

T. Shobha · C.L. Aravinda · L. Gomathi Devi
S.M. Mayanna

Preparation and characterization of oxides of Ni-Cu: anode material for methanol oxidative fuel cells

Received: 18 December 2001 / Accepted: 20 August 2002 / Published online: 30 April 2003
© Springer-Verlag 2003

Abstract Oxides of Ni-Cu were electrodeposited and characterized by SEM, IR and XPS techniques. These studies indicate that the coatings are mostly amorphous, made up of tiny particles of copper metal or a very low alloy with nickel in non-metallic phases with non-stoichiometric compositions. The deposited oxide films exhibit low overvoltages at 303 K for methanol oxidation and act as effective anode materials. Electrocatalytic activity of the deposited films depends on the composition of the coating. Under working conditions the deposits exhibit good corrosion resistance towards the electrolyte medium.

Keywords Oxides of Ni-Cu · Anode material · Methanol oxidation · Overvoltage · Corrosion resistance

Introduction

Methanol is a liquid fuel with a low-cost distribution system and is a potential candidate with high energy density to use in fuel cells [1]. It is a prospective power source since it is an easily refuelable power stack in electrically driven vehicles [2]. Unfortunately, methanol systems are on the verge of being abandoned because of the high cost of the noble metal catalysts and the lack of membranes which remove the cross-leaks of the methanol to the air electrodes [3]. Numerous materials have been used as electrodes for methanol oxidation [4, 5]. Although Pt offers a low overvoltage for methanol oxidation, surface inhibition by the adsorbed CO lowers the catalytic activity [6]. To overcome some of these drawbacks, alloys of Pt with Ru [6] and WO_3 [7] and alloys of Ru and Pd [8] are employed. However, the preparation

of these electrodes involves tedious procedures and is economically not viable. A recent review on the subject is noteworthy [9]. Considering these facts, it was felt that it might be feasible to deposit a simple mixture of oxides of Ni and Cu by an electrochemical method, using a suitable bath solution containing an oxidizing agent, to use as the anode material for methanol oxidation. Here we report the characterization of the surface composition and morphology of the deposits. The catalytic activity of the electrode material is evaluated by a polarization technique.

Experimental

Plating bath solutions were prepared by using AR grade chemicals and double distilled water. Oxides were deposited on copper foils (99.9%, $5 \times 2 \text{ cm}^2$ and 0.3 mm thick). Before deposition, the copper surface was cleaned with trichloroethylene, mechanically polished using different grades of emery paper and finally chemically polished [10]. The details of the pre-treatment of the electrode surface and experimental procedure have been described earlier [11].

The compositions of the deposits were obtained using an atomic absorption spectrometer (Perkin-Elmer PHI 590A). The surface morphology of the samples obtained under optimum deposition conditions was studied by scanning electron microscopy (SEM; JEOL JSM 840A). X-ray photoelectron spectra of the deposited thin films were recorded using an ESCA-3 mark II spectrometer (VG Scientific, UK) using Al K_α radiation (1486.6 eV). Galvanostatic polarization measurements were carried out in a current density range of 1–100 mA cm^{-2} at 303 K using a potentiostat/galvanostat (PAR 270 EG&G, NJ, USA) and a three-compartment glass cell with a saturated calomel and platinum foil as the reference and auxiliary electrodes, respectively. Catalytic activity of the coatings as an anode material was evaluated in methanol (1 M) containing H_2SO_4 (0.5 M), which is widely used as an electrolyte in methanol oxidation fuel cells [12].

Results and discussion

Attempts were made to develop complex plating bath solutions to obtain good quality coatings of the oxides of Ni and Cu. Several organic compounds containing oxygen, nitrogen and sulfur were examined individually

T. Shobha · C.L. Aravinda · L. Gomathi Devi · S.M. Mayanna (✉)
Department of Post-Graduate Studies and Research in Chemistry,
Central College Campus, Bangalore University,
Bangalore-560001, India
E-mail: mayanna@vsnl.net

and in combination to complex both Ni and Cu ions in the bath solution. Among these compounds, only triethanolamine (TEA) in slightly acidic solution acted as an effective complexing agent. Boric acid (H_3BO_3) and ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ were used as buffering agent and oxidizing agent, respectively. The pH of the bath solution was maintained at 5.0. Experiments were carried out to study the effect of plating variables [metal ions ratio, current density (c.d.), temperature and the concentration of TEA] on the composition of the coating. Based on the obtained results, the bath composition and deposition conditions were optimized to obtain good quality coatings of Ni and Cu oxides (Table 1). Under certain experimental conditions, the Cu content in the deposit was nearly the same as that in the bath solution (Table 2).

