

# Initial Corrosion Behavior of a Copper-Clad Plate in Typical Outdoor Atmospheric Environments

Pan Yi,<sup>1</sup> Kui Xiao,<sup>1,\*</sup> Kangkang Ding,<sup>1,2</sup> Lidan Yan,<sup>1</sup> Chaofang Dong,<sup>1</sup> and Xiaogang Li<sup>1,3</sup>

<sup>1</sup>Corrosion and Protection Center, University of Science and Technology Beijing, Beijing, 100083, P. R. China

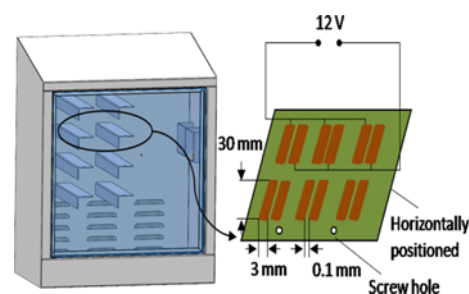
<sup>2</sup>State Key Laboratory for Marine Corrosion and Protection, Luoyang Ship Material Research Institute, Qingdao, 266101, P. R. China

<sup>3</sup>Ningbo Institute of Material Technology & Engineering, Chinese Academy of Sciences, Ningbo 315201, P. R. China

(received date: 21 July 2015 / accepted date: 12 October 2015 / published date: 10 January 2016)

A copper-clad printed circuit board (PCB-Cu) was subjected to long-term exposure test under typical Chinese atmospheric environments to study corrosion failure mechanisms. The corrosion behavior was investigated by analyzing electrochemical impedance, scanning Kelvin probes, stereo and scanning electron microscopes, and energy-dispersive spectra. Results showed that the initial surface potential was unevenly distributed. The outdoor PCB-Cu samples suffered severe corrosion caused by dust particles, contaminated media, and microorganisms after long-term atmospheric exposure. The initial localized corrosion was exacerbated and progressed to general corrosion for samples in Turpan, Beijing, and Wuhan under prolonged exposure, whereas PCB-Cu in Xishuangbanna was only slightly corroded. The tendency for electrochemical migration (ECM) of PCB-Cu was relatively low when applied with a bias voltage of 12 V. ECM was only observed in the PCB-Cu samples in Beijing. Contaminated medium and high humidity synergistically affected ECM corrosion in PCB-Cu materials.

**Keywords:** copper-clad plate, atmospheric corrosion, outdoor exposure, electrochemical migration



## 1. INTRODUCTION

Copper and its alloys exhibit excellent electrical and thermal conductivity, low cost, and high solder joint reliability<sup>[1]</sup> and are thus widely used as substrates for printed circuit boards (PCB). The printed foil in PCB is called the copper-clad laminate (PCB-Cu or CCL), which is prone to oxidation or corrosion. The corrosion of PCB-Cu in the actual service environment is affected by temperature and humidity,<sup>[2-4]</sup> contaminated media (Cl<sup>-</sup>, SO<sub>2</sub>, and H<sub>2</sub>S),<sup>[5-8]</sup> dust,<sup>[9]</sup> microorganisms,<sup>[10]</sup> and electromagnetic fields.<sup>[2,11,12]</sup> At the early stage of atmospheric exposure, a layer of the dense Cu<sub>2</sub>O film is quickly formed on the copper surface and

inhibits corrosion to a certain extent.<sup>[6,13,14]</sup> However, outside erosion gradually converts the outer surface of the Cu<sub>2</sub>O film into Cu<sub>3</sub>SO<sub>4</sub>(OH)<sub>4</sub>, CuSO<sub>4</sub>, Cu<sub>2</sub>(OH)<sub>3</sub>Cl, Cu<sub>2</sub>(OH)<sub>3</sub>NO<sub>3</sub>, Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>, and other corrosion products, which form a two-layered structure.<sup>[8]</sup> Ion migration occurs between the two neighboring plates under the effect of different voltages when the adsorbed water film covers the separating copper conductors; this phenomenon causes electrochemical migration (ECM) corrosion.

