

Full Paper

Electrochemical Investigation of Ni(II) Ions in Nickel Chloride and Nickel Sulfate at Carbon Paste Electrode: A Cyclic Voltammetric Study

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Abstract- Nickel bearing compounds exhibit excellent electrochemical properties in an alkaline medium due to the reversible one-electron redox process of the couple Ni(III)/Ni(II). Nickel(II) ions were investigated in the compounds like nickel chloride and nickel sulfate at carbon paste electrode by using cyclic voltammetric technique. The well-defined redox peaks were observed for both nickel chloride and nickel sulfate compounds in 0.1 M KOH solution as supporting electrolyte at scan rate of 100 mVs⁻¹. The effect of scan rates and concentrations were studied and the effects show good linear relationship with the peak currents. The cyclic voltammetric behavior of Ni(II) ions were also examined in 1 M KCl solution as supporting electrolyte. The Ni(II) ions shows well defined redox peaks in presence of potassium ferricyanide as a mediator.

Keywords- Nickel sulfate, Nickel chloride, Potassium ferricyanide, Carbon paste electrode, Cyclic voltammetry

1. INTRODUCTION

Metal ions are generally non-degradable. They have infinite lifetimes, and build up their concentrations in food chains to toxic levels. In recent years, arrays of industrial activities have been disturbing the geological equilibrium of metal ions through release of large quantities of toxic metal ions into the environment [1].

Metallic nickel is not affected by water but is slowly attacked by dilute hydrochloric or sulfuric acid and is readily attacked by nitric acid. Fused alkali hydroxides do not attack nickel. Several nickel salts, such as the acetate, chloride, nitrate, and sulfate, are soluble in water, whereas carbonates and hydroxides are far less soluble and sulfides, disulfides, subsulfides and oxides are practically insoluble in water [2,3].

The primary source of nickel in drinking-water is leaching from metals in contact with drinking-water, such as pipes and fittings. However, nickel may also be present in some groundwater as a consequence of dissolution from nickel ore-bearing rocks. Nickel is used principally in its metallic form combined with other metals and nonmetals as alloys. Nickel alloys are characterized by their hardness, strength, and resistance to corrosion and heat. Nickel is used mainly in the production of stainless steels, non-ferrous alloys, and super alloys. Other uses of nickel and nickel salts are in electroplating, as catalysts, in nickel-cadmium batteries, in coins, in welding products, and in certain pigments and electronic products [4]. Nickel occurs predominantly as the ion $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ in natural waters at pH 5–9. Complexes with ligands, such as OH^- , SO_4^{2-} , HCO_3^- , Cl^- , and NH_3 , are formed to a minor degree in this pH range. Nickel concentrations in bottled mineral water will depend on the source and any treatment applied. Levels of nickel in a selection of bottled mineral waters were below the detection limit of $25 \mu\text{g L}^{-1}$ [5].

A number of studies on the carcinogenicity of nickel compounds in experimental animals are available [6]. Generally, tumors are induced at the site of administration of the nickel compound. For instance, several nickel compounds induce injection-site sarcomas [7]. A marked variation in the incidence of injection-site sarcomas between different strains of mice has been reported [8]. There are only a limited number of studies on carcinogenic effects after oral exposure to nickel compounds [9]. As well, no difference in tumor incidence was observed in a lifetime study in rats exposed to 5, 50, or 125 mg of nickel per kg of body weight per day in the feed compared with controls. Owing to the high death rate and lack of information on cause of death, this study is of minor value in evaluating carcinogenicity after oral exposure to nickel. A similar 2 year study in dogs also revealed no increase in tumors [10].

The detection and assessment of the heavy metal ions in water supplies or effluent streams or in specific processes are important tasks in environmental protection and human health. Currently, although there are several methods commonly employed in metal ions analysis, e.g., atomic adsorption spectroscopy [11], electrochemical separation techniques

[12], high-performance liquid chromatography [13], and capillary electrophoresis [14], while atomic adsorption method is offer good analytical performance in terms of precision and accuracy, nevertheless expensive from the viewpoint of reagent consumption and instrumentation capital cost. Accordingly, there is considerable interest in developing simple, rapid and economically viable methods that will afford facile analyses of heavy metal ions. The carbon paste electrode based sensor-based analysis is an alternative method which can provide real-time analysis, low cost in instrumentation.