Surface analysis of the deposit was carried out by using the SEM technique. SEM micrographs of oxides of Ni and Cu obtained from bath solutions containing different amounts of Cu (2.5–30% Cu) at 30 mA cm^{-2} and a temperature of 303 K are shown in Fig. 1 (A and B). Micronodular growth is noticed with 2.5% Cu in the bath solution. With an increase in the copper content (10%) there is an increase in the size of the micronodules (Fig. 1A). With 30% Cu in the bath solution a dense agglomerate type of coating is noticed (Fig. 1B). These micrographs showed that the coating consists of tiny particles with porous regions with well-defined grain boundaries. Figure 1C shows the typical EDAX dot mapping recorded for the coating containing 10% Cu. These data indicated that there was uniform chemical composition throughout the deposit.

Table 1 Bath composition^a

Bath composition	Concentration (M)
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	0.15
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.01
TEA	0.15
H_3BO_3	0.32
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	0.04

^aOperating conditions: anode, SS316; substrate, copper foil; c.d., 30–50 mA cm^{-2} ; pH, 5.0; time, 15 min; temperature, 303 K

Table 2 Electrochemical parameters for methanol oxidation^a on oxide coatings of Ni-Cu at 303 K

Cu in the bath (%) ^b	ba (mV dec^{-1})	$\eta(100 \text{ mA cm}^{-2})$ (mV)	i_{corr} ($\mu\text{A cm}^{-2}$)
50.0	75.0	340.0	3.2
30.0 (36.0)	98.0	275.0	8.5
10.0 (12.0)	70.0	230.0	5.6
2.5	130.0	590.0	1.2
100.0	180.0	440.0	11.0
0.0	98.0	2090.0	0.5

^aElectrolyte: 1 M methanol + 0.5 M H_2SO_4

^bThe values of the percent Cu in the alloy are given in parentheses

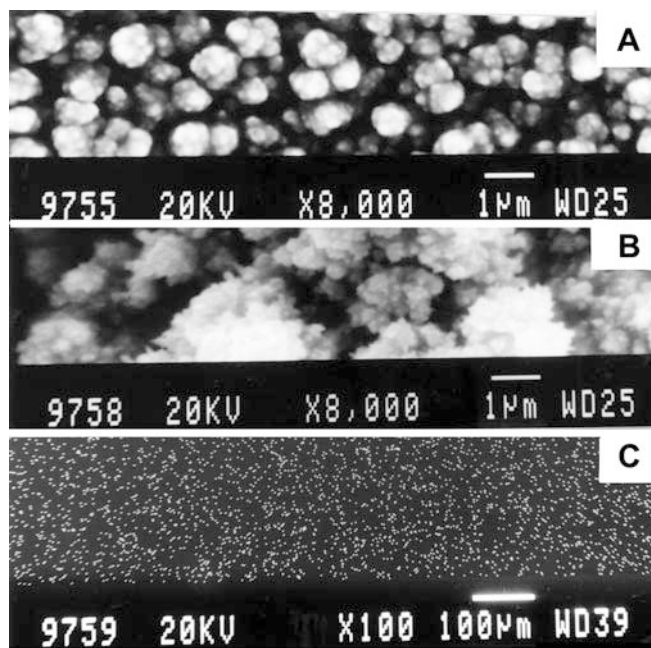


Fig. 1 SEM photographs of Ni-Cu oxide coatings obtained from bath solutions containing different amounts of Cu: **A** 10%; **B** 30%. **C** EDAX: Cu dot mapping

XRD studies were made using a few deposited coatings on a molybdenum surface to obtain microstructural information. These data revealed that the deposits are amorphous in nature. Hence the nickel and copper compounds (especially oxides) were not visible under XRD. Figure 2 shows XPS results for the Cu(2p) region of the as-prepared film as well as after 10 and 20 min intermittent sputtering. For the as-prepared film, Cu(2p_{3/2,1/2}) peaks (Fig. 2a) are observed at 932.6 and 952.4 eV, indicating that Cu is in the +1 oxidation state and the peaks could be attributed to Cu₂O species. On the other hand, Cu(2p_{3/2,1/2}) peaks (Fig. 2b) at 933.0 and 953.1 eV after 10 min sputtering could be attributed to Cu metal only. The absence of satellite peaks in the spectrum indicates the absence of a CuO phase. The same trend (Fig. 2c) continues after 20 min sputtering also. From these data it is difficult to identify the actual copper compounds. The observed changes are attributed to Cu(NO₃)₂/Cu(OH)₂.