Previous research on PCB-Cu corrosion focused on indoor simulation experiments; as such, the actual corrosion behavior and the mechanism of PCB-Cu under outdoor environments must be investigated. In the current study, PCB-Cu was subjected to long-term exposure tests under typical Chinese atmospheric environments. This study contributes to the electrochemical theory of atmospheric corrosion and provides

\*Corresponding author: xiaokui@sina.com

©KIM and Springer

a database for the selection and assessment of PCB in actual service environments.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Material preparation and exposure test

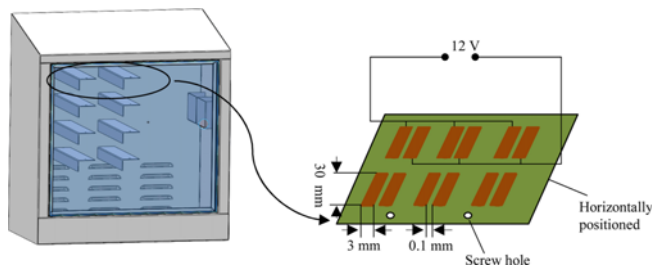
PCB-Cu samples were obtained from Sprine Co. (China). The basic parameters of the samples are listed in Table 1. The effective size of the printing plates is 30 mm × 3 mm, and the spacing between two neighboring plates is 0.1 mm. The PCB-Cu samples were positioned as shown in Fig. 1. The samples were fixed on angle irons by the screw in the box. Twelve sets of parallel samples were used, and only six sets were applied with an electrical bias voltage of 12 V to simulate the actual environment in the electronic components.

Boxes containing PCB-Cu samples were placed at the respective atmospheric corrosion test stations in Turpan, Xishuangbanna, Beijing, and Wuhan. The environmental characteristics of the four exposure sites are shown in Table 2. The experiment was started in April, and samples were withdrawn for further analysis after exposure for 1, 3, and 6 months.

**Table 1.** Basic processing parameters of PCB-Cu.

$M_{\text{board}}$	$T_{\text{board}}$	$T_{\text{copper}}$	$S$	$T_{\text{pro-layer}}$
FR-4	0.8 mm	35 $\mu\text{m}$	No surface treatment	No protective layer

Note:  $M_{\text{board}}$ , board materials;  $T_{\text{board}}$ , thickness of the board;  $T_{\text{copper}}$ , thickness of the copper layer;  $S$ , surface treatment;  $T_{\text{pro-layer}}$ , thickness of the protective layer.



**Fig. 1.** Schematic of the box.

**Table 2.** Typical environmental differences among exposure sites from meteorological and pollutant perspectives.

Location	Geographic position	NO <sub>2</sub> (mg· 100 m <sup>-2</sup> ·d <sup>-1</sup> )	H <sub>2</sub> S (mg· 100 m <sup>-2</sup> ·d <sup>-1</sup> )	SO <sub>3</sub> (mg· 100 m <sup>-2</sup> ·d <sup>-1</sup> )	NH <sub>3</sub> (mg· 100 m <sup>-2</sup> ·d <sup>-1</sup> )	Chlorides (mg· 100 m <sup>-2</sup> ·d <sup>-1</sup> )	Dust (g·m <sup>-2</sup> · month <sup>-1</sup> )	$T$ (°C)	Rainfall (mm)	RH (%)
Turpan	89°12'E, 42°56'N	–	–	–	–	–	–	29.5	0.19	17.1
XSBN	100°40'E, 21°35'N	–	–	0.0343	0.0294	0.0051	–	23.7	165.70	82.2
Beijing	116°16'E, 39°59'N	0.0958	0.0601	0.1390	0.0628	0.0199	9.2759	21.2	68.72	55.8
Wuhan	114°04'E, 30°36'N	0.1225	0.0815	0.3759	0.0462	0.0182	8.5968	25.3	149.77	68.8

Notes: Mean values were obtained from April to September. Given the limitations of the equipment, the environmental data for Turpan pollutants are incomplete but are expected to be between those of Beijing and Xishuangbanna. XSBN, Xishuangbanna.

### 2.2 Electrochemical measurements

Electrochemical tests were conducted in a conventional three-electrode system with a PAR VMP3 multi-channel electrochemical workstation. The counter electrode is platinum foil, and the reference electrode is a saturated calomel electrode. Electrochemical impedance spectroscopy (EIS) measurements were performed at open-circuit potentials with a perturbation of 10 mV. The measuring frequency ranged from 100 kHz to 10 mHz. All electrochemical measurements were performed in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution. ZSimpWin V3.20 was applied for EIS data fitting at the end of the test.

The voltage potential of the sample surface was measured with an M370 scanning Kelvin probe (SKP) at a working distance of 100 ± 2  $\mu\text{m}$  and a step size of 100  $\mu\text{m}$ . All the experiments were conducted in a stable laboratory environment at 20°C and 50% RH. Each test was performed three times.

