



Study on the Friction Behaviors of Copper Nanowires in Ionic Liquids under External Voltages

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(Submitted April 17, 2020; in revised form July 22, 2020)

The effects of copper nanowires (Cu NWs) and ionic liquid (1-butyl-3-methylimidazolium perchlorate, in short [BMIM][ClO₄]) on the tribological properties of ionic liquid under external voltages were explored using friction tests in this paper. The results showed that the ionic liquid with 0.15 wt.% Cu NWs after 60 days exhibited better lubricating property at a low voltage of 0.5 V. The worn surfaces characterized by SEM and XPS illustrated that the existence of the Cu₂O could increase wear of friction pairs when Cu particles were oxidized. How the different forms of copper affect the lubrication of ionic liquid under external voltages were further discussed. This work provides a new thought of using metal ions to improve the lubrication performance of ionic liquids under external voltages.

Keywords copper nanowires, external voltages, ionic liquid, lubricating property

1. Introduction

Nowadays, with the development of electrification engineering, an increasing amount of electronic components are used in industry and our daily life, such as electrical switches, high-speed railways, electric cars and power transmission systems of public tram (Ref 1, 2). However, some questions are exposed in these fields. In these applications, the sliding electrical contacts play an essential role in transmitting electrical energy and signal. During the sliding process, wear performance of friction pairs is able to be improved by low tribological properties, low electrical conductivity of the contacting materials and high temperature at the interface. Besides, the electric erosion can also cause a series of wear behavior for friction pairs (Ref 3, 4). In the past decades, some researches have been conducted to explore the relationship between friction and electric charges at the micro-level (Ref 5), as well as the improved performance of sliding electrical contacts. These methods which are used to enhance the performance include lubricants, coatings and other innovative contact materials (Ref 1-4, 6-8).

At present, there are mainly two kinds of lubricants that are widely used in industrial circle: lubricating oil and grease. Conventional lubricants are mainly used to reduce wear and

friction, while under external voltages, electrical conductivity and thermal stability also take significant parts (Ref 2). Much work has been done to improve the lubrication properties of traditional lubricants. As a new type of lubricant, room temperature ionic liquids have excellent tribological properties and also possess extraordinary properties such as wide electrochemical window, non-volatility, thermal stability and high conductivity (Ref 9-14). In theory, all varieties of anions can function as ionic liquids, so there could be thousand kinds of ionic liquids (Ref 15, 16). Recently, several researches have showed that ionic liquids can be used as additives in lubricants, base oil to synthesize conductive lubricating grease and lubricating oil as well (Ref 17-20). Fan et al. synthesized three kinds of new conductive lubricating greases by using three kinds of ILs ([Li(PEG)]BF₄, [Li(PEG)]PF₆ and [Li(PEG)]NTf₂) as base oil and illustrated that the greases showed high conductivity and outstanding tribological properties due to the ion migration under an applied external voltage and the formation of boundary protective film (Ref 21). Additionally, in the work of Ge et al., lithium salts and organic solvents were mixed to obtain lithium-based ionic liquid greases, which can be used in lubricating steel contacts (Ref 22). In terms of lubricating oil, Cao et al. compared the tribological properties and electrical contact resistance in the case of electrification of multiply-alkylated cyclopentanes, 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate and proved that ILs can reduce the coefficients of friction (COF), electrical contact resistance (ECR) and wear volume, which can be attributed to the protective film generated on the worn surfaces (Ref 2). Considering the impact of different loads and current intensity, Huang et al. applied two normal loads of 1 and 5 N in the friction tests and discovered that ILs possessed excellent tribological properties whether under low- or high-load condition. They also found that the COF and contact resistance would vary with changing the strengths of applied current, and the breakdown of ion lubrication film at the contact interface may be the main reason for the phenomenon (Ref 3).

Meanwhile, some researches reported that additives in ILs can effectively improve the lubricating properties. Recently, He et al. dispersed modified graphene oxide (MGO) into

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hydrophobic IL and prepared stable colloidal suspension as a lubricant. They found that the proper concentration of MGO could reduce COF value efficiently and discovered that the lubricant obtained better lubricity than pure IL (Ref 23). On the other hand, nanoparticles are frequently explored as additives in this field. Vinay Sharma et al. mixed modified polytetrafluoroethylene (PTFE) nanoparticles with IL, and the friction tests showed a low COF, for the PTFE nanoparticles produced small amount of fluorine and silicon chemistry in the transfer film which was formed during friction, in conjunction with the ILs facilitated lubrication (Ref 24). As for the electrical conductivity of ILs with additives, by adding copper or silver nanoparticles with excellent current conduction capacity to IL and polyalphaolefin (PAO), respectively, metallic nanoparticles in IL could reduce the electrocorrosion phenomenon and enhance the rolling effects of particles in the contact area, and promote electrical conductivity and lubrication characteristics at the same time (Ref 25, 26), while neither the reaction between metal nanoparticles and IL, nor the properties of the mixture after reaction have been observed.