Figure 3 shows XPS spectra of the Ni(2p) core level region of the as-deposited film, as well as after 10 and 20 min intermittent sputtering. Ni(2p_{3/2,1/2}) peaks (Fig. 3d) at 854.5 and 872.4 eV (with satellite peaks) indicate that Ni is in the +2 oxidation state and the peaks could be attributed to NiO species [13]. Ni(2p_{3/2,1/2}) peaks (Fig. 3e and f) at 852.6 and 870.3 eV, with weak satellite peaks at 860.6 and 878.8 eV, of the same film after 10 and 20 min sputtering can be assigned to Ni metal. There is no signature for NiO in the spectrum of the sputtered film. The presence of oxide species is further confirmed by IR data (Fig. 4). Pure samples of CuO and NiO species exhibit vibrational bands at 426 cm^{-1} ; however, the metal-oxide vibrational band in the IR spectra

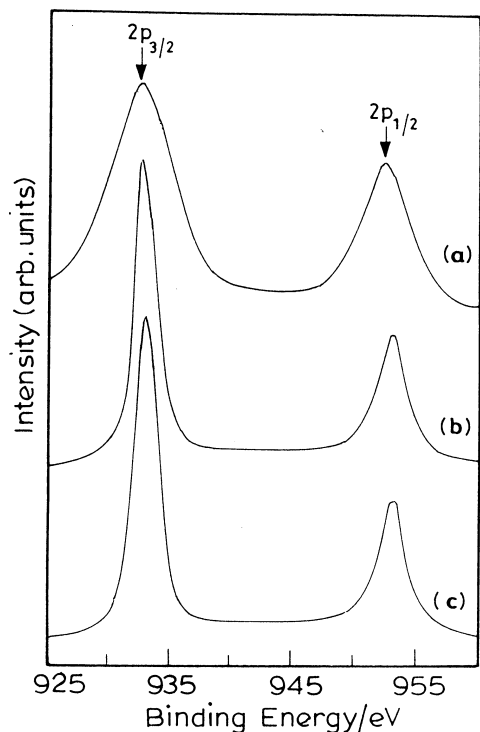


Fig. 2 XPS spectra of the Cu(2p) core level region in a Cu-Ni oxide coating (a) as-prepared, (b) after 10 min sputtering and (c) after 20 min sputtering

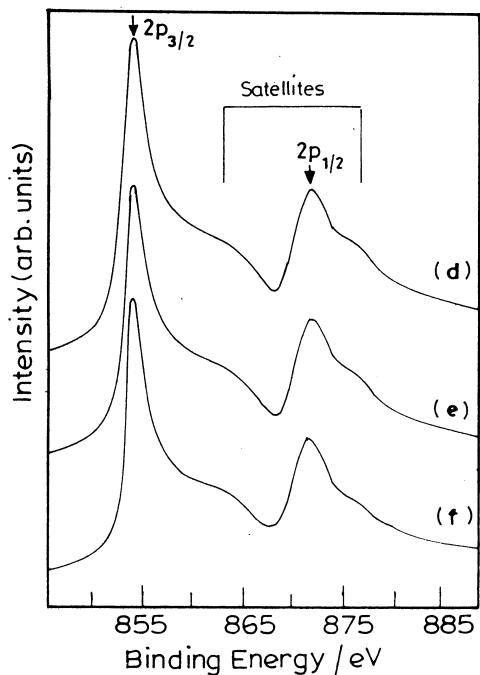


Fig. 3 XPS spectra of the Ni(2p) core level region in a Cu-Ni oxide coating: (d) as-prepared, (e) after 10 min sputtering and (f) after 20 min sputtering

obtained for the coating is shifted to 447 cm^{-1} [14]. The presence of a sulfato complex in the coating was also noticed at 1103 and 628 cm^{-1} [15].