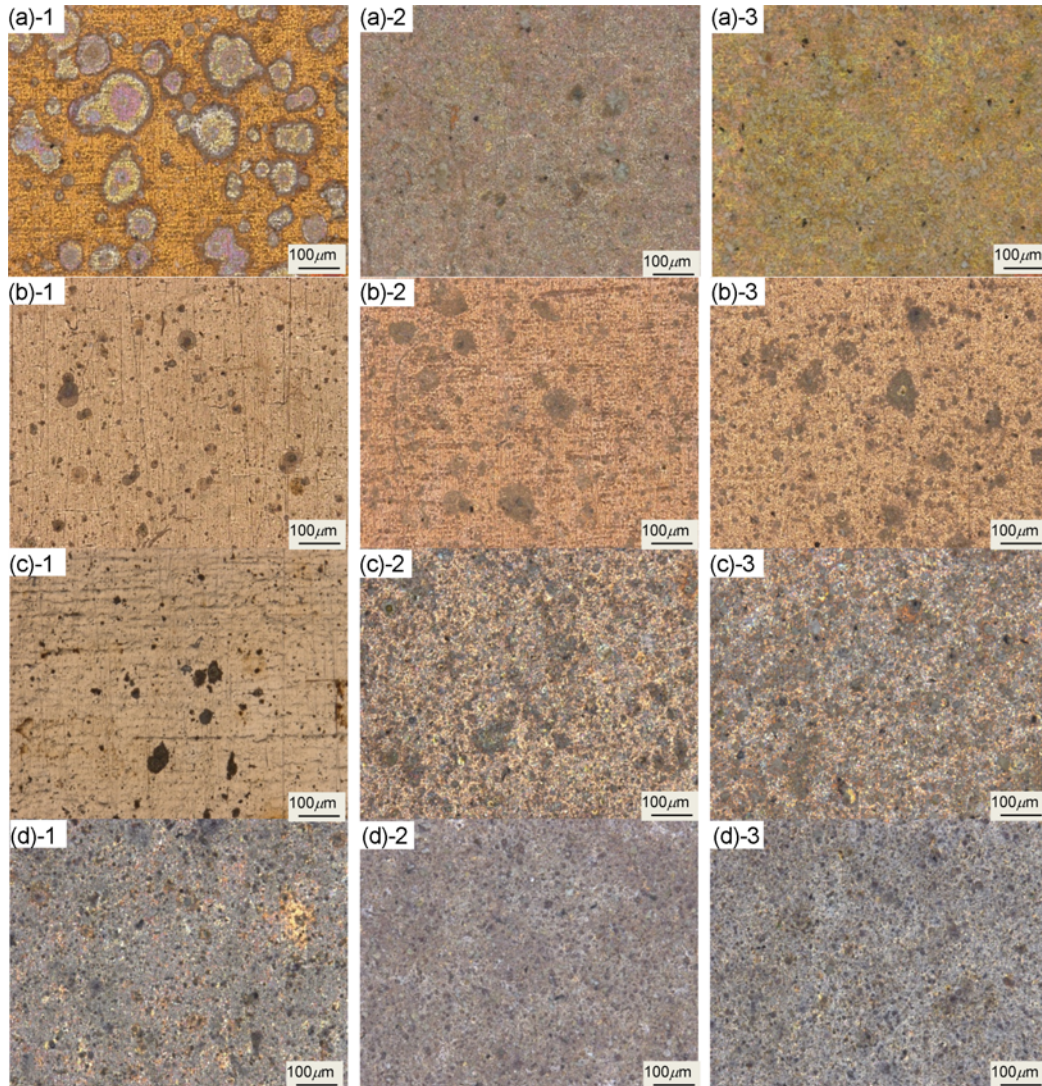
### 2.3 Corrosion morphology observation and elemental analysis

A stereo microscope (Keyence VHX-2000) and an environment scanning electron microscope (FEI Quanta 250) were used to observe the corrosion morphology. An energy-dispersive spectrometry (EDS) analyzer was used to determine element distribution on the surface.

## 3. RESULTS AND DISCUSSION

### 3.1 Corrosion morphology observation

Optical macroscopic photographs of the PCB-Cu samples exposed outdoors for 1, 3, and 6 months are shown in Fig. 2. The surface color of PCB-Cu sample exposed for 1 month in Turpan became darker. Localized corrosion occurred, and halo-shaped purple corroded regions were distributed and scattered on the sample surface. The purple regions extended over the entire surface after 3 months. Corrosion was exacerbated after 6 months, and the entire surface was covered with a layer of green corrosion film. Meanwhile, relatively slight overall corrosion was observed in the Xishuangbanna PCB-Cu samples (Fig. 2b). The surface color deepened, and the halo-shaped corrosion morphology similar to that of the Turpan PCB-Cu sample appeared



**Fig. 2.** Optical micrographs of the PCB-Cu samples exposed outdoors for (1) 1, (2) 3, and (3) 6 months in (a) Turpan, (b) Xishuangbanna, (c) Beijing, and (d) Wuhan.

without any expansion after prolonged outdoor exposure. At the early exposure stage, corrosion in the Beijing and Wuhan samples originated from local activation areas on the surface. Corrosion gradually developed over the entire surface and became uniform. However, the Wuhan PCB-Cu samples were severely corroded. The entire surface of the samples exposed for 1 month was already covered with a layer of ash-black corrosion products; this condition became more severe compared with that of the Beijing samples after exposure for 3 months. The difference in the corrosion morphology between the Beijing and Wuhan samples can be attributed to the varied weather conditions during the first month of sample collection. During this period, Beijing has windy and drought-like weather, whereas Wuhan experiences higher humidity because it is positioned near the south, which has a well-developed river system. Therefore, humidity

plays an important role in the corrosion of outdoor PCB-Cu.