Although electroanalytical methods in general and stripping techniques in particular provide very sensitive routes to the quantitation of many trace metals, widespread utilization of this family of techniques for the solution of practical analysis problems has been extremely limited. This situation is primarily explained by the availability of alternate spectrometric and neutron activation methods for trace-metal determination that are considerably more selective than stripping procedures. Further, because of problems ranging from inordinately negative reduction potentials and slow electron transfer kinetics to the formation of intermetallic compounds upon electrodeposition, numerous metal ions of analytical interest simply are not accessible to the stripping approach as it is conventionally carried out. However, in view of the high sensitivity afforded by analyte accumulation prior to measurement, the development of electroanalytical techniques analogous to the stripping approach but possessing more selective analyte collection mechanisms represents an extremely enticing goal [15]. Recently, a number of investigators have demonstrated a new variation of electrochemical trace-metal analysis in which analyte preconcentration was carried out at chemically modified electrodes (CMEs), with surfaces specifically designed for the ability to react with and bind the target solute [16-23].

In this work, carbon paste electrode was used for the electrochemical studies of Ni(II) ions present in nickel sulphate and nickel chloride by using cyclic voltammetric technique (CV) and the adopted method is very simple.

2. EXPERIMENTAL

2.1. Apparatus and procedure

Electrochemical measurements were carried out with a CHI model 660c. Electrochemical workstation connected to a personal computer for control and data storage. All electrochemical experiments were performed in a standard three-electrode cell. The carbon paste electrode was used as a working electrode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. All potentials reported were versus the SCE.

2.2. Reagents

Nickel sulphate, nickel chloride and silicone oil were purchased from Himedia chemicals. The graphite powder, potassium ferricyanide, potassium chloride and potassium hydroxide procured from Merk chemical and all aqueous solution were prepared with double distilled water.

2.3. Preparation of carbon paste electrode

The carbon paste electrode was prepared by mixing 70% graphite powder and 30% silicone oil in an agate mortar for 30 min. The mixture was then packed into a homemade Teflon cavity and polished using smooth paper.

3. RESULTS AND DISCUSSION

3.1. Electrocatalytic response of Ni(II) ion present in nickel sulphate and nickel chloride at carbon paste electrode in 0.1 M KOH solution

The electrochemical behaviour of Ni(II) ion present in nickel sulphate and nickel chloride at carbon paste electrode was studied by using CV technique. Fig. 1 represent the cyclic voltammograms for 1mM Nickel sulphate (curve b) and for blank solution (curve a) at carbon paste electrode in 0.1 M KOH at sweep rate 100 mVs^{-1} . In the Fig. 2 shows the cyclic voltammetric response for 1 mM nickel chloride (dashed line) and for blank solution (solid line) at carbon paste electrode in 0.1 M KOH at sweep rate 100 mVs^{-1} . The well-defined redox peaks were observed for both nickel sulphate and nickel chloride compounds oxidation of Ni(II) to Ni(III). For both Nickel sulphate and Nickel chloride the Ni(II) ions oxidised to Ni(III) at potential of 454mV and reduction of Ni(III) ion at potential of 366 mV respectively. The redox peak potential difference (ΔE_p) was 88 mV. The carbon paste electrode shows conductivity during oxidation of Ni(II) to Ni(III) by one electron transfer.

3.2. Electrochemical behavior of Ni(II) ion present in nickel sulphate and nickel chloride at carbon paste electrode in 1M KCl solution

The electrochemical behaviour of Ni(II) ion present in the nickel sulphate and nickel chloride at carbon paste electrode was recorded in 1 M KCl solution at sweep rate 50 mVs^{-1} . Fig. 3 and Fig. 4 shows the cyclic voltammetric response for respectively 1 mM nickel sulphate and 1 mM nickel chloride in the presence of 1 mM potassium ferricyanide (curve b) and for the absence of 1 mM potassium ferricyanide (curve a) at scan rate 50 mVs^{-1} in 1 M KCl solution.