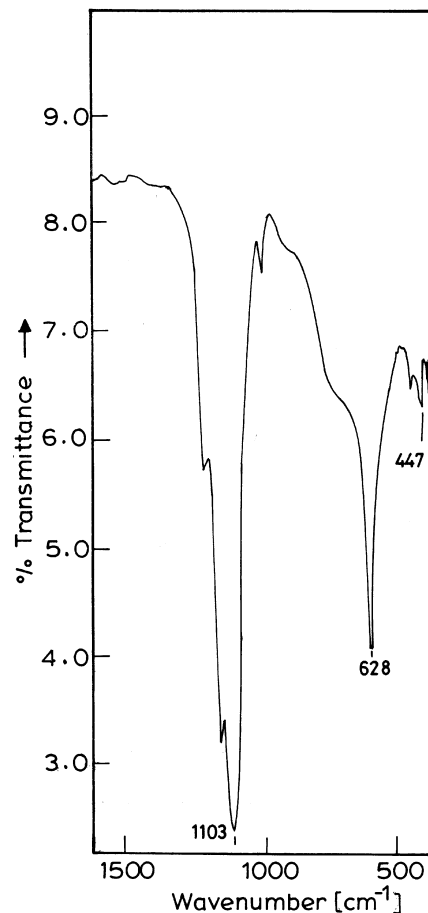


Fig. 4 IR spectrum of the Ni-Cu oxide coating

The coatings obtained under different conditions were tested for catalytic activity as anode materials for methanol oxidation. H_2SO_4 is widely used as the electrolyte in methanol oxidation fuel cells. Galvanostatic polarization measurements were carried out on oxides of Ni-Cu with different compositions in H_2SO_4 (0.5 M) containing methanol (1 M) at 303 K in the current density range $1\text{--}100\text{ mA cm}^{-2}$. Figure 5 shows the polarization curves for methanol oxidation on coatings having different Cu contents and Table 2 gives the corresponding electrochemical parameters. Under comparable experimental conditions, pure Cu and pure Ni did not act as good anodes for the methanol oxidation reaction. However, the electrocatalytic activity of the anode increases with a decrease in Cu content in the coating. A better catalytic activity is noticed with 10% Cu. A further decrease in Cu content ($<10\%$) does not improve the catalytic activity. The dependence of catalytic activity on the composition of the coating is perhaps due to the variation in surface area and the microstructure of the coating.

The Tafel diagrams (Fig. 5) consist of two Tafel regions, which indicates the different reaction mechanisms for methanol oxidation in the c.d. range chosen. The coatings offer good corrosion resistance towards the

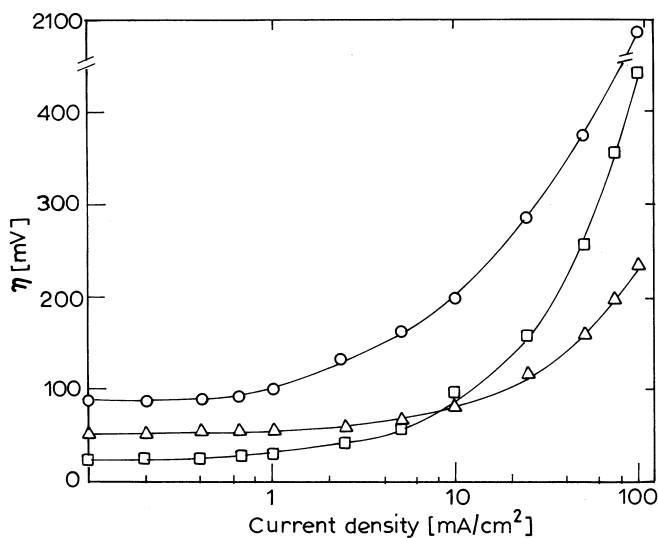


Fig. 5 Galvanostatic polarization diagrams for methanol oxidation on a Cu-Ni oxide coating with different compositions in 0.5 M H_2SO_4 at 303 K: circles: 100% Ni; squares: 100% Cu; triangles: 10% Cu

electrolyte medium (Table 2). The electrode material obtained from the bath solution containing 10% Cu exhibits a sufficiently low overvoltage (230 mV) in the stationary electrolyte medium even at 100 mA cm^{-2} and a temperature of 303 K for up to 60 h of operation, which is much lower than the value obtained with other electrode systems [16]. This shows the stability of the anode material for prolonged methanol oxidation, which is one of the important characteristics of a stable anode material.

Electrooxidation of methanol is retarded by the strong adsorption of reaction intermediates (CO , HCHO , HCO_2H , etc.) on the electrode surface [17]. Cyclic voltammetric investigation of acidic zinc sulfate in the presence of formaldehyde gives a characteristic peak on platinum electrodes [18]. This experimental approach was used to identify the formation of formaldehyde as an intermediate in the present system. The H_2SO_4 /methanol mixture was electrolysed for 2 h at 100 mA cm^{-2} using the deposited film as the anode material. The resulting reaction mixture was taken as the medium for zinc sulfate and a cyclic voltammetric experiment was carried out on a platinum electrode. The cyclic voltammograms obtained with reference to formaldehyde and in the presence of the oxidation mixture were almost identical (Fig. 6). This is further confirmation for the participation of formaldehyde as an intermediate during electrooxidation of methanol on a deposited oxide film of Ni-Cu.