The microscopic morphology of the PCB-Cu samples exposed outdoors for 6 months was further observed by SEM (Fig. 3). Areas around dust particles were severely corroded. The corrosion products were porous with low density in the Turpan sample. EDS analysis showed that dust may contain  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$ , and other electrolytes. The area deposited with dust can easily generate an electrolyte layer because of moisture absorption. This condition can cause serious electrochemical corrosion, thereby causing the observed corrosion morphology. Similarly, the corrosion of the Wuhan PCB-Cu samples assumed the shape of mounds with dust particles as their cores (Fig. 3d). The corrosion products presented relatively dense structures with high sulfur content (Table 3). This finding agrees with the sulfur-rich atmospheric environment in Wuhan. The corrosion

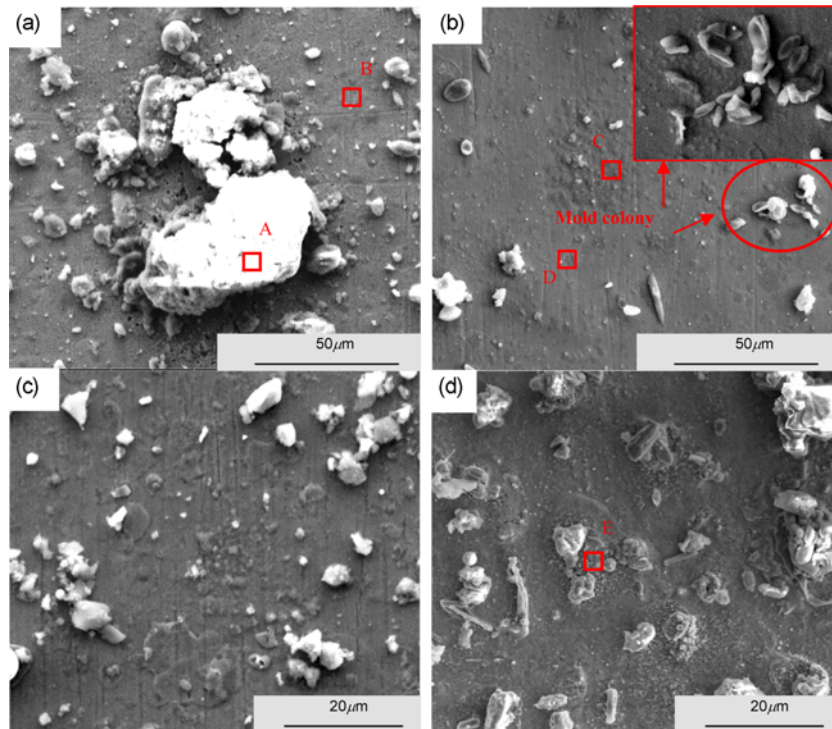


Fig. 3. SEM of the PCB-Cu samples exposed outdoors for 6 months in (a) Turpan, (b) Xishuangbanna, (c) Beijing, and (d) Wuhan.

Table 3. EDS results of outdoor PCB-Cu samples exposed for 6 months (at. %).

Element	O	Cu	S	C	Si	Cl	K, Ca, Mg	others
Area A	38.38	4.77	1.74	28.43	11.32	3.92	4.83	6.61
Area B	14.9	85.1	-	-	-	-	-	-
Area C	19.03	80.79	-	-	-	-	-	-
Area D	4.88	95.12	-	-	-	-	-	-
Area E	49.34	16.82	13.32	8.67	1.68	-	9.06	1.1

morphology of the Beijing PCB-Cu sample was similar to that of the Wuhan sample but presented a slightly higher degree of corrosion. A comparison of the corrosion morphology showed that the PCB-Cu sample in Xishuangbanna was the least corroded, with a slight accumulation of corrosion products in local areas. Meanwhile, the EDS spectra at points B, C, and D revealed that the PCB-Cu surface in Xishuangbanna was mildly oxidized because oxygen content increased in the local corrosion areas, whereas the entire surface of the Turpan sample was severely corroded. The clusters of mold spore analogs were also found on the Xishuangbanna PCB-Cu surface, and severe corrosion occurred around the adhesion areas. Corrosive products (e.g., sulfuric acid, organic acid, sulfide, and ammonia) were produced because of the growth and metabolism of mold spores. Thus, the corrosion environment on the metal surface worsened. The adhesion area was also in the activated state, which is preferentially corroded.

