

3.1 Characterization of the Nickel Coated Carbon (NiC) Micro Particles

Several batches of the NiC particles were prepared and used for composite electrode making. One of them that upon fabrication gave composite electrodes that performed well for CO_2 reduction in aqueous 30 % MEA solution were selected and investigated with different methods.

The average Ni content of the NiC particles was measured by acetylene-air flame atomizer of PerkinElmer PinAAcle 900T atomic absorption spectrometer controlled by WinLab32™ for AA software. For calibration 1000 mg/dm^3 AAS standard (Merck) was diluted and used. The calibration was linear in the 0–5 ppm range,

with 0.9999 correlation coefficient and slope of 0.0129 A/ppm. For analysis 20–25 mg NiC samples were treated with 5 cm^3 cc HNO_3 . After 30 min time, the samples were filtered and the filtrates were diluted with double deionized water and analyzed. According to the AA measurements the NiC composite particles contained 10.1 w/w% Ni.

In further experiments the particle size distribution of the carbon powder and that of the particulate matter obtained after preparation of catalytic Ni particles were compared. The diagrams are shown in Figure 1. They were made by detecting the Mie scattering in aqueous suspension using the Malvern Instruments Mastersizer apparatus. It was questionable whether the Ni metal particles developed in suspension form separate particles or they get attached onto suspended carbon particles. Since the reduction was made in suspension the direct estimation of sizes of the catalytic Ni particle could not also be done easily. As it can be seen in Figure 1. (blue line) the graphite powder is mono disperse with about 26 μm most numerous particle size. The information given by the Aldrich company about of their graphite powder is particle size $< 20\text{ }\mu\text{m}$.

The prepared NiC powder shows also mono disperse character with a bit broader distribution. The most numerous particulate size is about 33 μm as it can be seen in Figure 1. (red line). From the percentage of Ni obtained with AA measurements and from this size distribution we can guess that major part of the Ni is attached to carbon particles. The increase of the most numerous size cannot be used however, for guessing the size of the Ni particles. Figure 1. suggests that may be just a very small amount of nano size separate Ni particles, as well as some associated NiC grains with sizes over 100 μm were formed during the NiCl_2 reducing reaction.

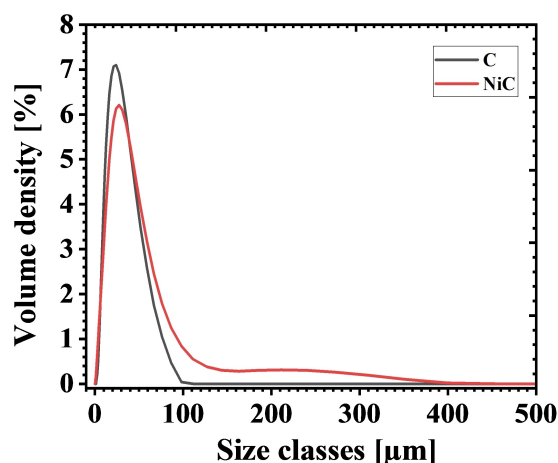


Fig. 1. Particle size distribution of the carbon powder (blue line) and the particulate matter obtained after preparation of catalytic Ni particles (red line).

3.1.1 Raman Spectroscopic Investigation

In Figure 2, the Raman spectra of the graphite powder and the Ni coated graphite powder can be seen. On the graphite spectrum the characteristic G band can be seen at 1570 cm^{-1} corresponding to the sp^2 stretching vibration. At 1330 cm^{-1} the induced defect mode of the aromatic and olefin stretching vibration can be seen and its harmonics between $2600\text{--}2700\text{ cm}^{-1}$ [28]. The blue curve however, shows these peaks to be suppressed that is because of the nickel coating. The appearance of these peaks, on the other hand, indicates that the coating is not entire, there are spots on the surface that is not coated. This was further investigated using SEM combined with EDS.