Conclusions

The deposited oxide coatings of Ni-Cu using suitable plating baths and working conditions exhibit good

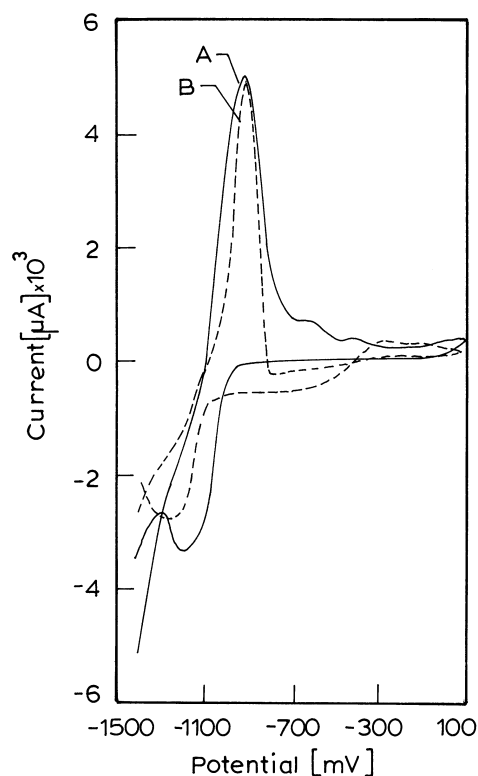


Fig. 6 Cyclic voltammograms obtained in zinc plating bath solution ($0.02 \text{ M ZnSO}_4 + 0.01 \text{ M Na}_2\text{SO}_4$) at a scan rate of 100 mV s^{-1} ; temperature 298 K and pH 3.0: A, with HCHO; B, with the reaction mixture ($\text{CH}_3\text{OH} + \text{H}_2\text{SO}_4$)

catalytic activity for the anodic oxidation of methanol, with a low overvoltage even at sufficiently low temperatures. XPS studies of the coating show that the oxidation state of both Cu and Ni species at the surface differs from that of the bulk. A decrease in Cu content in the coating increases the catalytic activity. The coatings offer good corrosion resistance towards H_2SO_4 medium. A cyclic voltammetric study shows the existence of formaldehyde as one of the intermediates during the methanol oxidation.

Acknowledgement One of the authors (S.M.M.) thanks the UGC, New Delhi, for financial assistance to carry out this work.

References

1. Kordesch K, Simader G (1996) Fuel cells and their applications. VCH, Weinheim, pp 251–295
2. Kantha S, Grimes P (1994) *Phys Today* 47:54
3. Baker BS (ed) (1965) Hydrocarbon fuel cell technology. Academic Press, New York
4. Parsons R, Vander Noot T (1988) *J Electroanal Chem* 257:9
5. (2001) Proceedings of the conference on advances in R and D for the commercialization of small fuel cells and battery technologies for use in portable applications, Washington DC
6. Baldauf M, Preidel W (1999) *J Power Sources* 84:161
7. Shen PK, Tseung ACC (1994) *J Electrochem Soc* 141:3082
8. He Chunzhi, Kunz HR, Fenton JM (1997) *J Electrochem Soc* 144:970

9. Heinzel A, Barragan VM (1999) *J Power Sources* 84:70
10. Dinnappa RK, Mayanna SM (1979) *J Electrochem Soc India* 28:191
11. Maruthi BN, Ramesh L, Mayanna SM, Landolt D (1999) *Plat Surf Finish* 3:85
12. Burstein GT, Barnett CJ, Kucernak ARJ, Williams KR (1996) *J Electrochem Soc* 113:L139
13. Briggs D, Seals MP (1984) *Practical surface analysis by Auger and X-ray photoelectron spectroscopy*. Wiley, New York
14. Ferraro JR (1971) *Low-frequency vibrations of inorganic and co-ordination compounds*, Plenum Press, New York
15. Nakamoto K (1963) *Infrared spectra of inorganic coordination compounds*. Wiley, New York
16. Watanabe M, Uchida M, Motoo S (1987) *J Electroanal Chem* 229:395
17. Matsui H, Kunugi A (1990) *J Electroanal Chem* 292:103
18. Shabanna Begum S, Muralidharan VS, Mayanna SM (2001) *J Port Electrochim Acta* 19:121