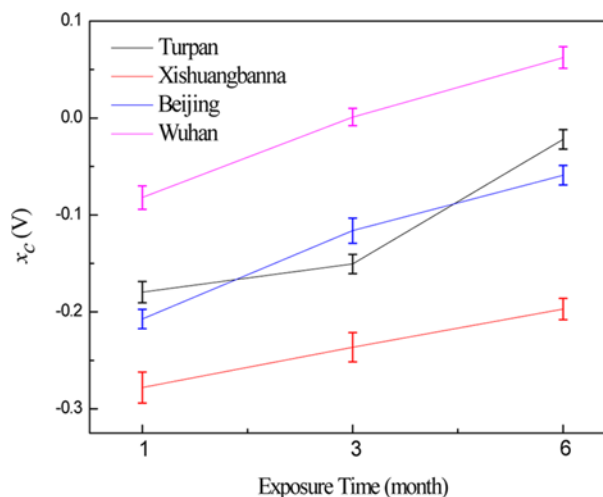


Fig. 4. Expected surface  $E_{kp}$  versus exposure time for outdoor PCB-Cu ( $\mu = -0.2860$  V for the blank sample).

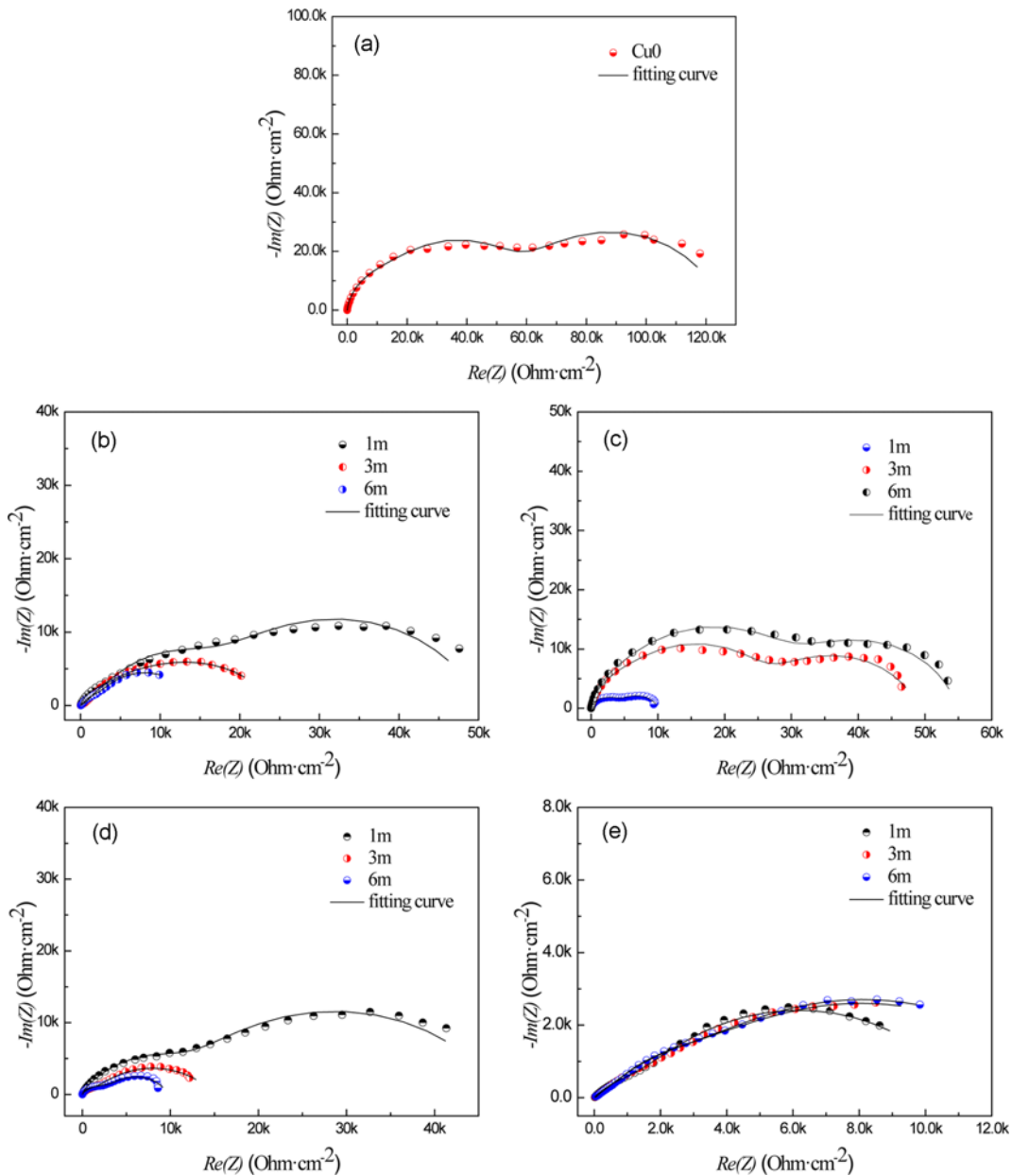
### 3.2 SKP analysis

The surface Kelvin potential (E<sub>kp</sub>) was measured after the exposure test to study the corrosion behavior and law of PCB-Cu exposed to different atmospheric environments. Gauss fitting was performed on the surface E<sub>kp</sub> map distribution at different periods.

The expected E<sub>kp</sub> values of PCB-Cu exposed at different periods are shown in Fig. 4. Similar overall evolution rules were observed with time for the surface E<sub>kp</sub> of PCB-Cu samples exposed in the four areas. E<sub>kp</sub> increased with prolonged exposure, thereby indicating that surface oxidation was continuously exacerbated. The films of the oxide and/or

corrosion product hindered electronic escape on the sample surface.<sup>[15]</sup>

The expected surface E<sub>kp</sub> of the Wuhan PCB-Cu sample was higher than those of the other locations during the entire exposure period (Fig. 4). The expected potential reached 0.0624 V, which indicates that the Wuhan PCB-Cu sample was severely corroded and accumulated large amounts of corrosion products. By contrast, the expected potential of the Xishuangbanna PCB-Cu sample was lower, and the sample surface was only mildly oxidized. The corrosion conditions of the Beijing and Turpan samples ranged between those of Wuhan and Xishuangbanna. However, the E<sub>kp</sub> value was



**Fig. 5.** EIS measurements and fitting curves for PCB-Cu: (a) blank sample and samples exposed outdoors in (b) Turpan, (c) Xishuangbanna, (d) Beijing, and (e) Wuhan.

higher in the Turpan sample at the early exposure stage. This finding indicated that the PCB-Cu samples are prone to serious oxidization or corrosion at springtime when they are exposed to the Turpan atmospheric environment.

