

Effect of Pulse Frequency on the Deposition of Cu-Fe Alloy via Pulsed Current Electrodeposition Method

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Abstract. In an attempt to reduce the oxidation and Cr evaporation rates of solid oxide fuel cells (SOFCs) interconnect, Cu-Fe coating was developed on the AISI 430 ferritic stainless steel substrate by a pulsed current electrodeposition method. Effects of pulse frequency on properties and performance of the fabricated coating were investigated. Results show that Cu-Fe alloy was successfully fabricated using pulse deposition methods. The variation of pulsed frequency during pulse current deposition strongly influence the coating morphology and its composition. The increase of pulse frequency tend to increase the Cu-Fe grain size. Moreover, the amount of Cu particles decreases with the increase of pulse frequency.

Introduction

Solid oxide fuel cells (SOFC) are regarded as highly efficient power generation systems for future application, owing to their high efficiency, low pollution and relatively flexible fuel choice [1]. Interconnect is an important component of the SOFC that separates the oxidant and fuel gases, distributes the gases to electrodes and provides electrical connections between single stacks. Because of high operating temperature, requirements for the interconnect materials, such as high temperature oxidation resistance, high electrical conductivity and thermal expansion compatibility with other cell components are essentially stringent [2-4]. Ferritic stainless steel as interconnect has more attention due to excellent formability, relatively higher toughness and mechanical strength, higher electrical and thermal conductivities compared to ceramic alternatives. Nevertheless, they have low resistance against Cr₂O₃ evaporation in the SOFC operation environment. The volatile chromium species such as CrO₃ and CrO₂(OH)₂ can contaminate the cathode and cause rapid degradation of cell performance [5].

One of the most effective way to improve the ferritic stainless steel interconnect performance is to apply a surface coating to increase electrical conductivity, reduce oxide scale growth and Cr volatility. Generally, spinels coating can be use as barriers to Cr cation migration and possess high electronic conductivity [2-3,6]. Various coatings, e.g., reactive element materials (REO) [7], perovskite [8,9] and spinel oxides [10,11] have been explored. Cu-Fe spinel coating are promising as one of suitable candidate due to their high electrical conductivity and compatible thermal expansion coefficient. Cu-Fe spinel conductivity can be improved by the presence of copper and iron elements because of their multiple valence.

Pulsed current deposition has been regarded as alternative deposition mode to DC plating. In pulsed deposition, three addition parameters can be varied independently for control over film quality, peak current density, on- and off-times [11]. It can also be used to control the composition and microstructures of depositions, as well as allowing for some additives to be replaced, and thus simplifying the deposition process [12-13].

In the present work, Cu-Fe alloys are deposited on stainless steel 430 substrate by pulsed current electrodeposition method. The effects of pulse frequency on the surface morphology, crystal size and composition of coatings are studied. The surface morphology of the coating and the amount of Cu-Fe deposited were characterized by scanning electron microscopy (SEM) and energy-dispersive spectrum (EDS). Moreover, the crystalline structure of the coating was characterized by X-ray diffraction (XRD).

Experimental

The substrate used for electrodeposition experiment was made of ferritic stainless steel (AISI 430) sheet. The specimens were cut to coupons of 10 x 15 x 1 mm, and set as a cathode. For anode, similar specimen with dimension of 25 x 25 x 1 mm was used. Prior to the electrodeposition, the specimens were ground up to 2000 grit and polished. Afterwards the specimens were degreased with NaOH and pickled with H₂SO₄ for 10 minutes at room temperature. The weight of coupon before and after plating were recorded.

The bath electrolyte used for the electrodeposition composed of 50 ml CuSO₄ 0.45 M, 50 ml FeSO₄ 0.9 M and H₂SO₄ 0.9 M. The detail electrodeposition parameters are given in Table 1. All experiment were carried out at room temperature and pH at 1.8. The deposition time was kept constant 11 minutes for pulse current (PC) and 8 minutes for direct current (DC). For this experiment, pulsed current was obtained from function generator coupled to Hokuto Denko HA-151B potentiogalvanostat. Pulse current at frequency of 1, 10 and 100 Hz, with square waveform and current density of 30 mA/cm² were supplied to the cathodes. The duty cycle are set at 75%, with the amplitude of 400 mV. The current profile during pulse current deposition are shown in Fig. 1 The on-time and off-time variation during pulse deposition are shown in Table 2.