3.1.2 Scanning Electron Microscopy Combined with EDS

In Figure 3.A and B the SEM images of the uncoated and coated graphite particles can be seen. The image of the uncoated carbon is lighter, whereas darker spots appear on the coated one. Those correspond to the particles of the heavier element, supposedly to nickel. Also, the

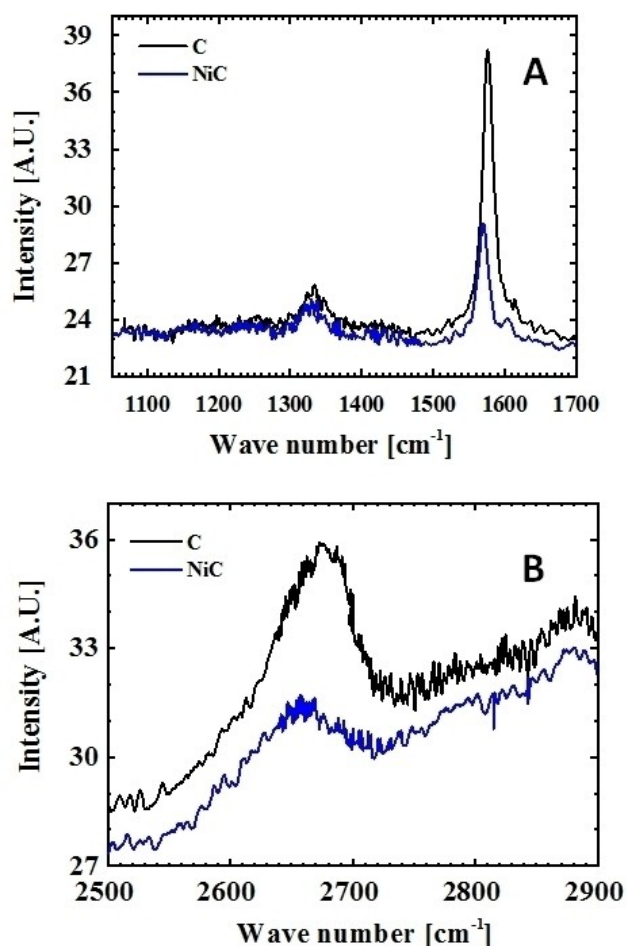


Fig. 2. Two segments of Raman spectra of the untreated graphite (black line) and the Ni coated electrode materials (blue line)

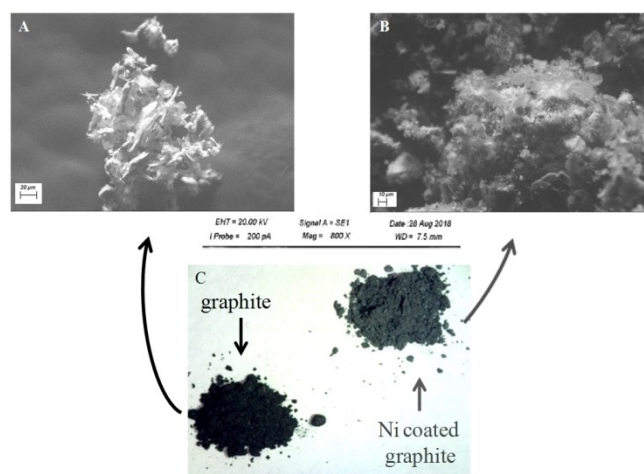


Fig. 3. Scanning electron microscopic images of the untreated graphite (A) and the Ni coated electrode powder samples materials (B). (C) Shows the optical images of the two powders.

structure changes after the coating. The sharp edges of the grains seem to disappear and dark gray deposit can be seen on the surface of the specimen. It is also readily observable that the coating is not entire. In the photographs (Figure 3.C) the color difference between the graphite and the Ni coated graphite is shown: the later has lighter grey color.