### 3.3 EIS results and analysis

The Nyquist diagram of the PCB-Cu samples exposed outdoors is shown in Fig. 5. The film of the corrosion product of Cu was formed under long-term exposure to atmospheric conditions; this film generally has a two-layered structure.<sup>[7]</sup> The inner layer is a relatively dense  $\text{Cu}_2\text{O}$  film, whereas the outer layer consists of Cu salts, whose components depend on the species of the atmospheric pollution medium. Therefore, the equivalent circuit in Fig. 6 was adopted to fit the EIS measurements.  $R_s$  represents the solution resistance.  $R_f$  and CPE-f represent the resistance and capacitor of the outer layer of corrosion product, respectively.  $R_o$  and CPE-o represent the resistance and capacitor of the inner oxide film, respectively. CPE-dl is the electric double-layer capacitance.  $R_{ct}$  is the charge transfer resistance.  $R_{ct}$  reflects the magnitude of the interface reaction resistance, which is used to characterize the corrosion reaction rate. High  $R_{ct}$  values indicate low corrosion rates. The  $R_{ct}$  values of the PCB-Cu samples at different periods are shown in Fig. 7. The corrosion rate of the Beijing and Turpan PCB-Cu samples tended to increase with increasing exposure time, which indicates that PCB-Cu exhibits poor corrosion resistance in these atmospheric environments. On the one hand, the exposure time transitioned during summer, when the

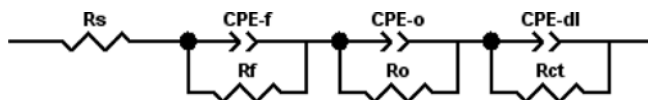


Fig. 6. EIS equivalent circuit for outdoor PCB-Cu.

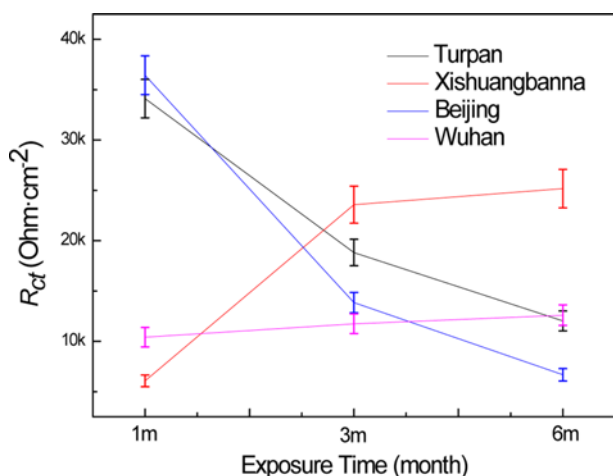


Fig. 7.  $R_{ct}$  versus exposure time for outdoor PCB-Cu ( $R_{ct} = 7356 \Omega \cdot \text{cm}^2$  for the blank sample).