Table 1 Electrodeposition Parameters for Fabrication Fe-Cu Alloy

Parameters	Value
Current density [mA/cm ²]	30
Temperature [°C]	25
Pulse frequency [Hz]	1, 10, 100
Amplitude [mV]	400
Duty cycle [%]	75%
Electrolyte	50 ml CuSO ₄ 0.45 M, 50 ml FeSO ₄ 0.9 M H ₂ SO ₄ 0.9 M
pH	1.8

To determine the suitable cathodic current density for pulse current electrodeposition, the sample was exposed to a potentiodynamic polarization test. The substrate was set as the working electrode, platinum as the counter electrode and standard calomel electrode (SCE) as the reference electrode. The surface morphology of the deposit was characterized using scanning electron microscope (SEM). The amount of Cu and Fe particles deposited in the coating was determined by EDS combined with SEM. To determine the crystalline orientation, XRD analysis were carried out with Cu K α radiation.

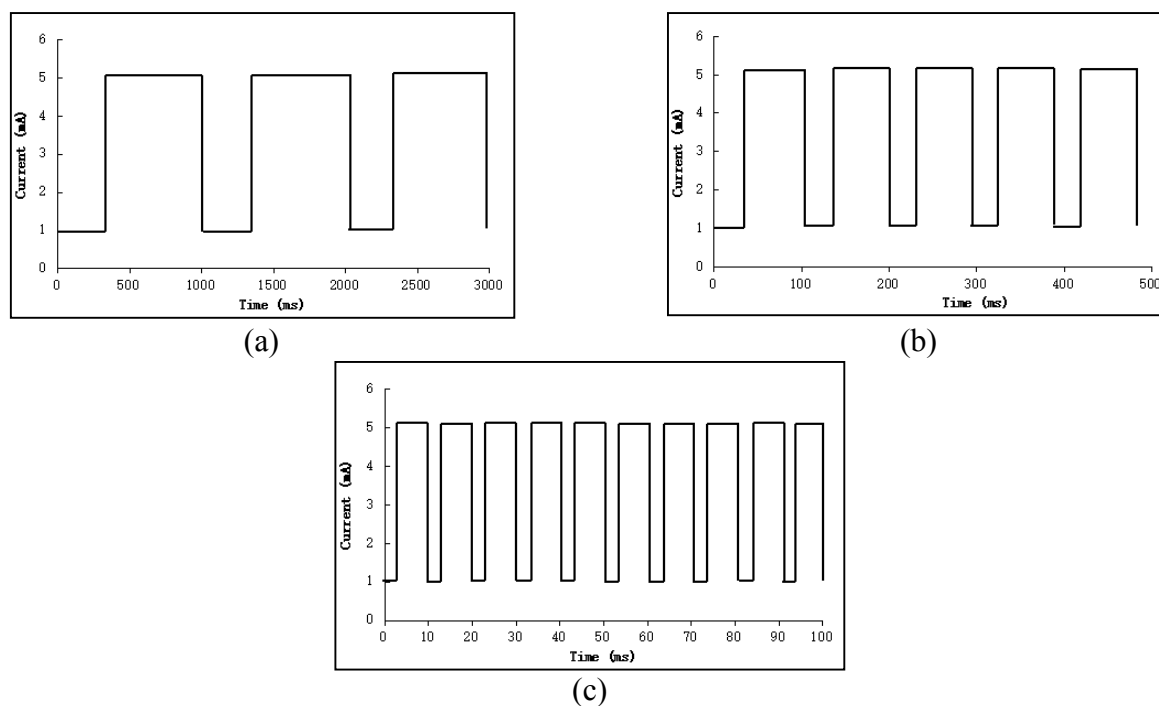


Fig. 1 Deposition current profile pulse current electrodeposition (a) 1 Hz, (b) 10 Hz, (c) 100 (Hz).

Table 2 On-time and off-time variation obtained at different frequencies.

Sample	T_{On} [ms]	T_{Off} [ms]	T_{total} [ms]
DC	-	-	480000
PE 1	750	250	640000
PE 10	75	25	640000
PE 100	7.5	2.5	640000

Results and Discussion

Determination of Current Density for Cu-Fe Alloy Deposition.