In Figure 4, the energy-dispersive X ray spectra (EDS) of the two specimens are shown. Based on those the relative abundance of different elements on the sample surfaces can be estimated. The EDS spectrum, shown in Figure 4. A has a single peak due to the 100 % C content. However, several peaks appear on the EDS spectrum of the Ni coated graphite (Figure 4.B). The three Ni peaks confirm the coating. However, significant intensities of O N and S peaks appear also. Most likely they resulted by the adsorbed oxygen, nitrogen and the sulfur that persisted after reduction of NiCl_2 .

The electrochemical surface area of the embedded electrodes was determined using cyclic voltammetry in 1 mM FcMeOH dissolved in 0.1 M aqueous KCl supporting electrolyte. The scanning rate was changed between 50 and 400 mV/s and the slope of the anodic peak current vs. square root of the scan rate was used for determination of the electrochemical surface area according to the Randles-Sevcik equation. It was found that the electrochemical active surface of NiC electrode was ca. 2.05 times higher than its geometric area.

3.1.3 Electrochemical Impedance Spectroscopic Investigation (EIS)

For the sake of examining the efficiency of the coating, the electrochemical impedance spectroscopy has been used for quantifying the corrosion resistance of composite electrodes made of coated and uncoated graphite. The measurements were made at open circuit potential in the

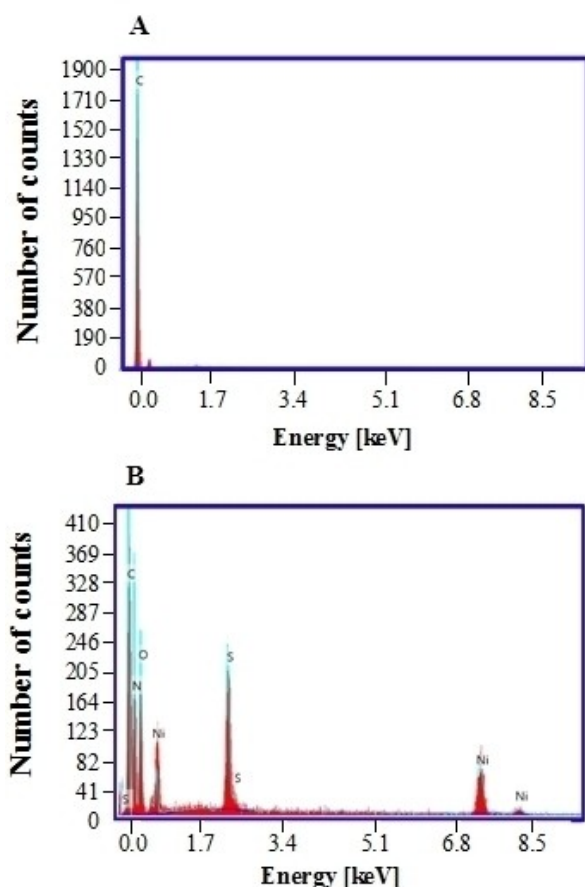


Fig. 4. EDS spectra of the untreated graphite (A) and the Ni coated electrode materials (B).

testing electrolyte (0.1 M KCl) in frequency range of 0.1–1 kHz. The results are presented as Bode and Nyquist plots in Figure 5. It is observed that the samples have similar experimental Bode diagram (discrete points) as seen in Figure 5.A, it shows a single peak display the presence of one time constant. The experimental Nyquist plots (discrete points) presented in Figure 5.B reveal two different depressed capacitive like-semicircles. As it can be seen, the diameter of the depressed capacitive like-semicircle is smaller for the electrode made with NiC, than for the one made with pure graphite. The diameter obtained for pure carbon composite electrode is about three times higher than that in the impedance spectrum of NiC based composite electrode.