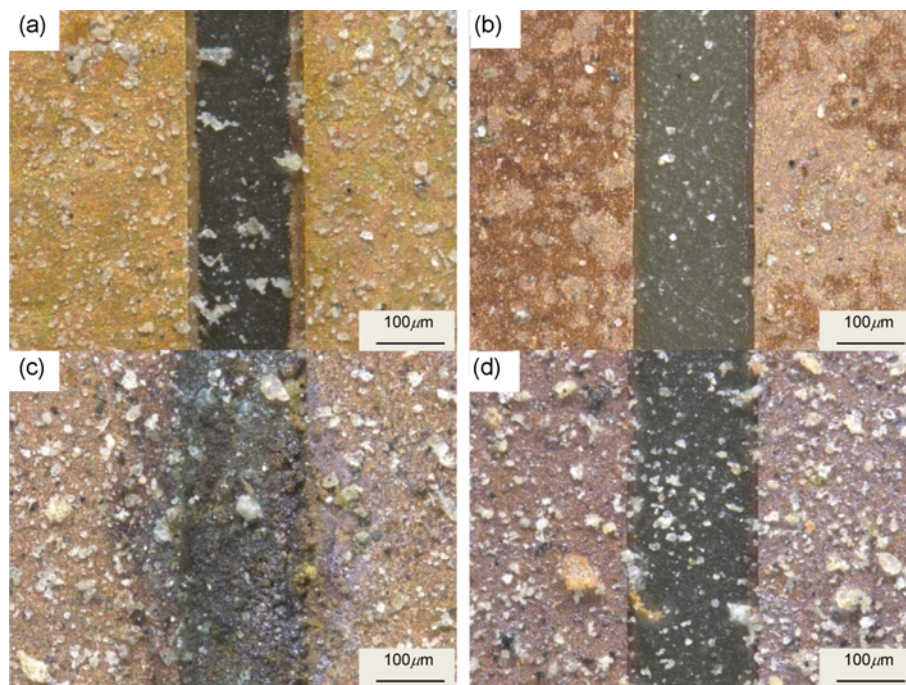
weather in Turpan was extremely warm. A large temperature difference exists between day and night, and condensation often occurs. This environment type can easily cause severe Cu oxidation. On the other hand, sandstorm weather frequently occurs in Turpan. The deposited dust particles containing  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$ , and other electrolytes exacerbated the corrosion process. The relatively dense  $\text{Cu}_2\text{O}$  film was gradually destroyed, resulting in the formation of porous corrosion products and reduced corrosion resistance. Given that the Beijing atmosphere contains much contaminated media, the outer surface of the  $\text{Cu}_2\text{O}$  film was gradually corroded and transformed to  $\text{Cu}_3\text{SO}_4(\text{OH})_4$ ,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ,  $\text{Cu}_2\text{NO}_3(\text{OH})_3$ , and other corrosion products,<sup>[5,8]</sup> thereby weakening the protective effect of the film on the substrate.

The atmospheric environment in Wuhan is similar to that in Beijing, but the evolution rule of  $R_{ct}$  relatively differs. Figure 7 shows that the  $R_{ct}$  of PCB-Cu in Wuhan remained low and did not change during the entire exposure period. This condition can be attributed to the sample surface, which was already covered with a thick film of corrosion products during the early exposure stage as a result of severe corrosion. The film also achieved a relatively stable structure. The dissolution and generation of the films of the oxide and/or corrosion product are in dynamic equilibrium. The morphology and corrosion rate ceased to significantly change with increasing exposure time.

Compared with the three other cities, the  $R_{ct}$  of the Xishuangbanna PCB-Cu sample showed a completely opposite trend. That is, corrosion gradually increased over time. The initial value of  $R_{ct}$  was low, which could be attributed to the corrosion reaction of the localized activated areas on the surface (Fig. 2b). Subsequently, the formation of a film with an effective electrolyte layer was difficult because of the slight air pollution in Xishuangbanna. The interfacial reaction resistance was relatively high, and the localized corrosion areas could not expand. Thus, the  $R_{ct}$  value increased. The corrosion resistance of the PCB-Cu samples exposed for 6 months was in the following order: Xishuangbanna > Wuhan = Turpan > Beijing. Given the corrosion morphology and severity of the actual atmospheric environment, PCB-Cu should be used in Xishuangbanna. The PCB-Cu corrosion in Beijing is currently less than that in Wuhan and Turpan. However, the corrosion process of the latter can be further exacerbated because of the low  $R_{ct}$  values. A relatively stable state similar to that of the Wuhan sample can be achieved because of the slow decrease of  $R_{ct}$ .