Fig. 2 shows the potentiodynamic cathodic polarization behavior of AISI 430 substrate in a solution 0.9 M FeSO_4 and 0.45 M CuSO_4 + 0.9 M H_2SO_4 . Cathodic polarization curve of Cu lies at less negative potentials than that of Fe. This indicates that Cu is nobler than Fe in the solution system. The polarization curve of Cu-Fe alloy lies between potentials those of the parent metals. The suitable current density for the co-deposition of Cu and Fe is achieved at 0.03 A/cm².

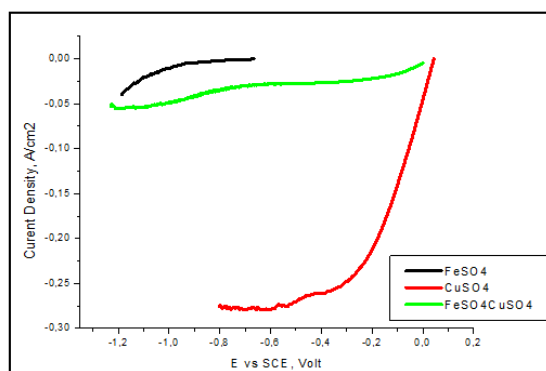


Fig. 2 Cathodic Polarization Curve for Fe, Cu, and Fe-Cu Deposition in FeSO_4 , CuSO_4 and (Fe, Cu) SO_4 Solution at pH=2.

Effect of Pulse Frequency on Cu-Fe Coating Composition.

The effect of pulse frequency on Cu-Fe coating composition are summarized in Table 3. The amount of Cu particles tend to decrease with the increase of pulse frequency. On the other hand, the amount of iron tend to increase with the increase of pulse frequency. This could be explained from its standard reduction potential value. The standard reduction potential value of iron and copper ($[\text{Cu}^{2+}/\text{Cu}] = 0.34$ vs SHE, $[\text{Fe}^{2+}/\text{Fe}] = -0.41$ vs SHE) clearly shows that copper is reduced preferentially during the deposition. However, the increase of pulse frequency during deposition tend to decrease the deposition on-time. As a results, a thinner deposit was obtained with the increase in pulse frequency, which results in less copper content in the deposit.

Table 3 Cu-Fe Content in the Electrodeposit Obtained at Different Frequencies.

Sample	% Mass		Mol		Mol fraction		Alloy
	Cu	Fe	nCu	nFe	xCu	xFe	
DC	88.96	11.04	1.41	0.20	0.88	0.12	CuFe_7
PC 1	96.9	3.10	1.47	0.05	0.97	0.03	CuFe_{32}
PC 10	95.32	4.68	1.51	0.08	0.95	0.05	CuFe_{19}
PC 100	91.62	8.38	1.42	0.15	0.91	0.09	CuFe_{10}

On the other hand, double layer discharge, concentration profile relaxation and hydrogen bubble released will occur during the off time. The increases in deposition off-time, will results in denser and compact coating due to hydrogen bubble release. However, this situation does not help copper deposition due to the concentration gradient relaxation. The off-time in pulsed current electrodeposition provides more chances for iron to arrive at the cathode, increasing the amount of adsorbed particles to deposit in the coating.

Effect of Pulse Frequency on Morphology and Structure of Cu-Fe Coating.

Fig. 3 shows the surface morphology of as-deposited Cu-Fe coating on AISI 430 substrate obtained from various pulse frequency during pulse deposition.