In the aim of interpreting the experimental data, a simple electric circuit has been proposed as shown in Figure 5.A, which considers the resistance of the electrolyte R_s and a parallel RC circuit where R_{ct} and C_{ct} are the charge transfer resistance and double layer capacitance, respectively. The parameters were determined using EC-Lab software and the quality of the fitting was evaluated based on the χ^2 values. The resistances of graphite and nickel coated graphite are $0.262 \text{ M}\Omega\cdot\text{cm}^2$ and $0.096 \text{ M}\Omega\cdot\text{cm}^2$, respectively. The significant diminution of

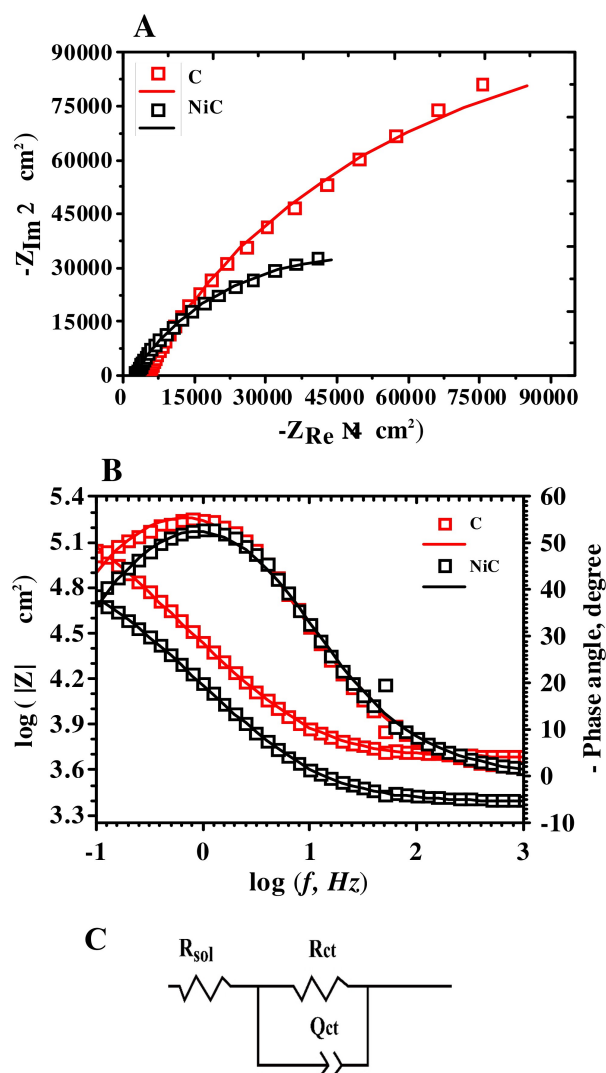


Fig. 5. Impedance spectra of the graphite and the Ni coated graphite electrodes carried out in 0.1 M KCl solution. (A) Nyquist and (B) Bode plots, and (C) circuit diagram.

the resistance after coating can be explained by the higher conductivity of the nickel compared to graphite.

3.1.4 Electrochemical Microscopy Test of the Catalytic Activity of Electrode Surfaces

The electrochemical surface characteristics of the composite electrode were further investigated using SECM in feedback mode. The testing electrolyte was the same medium used for carbon dioxide reduction, namely, 30 % MEA solution in 0.1 M KCl. Besides, the solution contained ferrocene-methanol (FcMeOH) in 0.5 mM concentration. It seemed to be a better choice to carry out constant distance 2D mapping instead of the regularly applied Z-approach curves, because the electrodes were prepared from mixture of the different graphite powders and the epoxy resin. Hence a slight heterogeneity of the surface could be expected. The electrodes were relatively

big, therefore to decrease the scanning time only their edges were mapped (only rough mapping were done). The vertical tip to sample distance was 20 μm and 25 μm step size was set. Relatively big, about 2000 $\mu\text{m} \times 2000 \mu\text{m}$ scanning areas were selected.

0.6 V vs. Ag/AgCl/KCl (3.5 M) potential on the Pt microelectrode was employed. In this way the detected current was resulted by electrochemical oxidation of the ferrocene-methanol. Interestingly, the electrodes prepared from the untreated and the Ni coated graphite powder showed very different behavior in the feedback mapping.