### 3.4 Effect of electrical bias on the ECM behavior

When the electrical bias was 12 V, the ECM behavior only occurred on the PCB-Cu samples in Beijing (Fig. 8). The edge region of the positive electrode plate was severely corroded, and the corrosion products migrated to the surface



**Fig. 8.** ECM corrosion morphology of PCB-Cu exposed outdoors for 6 months under the electrical bias of 12 V in (a) Turpan, (b) Xishuangbanna, (c) Beijing, and (d) Wuhan. Right, positive plate.

of the negative plate. This phenomenon caused a short circuit between the neighboring plates. This difference can be attributed to the different climate conditions in Beijing for the previous months, wherein the air had high humidity for a long period of time, with multiple thunderstorms during the late exposure stage (mainly in July and August). Severe corrosion occurred under the synergistic effect of humidity and gas pollutants. The distance between two neighboring plates at the ECM points decreased with further migration. This condition substantially increased the electric field strength and promoted ion migration between the two plates. By ranking the PCB-Cu samples according to their electrochemical corrosion tendency, the sample from Beijing was found to have most serious corrosion. By contrast, the corrosion in other areas was relatively weak. Overall, the tendency of PCB-Cu for ECM corrosion is generally low and requires the synergistic effect of high humidity and electrolyte ions.

#### 4. CONCLUSIONS

1. The surface potential was unevenly distributed in the PCB-Cu samples exposed outdoors. For samples in Turpan, Beijing, and Wuhan, localized corrosion occurred at the early stage and progressed into general corrosion with prolonged exposure. Corrosion was exacerbated by the synergistic effects of dust particles and contaminated media. The Xishuangbanna PCB-Cu sample was the least corroded,

and microbial corrosion was observed. The  $\text{Cu}_2\text{O}$  film on the PCB-Cu surface can be eroded by contaminated media, thereby losing its protective effect on the substrate.

2. Given an electrical bias of 12 V, the ECM corrosion tendency for PCB-Cu is relatively low and requires the synergistic effect of high humidity and electrolyte ions. According to the tendency for electrochemical corrosion of the PCB-Cu samples, corrosion is the most serious in Beijing but is relatively weak in other areas.

#### ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from National Basic Research Program of China (973 Program) (No. 2014CB643300) and the National Natural Science Foundation of China (No. 51271032). This work was also supported by the National Environmental Corrosion Platform.

#### REFERENCES

1. W. Y. Gen, X. Chen, A. M. Hu, and M. Li, *Microelectron. Reliab.* **51**, 866 (2011).
2. H. L. Huang, X. P. Guo, G. A. Zhang, and Z. H. Dong, *Corros. Sci.* **53**, 1700 (2011).
3. H. L. Huang, Z. H. Dong, Z. Y. Chen, and X. P. Guo, *Corros. Sci.* **53**, 1230 (2011).
4. R. P. B. Hernández, Z. Pászti, H. G. Mello, and I. V. Aoki,

- Corros. Sci.* **52**, 826 (2010).
5. C. Leygraf and T. Graedel, *Atmospheric Corrosion*, p. 152, Wiley and Sons, New York (2000).
  6. K. P. FitzGerald, J. Nairn, G. Skennerton, and A. Atrens, *Corros. Sci.* **48**, 2480 (2006).
  7. H. Strandberg, *Atmos. Environ.* **32**, 3511 (1998).
  8. H. Strandberg, *Atmos. Environ.* **32**, 3521 (1998).
  9. W. Wang, M. J. Huang, J. S. Zheng, K. C. Cheung, and M. H. Wong, *Sci. Total Environ.* **463**, 1201 (2013).
  10. C. A. C. Sequeira, *Brit. Corros. J.* **30**, 137 (1995).
  11. V. C. Noninski, *Electrochim. Acta* **42**, 251 (1997).
  12. J. Hu, C. F. Dong, X. G. Li, and K. Xiao, *J. Mater. Sci. Technol.* **26**, 355 (2010).
  13. T. E. Graedel, K. Nassau, and J. P. Franey, *Corros. Sci.* **27**, 639 (1987).
  14. S. P. Sharlna, *J. Electrochem. Soc.* **127**, 21 (1980).
  15. M. Rohwerder and F. Turcu, *Electrochim. Acta* **53**, 290 (2007).