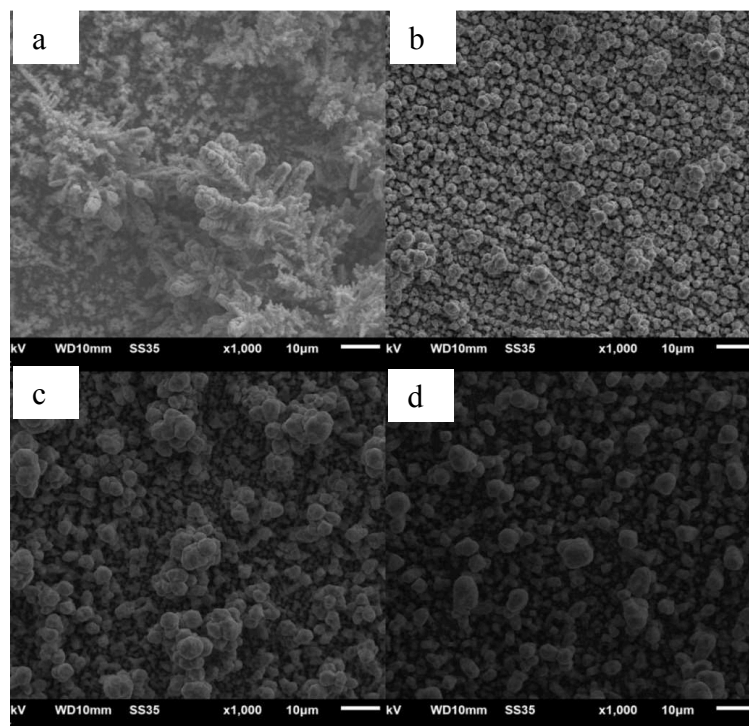


Fig. 3 SEM Image of as-deposited Cu-Fe alloy coating obtained at different Frequency
(a) 0 Hz, (b) 1 Hz, (c) 10 Hz, (d) 100 Hz.

The surface morphology of Cu-Fe coating obtained by pulse current deposition shows a spherical structure, completely different with that obtained with DC methods (0 Hz). The increase of pulse frequency tend to increase the Cu-Fe grain size. Agglomeration takes place with the increase in pulse frequency, resulted larger coating grain size.

Fig. 4 shows the XRD pattern of the prepared Cu-Fe alloy obtained under various frequencies. Cu-Fe alloy peak were identified in all specimen. The weak characteristic lines in the range of 2θ of 18° and 36° indicate the present of Fe_xCu_x phases. These peak were correspond to (111) and (222) planes. On the other hands, the strong characteristic lines in the range of 2θ of 43° , 50° and 75° indicate the present of FeCu_4 phases. These peak were correspond to (111), (202) and (220) planes.

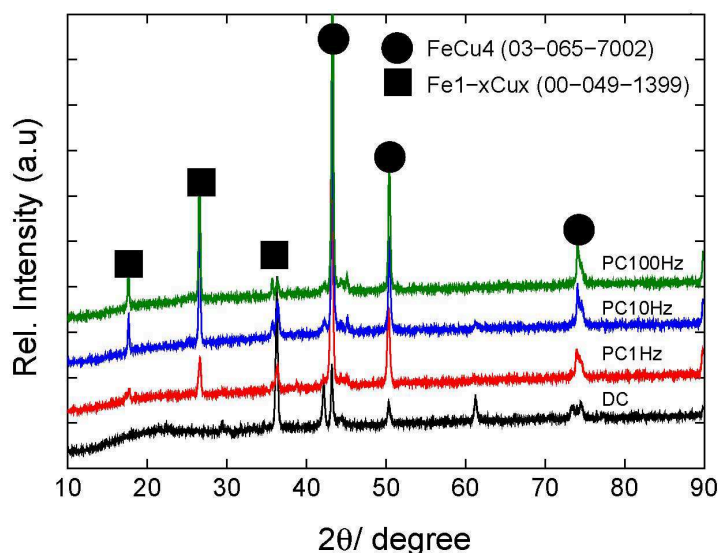


Fig. 4 XRD Spectra of Cu-Fe in the electrodeposit obtained at different Frequency
(a) 0 Hz, (b) 1 Hz, (c) 10 Hz, (d) 100 Hz.

The increase of pulse frequency tend to increase the peak intensity, especially at (111), (202) and (220) planes, indicates that the structure of the prepared coatings is predominantly face center cubic. The amount of the deposited Cu-Fe alloy increases with the increase in pulse frequency. The higher pulse frequency could generate a higher over potential, providing more energy for the adsorption of Cu-Fe alloy.

The estimation of Cu-Fe crystallite size by Scherers formula [14] from (111), (202) and (220) diffraction peak with varied pulse frequency are summarized in Table 4. The increase of pulse frequency tend to increase the coating crystallite size. Teoritically, the increase of pulse frequency could enhance the nucleation rate during deposition [15]. As a result, the coating crystallite size are usually small. On the contrary, agglomeration become easier with increasing nucleation rate, and it can consequently increase the grain size.

Table 4 Estimated Cu-Fe crystallite size obtained under various frequency.