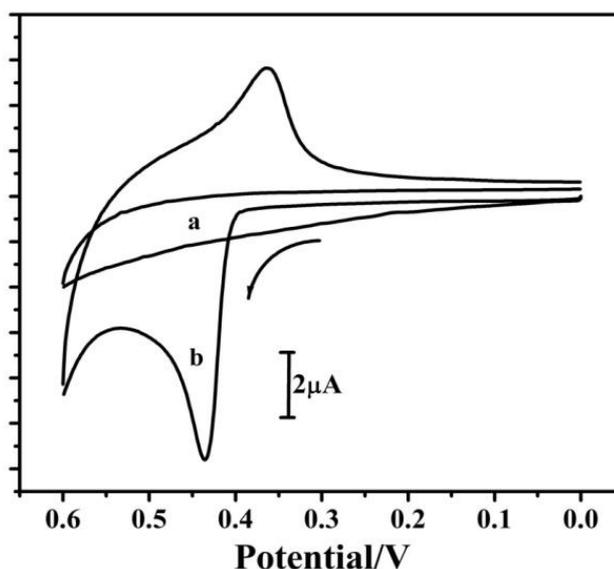


Fig. 1. Cyclic voltammograms for 1 mM nickel sulphate (curve b) and for blank solution (curve a) at carbon paste electrode in 0.1 M KOH at sweep rate 100 mVs^{-1}

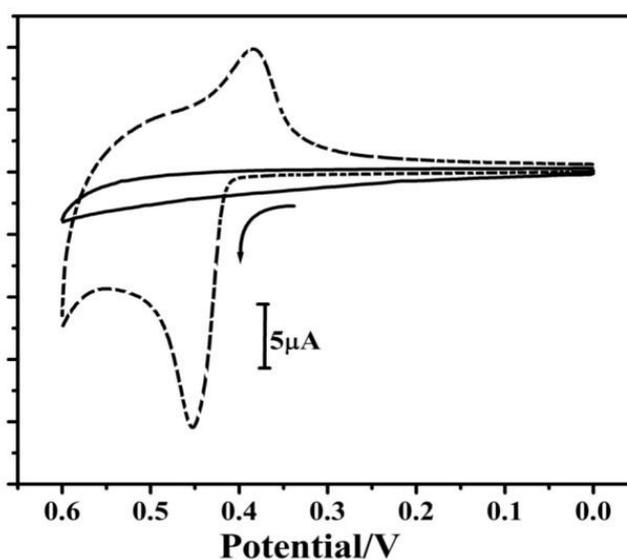


Fig. 2. Cyclic voltammograms for 1 mM nickel chloride (dashed line) and for blank solution (solid line) at carbon paste electrode in 0.1 M KOH at sweep rate 100 mVs^{-1}

In the absence of potassium ferricyanide nickel containing compounds does not reveal any peaks at potential window between 200 mV to 1000 mV at carbon paste electrode. In presence of potassium ferricyanide shows two redox peak couples at potential because of

formation of two types of nickel(II) hexacyanoferrate(Ni-CN-Fe). The formed film oxidized at potential 465 mV and 608 mV respectively and reduced at potential 581 and 444 mV respectively. The result shows nickel bearing compounds exhibit excellent electrochemical properties in an alkaline medium due to the reversible one-electron redox process of the couple Ni(III)/Ni(II) [24]. But in the neutral pH it required mediator for showing conductivity in KCl solution. In the presence potassium ferricyanide the carbon paste electrode shows electrochemical activity towards nickel(II) ions. The two redox couples are attributed to [Ni(II)-CN-Fe(III)]/[Ni(III)-CN-Fe(III)] and [Ni(II)-CN-(Fe(III))]/[Ni(II)-CN-Fe(II)] and the possible electrode mechanism for two redox couples to be represented as follows [25].