Figure 6.A shows image obtained over composite surface made of pure graphite, Figure 6.B is an image recorded over nickel coated graphite containing composite sample surface. As it can be seen in Figure 6, the pure graphite composite surface (Figure 6.A) showed a relatively uniform positive feedback character. The sample surface made of Ni coated graphite particles also provided positive feedback (see Figure 6.B) however, the effect was stronger, besides there appeared some more “active” areas on the surface. The current was more than two

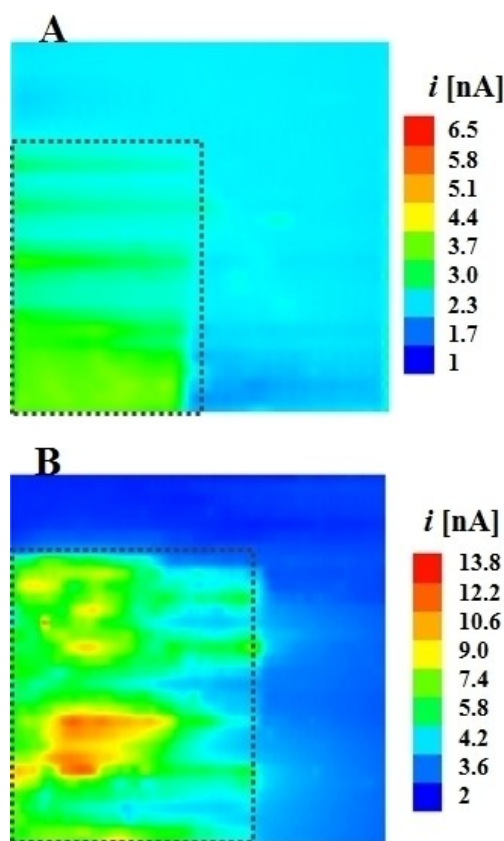


Fig. 6. Scanning electrochemical microscopic images obtained with 25 μm Pt microelectrode tip in 30 % aqueous MEA solution containing 0.5 mM ferrocene methanol and 0.1 M KCl. Scanning rate 25 $\mu\text{m/s}$, sample-tip vertical distance 20 μm , scanned areas 2000 $\mu\text{m} \times 2000 \mu\text{m}$; dotted rectangles indicate the actual location of the sample surfaces.

times higher at highest points of Figure 6.B than in Figure 6.A. This finding is in good accordance with electrochemical impedance spectroscopic measurements shown before.

3.2 Electrochemical Reduction of CO_2

3.2.1 Voltammetric Study

The electrochemical CO_2 reduction character of the electrode fabricated from NiC containing particles was tested in monoethanolamine media. In the experiments DC voltammograms were recorded in range range of 0–−1.5 V with electrodes made using pure carbon particles and with one made using NiC particles. The back ground electrolyte was aqueous 30 % monoethanolamine solution containing 0.1 M KCl. It was saturated with CO_2 by bubbling CO_2 gas through the solution for 1 minute s. The absorbed amount of CO_2 was estimated from the weight increase. A slight temperature raise of the saturated solutions was observed after the saturation step. The solution was left to cool down to room temperature. In Figure 6, two typical curves can be seen in the case of CO_2 saturated solution. Apparently, the nickel coating enhanced the cathodic current. The increase of the rate of the reduction processes started at lower negative overpotentials when the nickel coated electrode was used. As it is well-known, nickel has higher affinity to reduce hydrogen ions from the solution, thus a competition is expected between the CO_2 and H^+ reduction reactions. Therefore the increase of the voltammetric current shown in Figure 7, can be contributed by parallel hydrogen ion reduction.