Sample	Average Size [nm]
DC	15.67
PE 1	18.5
PE 10	24.83
PE 100	29

Conclusions

Cu-Fe alloy was successfully deposited using pulsed current electrodeposition method. The variation of pulsed frequency during pulse current deposition strongly influence the coating

morphology and its composition. SEM and XRD analysis strongly indicated that the increase of pulse frequency tend to increase the Cu-Fe crystallite size. Composition analysis by EDS shows that the amount of Cu particles decreases, while Fe increases with the increase of pulse frequency. Composition of fabricated Cu-Fe alloy was depended on the process parameter and require further optimization.

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References

- [1] Y.P. Fu, $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.4}\text{Ni}_{0.6}\text{O}_{3\delta}\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ as a potential cathode for intermediate-temperature solid oxide fuel cells, *Int J Hydrogen Energy*. 35 (2010) 8663-9.
- [2] B. Hua, J. Pu, W. Gong, J. Zhang, F. Lu, L. Jian, Cyclic oxidation of Mn-Co spinel coated SUS 430 alloy in the cathodic atmosphere of solid oxide fuel cells, *J. Power Sources*. 185 (2008) 419-422.
- [3] B. Hua, W. Zhang, J. Wu, J. Pu, B. Chi, L. Jian, A promising NiCo_2O_4 protective coating for metallic interconnects of solid oxide fuel cells, *J. Power Sources*. 195 (2010) 7375-7379.
- [4] A. Heidarpour, G.M. Choi, M.H. Abbasi, A. Saidi, A novel approach to co-sintering of doped lanthanum chromite interconnect on Ni-YSZ anode substrate for SOFC applications, *J. Alloys Compd*. 512 (2012) 156-159.
- [5] D.R. Ou, M. Cheng, X.-L. Wang, Development of low-temperature sintered Mn-Co spinel coatings on Fe-Cr ferritic alloys for solid oxide fuel cell interconnect applications, *J. Power Sources*. 236 (2013) 200-206.
- [6] W. Qu, J. Li, D.G. Ivey, Sol-gel coatings to reduce oxide growth in interconnects used for solid oxide fuel cells, *J. Power Sources*. 138 (2004) 162-173.
- [7] A. Balland, P. Gannon, M. Deibert, S. Chevalier, G. Caboche, S. Fontana, Investigation of La_2O_3 and/or $(\text{Co},\text{Mn})_3\text{O}_4$ deposits on Crofer22APU for the SOFC interconnect application, *Surf. Coat. Technol*. 203 (2009) 3291-3296.
- [8] N. Orlovskaya, A. Coratolo, C. Johnson, R. Gemmen, Structural characterization of lanthanum chromite perovskite coating deposited by magnetron sputtering on an iron-based chromium-containing alloy as a promising interconnect material for SOFCs, *J. Am. Ceram. Soc*. 87 (2004) 1981-1987.
- [9] C. Monterrubio-Badillo, H. Ageorges, T. Chartier, J.F. Coudert, P. Fauchais, Preparation of LaMnO_3 perovskite thin films by suspension plasma spraying for SOFC cathodes, *Surf.Coat. Technol*. 200 (2006) 3743-3756.
- [10] X.S. Xin, S.R. Wang, Q.S. Zhu, Y.J. Xu, T.L. Wen, A high performance nano-structure conductive coating on a Crofer22APU alloy fabricated by a novel spinel powder reduction coating technique, *Electrochem. Commun*. 12 (2010) 40-43.
- [11] X. Xin, S. Wang, J. Qian, C. Lin, Z. Zhan T. Wen, Development of the spinel powder reduction technique for solid oxide fuel cell interconnect coating, *Int. J. Hydrogen Energy*. 37 (2012) 471-476.
- [12] J.-Cl. Puipe, F. Leaman (Eds.), *Theory and Practice of Pulse Plating*, AESF Soc, Orlando, 1986.
- [13] S.K. Ghosh, A.K. Grover, G.K. Dey and M.K. Totlani, Nanocrystalline Ni-Cu alloy plating by pulse electrolysis, *Surf Coat Tech*. 126 (2000) 48-63.
- [14] B. D. Cullity, *Element of X-Ray Diffraction* second ed., UK:Addison Wesley Publishing, London, 1981.
- [15] Y. Yang, Y.F. Cheng, Electrolytic deposition of Ni-Co-SiC nano-coating for erosion-enhanced corrosion of carbon steel pipes in oilsand slurry, *Surface and coatings technology*, *Surf. Coat. Technol*. 205 (2011) 3198-3204.