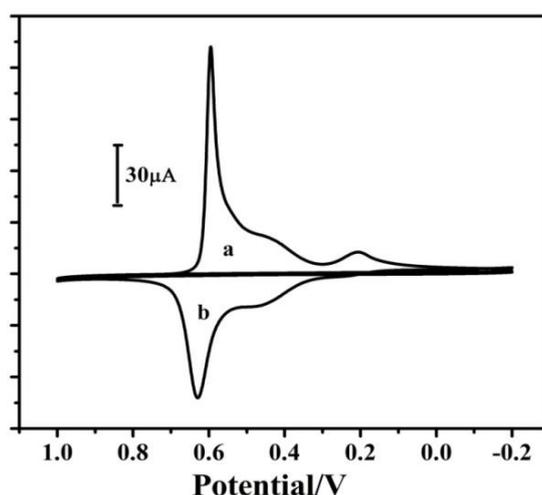
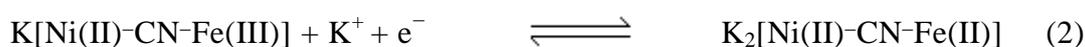
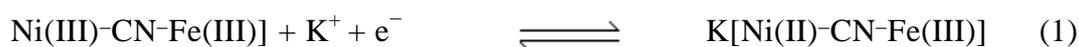


Fig. 3. Cyclic voltammograms for 1 mM nickel sulphate in the presence of 1 mM Potassium ferricyanide (curve b) and for 1mM nickel sulphate in the absence of 1 mM Potassium ferricyanide (curve a) at scan rate 50 mVs⁻¹ in 1 M KCl solution

3.3. Effect of scan rate on the peak current

Fig. 5A and Fig. 6A shows the cyclic voltammograms of 1 mM nickel sulphate and 1 mM nickel chloride at CPE in 0.1 M KOH solution at different scan rates. This was carried out in order to investigate the kinetics of the electrode reactions and verify whether diffusion is the only controlling factor for mass transport or not.

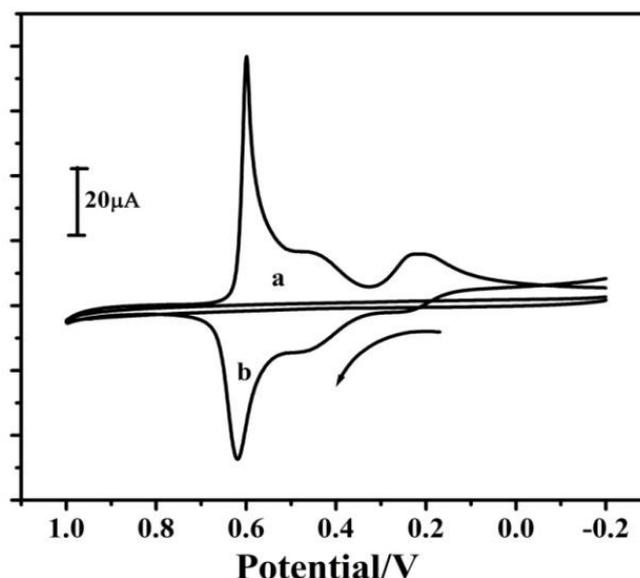


Fig. 4. Cyclic voltammograms response for 1 mM nickel chloride in the presence of 1 mM Potassium ferricyanide (curve b) and for 1 mM nickel sulphate in the absence of 1 mM Potassium ferricyanide (curve a) at scan rate 50 mVs⁻¹ in 1 M KCl solution

The observation shows that with the increased scan rate, the redox peak current also increased gradually (Fig. 5A, Fig. 6A). The graph of anodic peak current (I_{pa}) vs. square root of scan rate ($v^{1/2}$) was plotted (Fig. 5B, Fig. 6B). The graph obtained was good linearity between the square root of scan rate ($v^{1/2}$) and I_{pa} . In the range from 100 to 500 mVs⁻¹ the redox peak currents were proportional to the square root of scan rate ($v^{1/2}$) and the obtained correlation coefficient was 0.9960 and 0.9994 for nickel sulphate and nickel chloride respectively, which indicates that the electron transfer reaction was diffusion-controlled [26].

3.4. Effect of concentration of nickel

As the concentration of nickel sulphate and nickel chloride was varied from 0.1 to 0.5 mM and cyclic voltammograms were recorded (Fig.7A, Fig. 8A) in 0.1 M KOH solution at scan rate 100 mVs⁻¹. The anodic peak current increases linearly with increase in concentration of nickel compounds and the obtained correlation coefficient were found to be 0.9932 and 0.9985 for nickel sulphate and nickel chloride respectively (Fig. 7B, Fig. 8B).