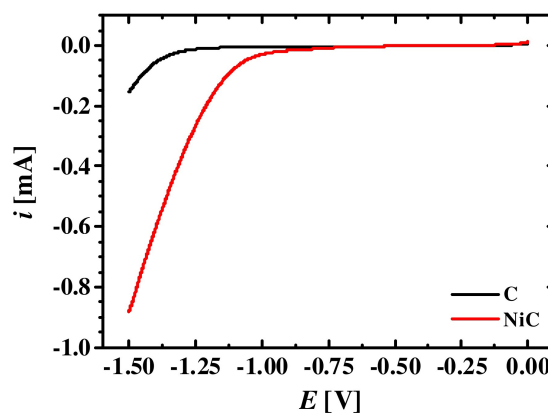


Fig. 7. Linear sweep voltammograms, taken at 25 mV/s scanning rate in 30 % MEA solution saturated with CO_2 and containing 0.1 M KCl. The working electrodes were the graphite (black line) and the Ni coated graphite (red line) electrode, the reference was Ag/AgCl/KCl (3.5 M) and the counter electrode was a platinum mesh.

3.2.2 Scanning Electrochemical Microscopic Studies of the CO₂ Reduction

As it was mentioned earlier, the carbon dioxide reduction and the hydrogen evolution are two competing processes that can proceed, parallel at sufficiently negative overpotentials. In order to see the extent of hydrogen evaluation separately, sample generator-tip collector (SG/TC) mode experiments with the SECM were made employing different polarization potential on the NiC composite electrode embedded in epoxy. In these experiments the platinum microelectrode tip was used to detect the hydrogen evolved on different areas of the polarized sample surface. The potential of it was set at -0.05 V vs. Ag/AgCl/KCl (3.5 M) that is typically used in H₂ measurements with the SECM [29].

The Pt tip was positioned above the insulating resin and at constant height (20 μ m) and line scans were recorded as the tip traveled above the graphite electrode whose potential was set constant throughout scan.

In Figure 8 comparative line scans can be seen taken at different sample polarization potentials in background solution without CO₂ (Figure 8.A) and in CO₂ saturated one (Figure 8.B). Figure 8.B shows that in absence of CO₂ above the polarized NiC composite electrode surface considerable amount of hydrogen concentration is detected. Higher the employed negative polarizing potential higher the hydrogen concentration. At -1.5 V polarization, specially high hydrogen reduction current could be recorded. Interestingly at the two sides above the NiC composites steep maxima show up. Most likely they are resulted by the enhanced mass transport of the reducing species as it is expected. The hydrogen evolution is quite high even at polarizing potential of -1.2 V vs. Ag/AgCl/KCl (3.5 M) applied on the electrode. The tendencies are very similar in Figure 8.B however, the extents of the changes in currents are significantly different. It seems that the presence of CO₂ in the electrolyte suppresses the hydrogen evolution reaction. The current change of the -1.500 V polarization results in less increase in the local current than the -1.200 V polarization in Figure 8. A.

Comparing the experimental findings shown in Figure 8.A and Figure 8.B it can be assumed that in potential range of -1200 – 1500 mV vs. Ag/AgCl/KCl (3.5 M), the carbon dioxide reduction is the major electrode reaction in 30 % aqueous monoethanol amine solution containing CO₂.

For a better comparison, the average current values corresponding to the H₂ evolution reaction measured with the Pt microelectrode above the NiC electrode are shown in Figure 9. The values were taken from the line scans in Figure 9 from the 500–3700 μ m range where the NiC electrode actually were located.

4 Conclusion

In this contribution, we present a new electrode optimized for carbon dioxide electrochemical reduction in the