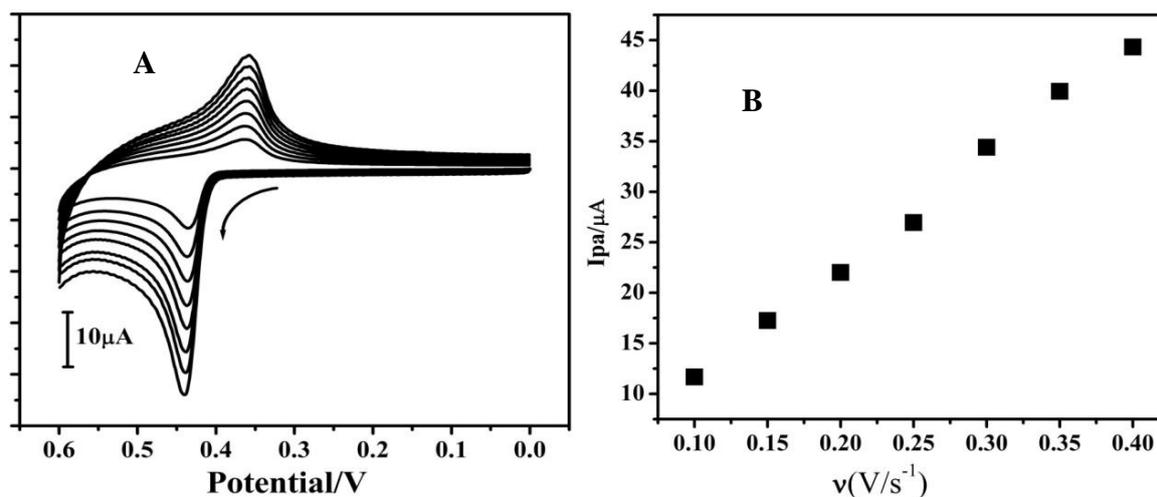


Fig. 5. (A) Cyclic voltammograms of 1 mM nickel sulphate at CPE in 0.1 mM KOH solution at different scan rates (0.1-0.4 Vs^{-1}). (B) Graph of anodic peak current vs scan rate

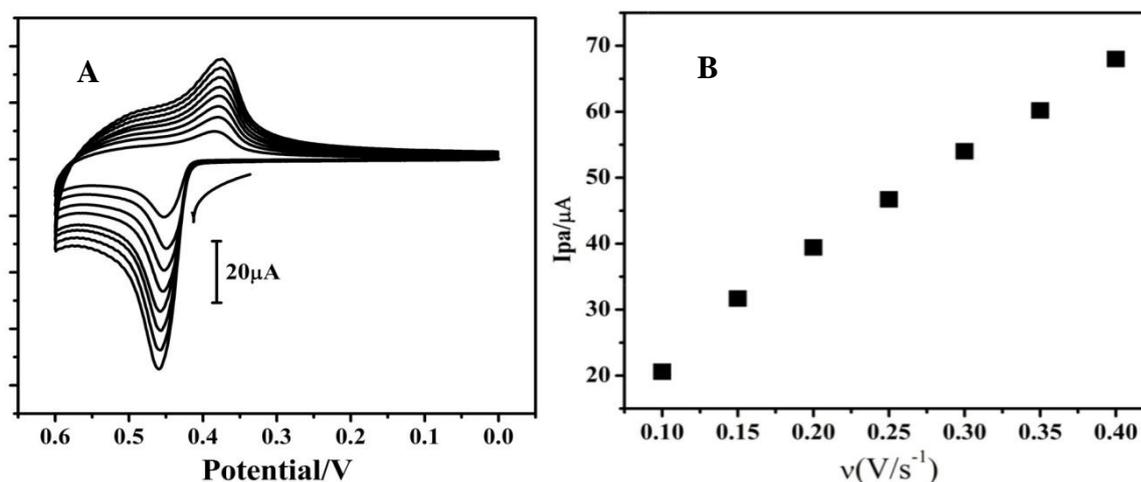


Fig. 6. (A) Cyclic voltammograms of 1 mM nickel chloride at CPE in 0.1 mM KOH solution at different scan rates (0.1-0.4 Vs^{-1}). (B) Graph of anodic peak current vs. scan rate