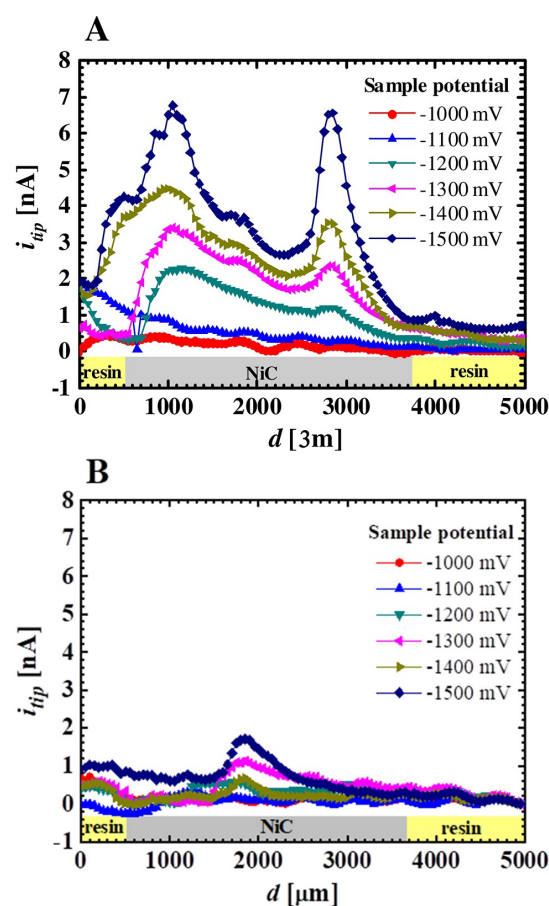


Fig. 8. Scanning electrochemical microscopic H₂ line scans above the Ni coated graphite electrode in the absence (A) and in the presence of carbon dioxide (B). The solution was 30 % aqueous MEA, containing 0.1 M KCl. The SECM tip was a 25 μ m Pt microelectrode. The sample was polarized against Ag/AgCl/KCl (3.5 M) and the counter electrode was a platinum mesh. The scanning rate was 25 μ m/s, the tip sample vertical distance was 20 μ m.

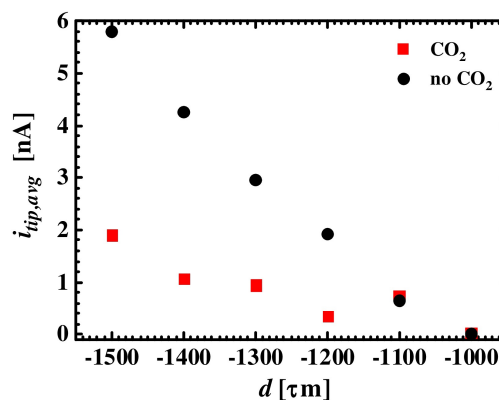


Fig. 9. Average current values plotted against polarizing potential. The current values were taken from Figure 7. measured in solution containing CO₂ (red spots) and in one without CO₂ (black spots). The decrease of H₂ evolution rate resulted by CO₂ saturation can be seen.

frequently employed capturing medium, aqueous mono-ethanol amine solution. Along with conventional electrochemical techniques, surface investigating techniques, electrochemical impedance spectroscopy and scanning electrochemical microscopic studies was demonstrated the superior performance of the composite electrode made of catalytic nickel micro-particle coated graphite over the same kind of graphite electrode made of pure graphite. The new electrode showed a better affinity for carbon dioxide reduction in the medium used. The hydrogen evolution in the applied potential range was investigated with scanning electrochemical microscopy and it was revealed that the carbon dioxide reduction suppresses the hydrogen evolution reaction. Embedding the described NiC microparticles in epoxy binder different size and shape electrodes can be fabricated. Those can be used for reducing CO₂ right in the media that are broad scale used for capturing it. It is hoped that useful product with lower expense can be achieved.

In our earlier work [21] the applicability of copper based electrodes for reduction in MEA containing media was checked. Unfortunately hard corrosion of the electrode surface was observed. The electrode we propose is stable in the CO₂ capturing MEA solution. The behavior of existing but non nano copper based electrodes in MEA media is not known. Furthermore the fabrication of the proposed electrode is cost efficient. It does not need expensive chemicals or special equipment. Considering industrial application, it can be an important advantage that working electrodes with large surface area, as well as with special shapes can be made using similar procedure.

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Data Availability Statement

The authors confirm that the data supporting this research work and are available in this article can be shared.

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