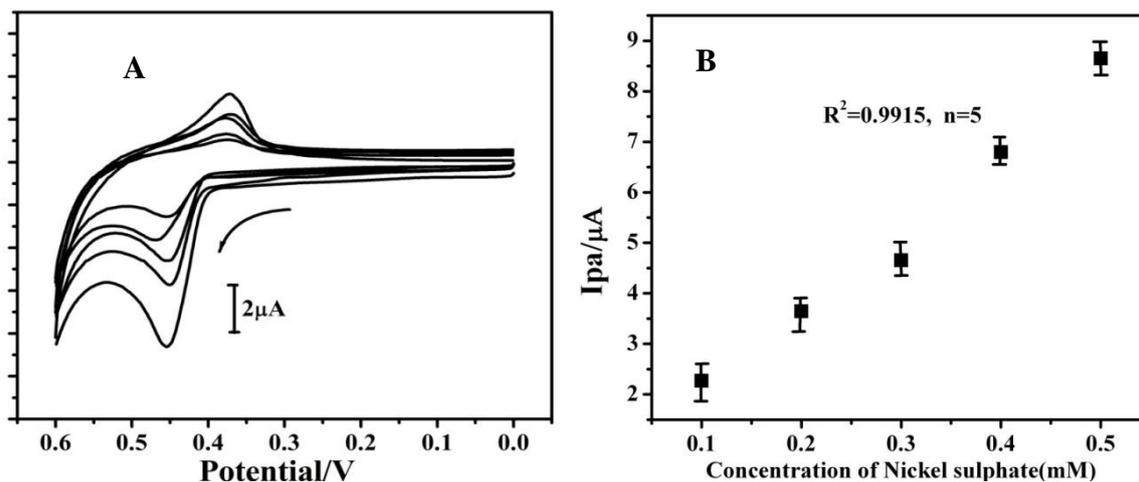


Fig. 7. (A) Cyclic voltammograms for different concentration of nickel sulphate (0.1-0.5 mM) at CPE in 0.1 M KOH solution. (B) Graph of I_{pa} vs. concentration of nickel sulphate

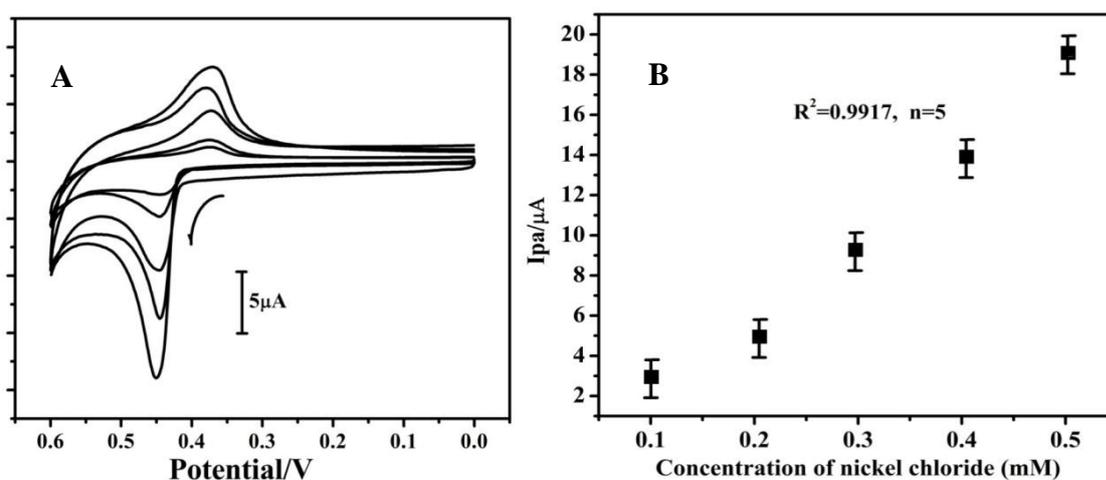


Fig. 8. (A) Cyclic voltammograms for different concentration of nickel chloride (0.1-0.5 mM) at CPE in 0.1 M KOH solution. (B) Graph of I_{pa} vs. concentration of nickel chloride

4. CONCLUSION

In this work, nickel(II) ions were investigated in the compounds like nickel chloride and nickel sulfate at carbon paste electrode by using cyclic voltammetric technique. The well-defined redox peaks were observed for both nickel chloride and nickel sulfate

compounds in 0.1 M KOH solution as supporting electrolyte at scan rate of 100 mVs⁻¹. The effect of scan rate and concentration was studied, which indicates that the electron transfer reaction was diffusion controlled. The electrochemical behaviour of nickel ion can be studied in neutral pH and the CPE shows well defined redox peaks in presence of potassium ferricyanide as a mediator in 1 M KCl solution. The method is very simple to identify the electrochemical behaviour of Ni(II) ions.

REFERENCES

- [1] D. Chen, and A. K. Ray, Chem. Engin. Sci. 56 (2001) 1561.
- [2] L. G. Morgan, and G. N. Flint, Nickel alloys and coatings: release of nickel. In: Maibach HI, Menné T, eds. Nickel and the skin: immunology and toxicology. Boca Raton, FL, CRC Press, (1989) p. 45.
- [3] P. Haudrechy, J. Foussereau, B. Mantout, and B. Baroux. Contact Dermatitis 31 (1994) 249.
- [4] (IARC) Nickel and nickel compounds. In: Chromium, nickel and welding. Lyon, International Agency for Research on Cancer, (1990) p. 257 (IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Vol. 49).
- [5] H. E. Allen, M. A. Halley-Henderson, and C. N. Hass, Arch. Environ. Health 44 (1989) 102.
- [6] A. Aitio, Nickel and nickel compounds. Stockholm, National Institute of Working Life, Nordic Council of Ministers, The Nordic Expert Group for Criteria Documentation of Health Risks from Chemicals, (1995), p. 61 (Arbete och hälsa 26).
- [7] F. W. Sunderman Jr., Carcinogenicity of nickel compounds in animals. In: Sunderman FW Jr, ed. Nickel in the human environment. Lyon, International Agency for Research on Cancer, (1984), p. 127 (IARC Scientific Publications No. 53).
- [8] R. E. Rodriguez, M. Misra, B. A. Diwan, C. W. Riggs, and K. S. Kasprzak, Toxicology 107 (1996) 131.
- [9] H. A. Schroeder, M. Mitchener, A. P. Nason, J. Nutrition 104 (1974) 239.
- [10] A. M. Ambrose, P. S. Larson, J. R. Borzelleca, and G. R. Hennigar, Jr., J. Food Sci. Tech. 13 (1976) 181.
- [11] T. J. Hwang, and S. J. Jiang, J. Anal. At. Spectrosc. 11 (1996) 353.
- [12] F. Hissner, J. Mattusch, G. F. Werner, J. Anal. Chem. 354 (1996) 718.
- [13] R. Das, A. k. Chakraborty, M. L. Cervera, and M. Delaguardia, Mikrochim. Acta 122 (1996) 209.
- [14] J. Wen, and R. M. Cassidy, Anal. Chem. 68 (1996) 1047.
- [15] R. P. Baldwin, J. K. Christensen, and L. Kryger, Anal. Chem. 58(1986) 1790.
- [16] G. T. Cheek, and R. F. Nelson, Anal. Lett. 11 (1978) 393.
- [17] J. A. Cox, and M. Majda, Anal. Chem. 52 (1980) 861.

- [18] K. H. Lubert, M. Schnurrbusch, and A. Thomas, *Anal. Chim. Acta* 144 (1982) 123.
- [19] K. Izutsu, T. Nakamura, R. Takizawa, and H. Hanawa, *Anal. Chim. Acta.* 149 (1983) 147.
- [20] A. R. Guadalupe, and H. D. Abruna, *Anal. Chem.* 57 (1985) 142.
- [21] J. A. Cox, and P. J. Kulesza, *Anal. Chim. Acta* 754 (1983) 71.
- [22] J. Wang, B. Greene, and C. Morgan, *Anal. Chim. Acta* 158 (1984) 15.
- [23] J. F. Price, and R. P. Baldwin, *Anal. Chem.* 52 (1880) 1940.
- [24] M. Li, S. Xu, F. Ni, Y. Wang, S. Chen, and L. Wang, *Microchim. Acta* 166 (2009) 203.
- [25] S. M. Chen, *J. Electroanal. Chem.* 521 (2002) 29.
- [26] T. V. Sathisha, B. E. K. Swamy, B. N. Chandrashekar, N. Thomas, and B. Eswarappa, *J. Electroanal. Chem.* 674 (2012) 57.