In the present work, Cu NWs with different contents were added into [BMIM] [ClO₄]. The electrical conductivity and lubrication performance were evaluated under external voltages of the lubricants. Since Cu NWs would react with the anion of IL along with time, the tribological properties of the lubricants at different periods were also assessed. Moreover, the friction under different voltage directions and loads was also studied.

2. Experimental Details

2.1 Materials

The additive in this study was Cu NWs (diameter 50-200 nm; length 10-30 μm ; concentration 10 mg mL⁻¹; solvent ethanol), purchased from Suzhan intelligent technology co. LTD (Nanjing, China). The appearance of Cu NWs was observed by FEI Quanta 450 scanning electron microscopy (SEM) at an operating voltage of 30 kV. Figure 1 shows the characteristics of Cu NWs. The chosen ionic liquid is 1-butyl-3-methylimidazolium perchlorate ([BMIM] [ClO₄], 99%), purchased from Zhongke ketko trade Co., Ltd (Lanzhou, China). Table 1 gives the physical properties of the ionic liquid.

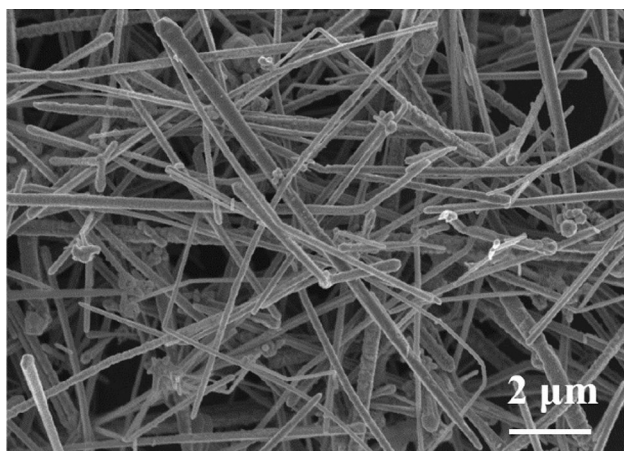


Fig. 1 SEM morphology of the Cu NWs

Firstly, the Cu NWs dispersion liquid was ultrasonically treated for 3 min, and the dispersion liquid of 510 μL , 1020 μL and 1530 μL was then dissolved into 3 mL [BMIM] [ClO₄]. After 5 min of stirring, the mixed solution was ultrasonically treated for 5 min. Then, ionic liquid and Cu NWs mixture solutions with different concentrations were prepared (0.15, 0.3 and 0.45 wt.%). Each solution was placed at a temperature of 28 °C for 10 min to remove ethanol, then poured into an Eppendorf tube and kept sealed for the tests. After friction tests, the samples were stored under seal and shading at room temperature for 60 days, and the tests were repeated. Considering [BMIM] [ClO₄] can be stored stably at room temperature, the test was omitted.

2.2 Characterization of the Lubricants

The lubricant molecular structure was analyzed using FTIR spectra (NICOLET6700, Thermo Scientific, USA). The scattering frequency of each spectrum was 15 times s⁻¹. The thermogravimetric analysis (TGA) of the lubricants was performed using a Q500 TGA (TA instruments) at a heating rate of 10 °C min⁻¹ in nitrogen atmosphere. The contact resistance of friction process was analyzed using the electrochemical workstation (CHI600E, Shanghai Chenchua, China). The conductivity was tested by conductivity meter CT-3031 (Aipu instrument; Zhejiang, China; resolution ratio 0.01 mS cm⁻¹).

2.3 Friction Test under External Voltages

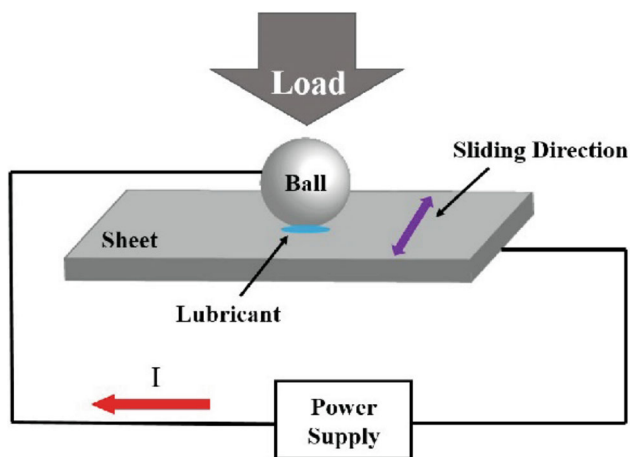
The tribological behaviors were tested using the CETR tribometer (UMT-3 model by CETR Corporation Ltd, USA) under room temperature, and COF values were recorded automatically by the tester. Figure 2 shows a schematic diagram of the experimental device. Electrochemical workstation was used as a DC supply to provide a stable voltage and feedback current in real time. The values of the voltage on the lubricant were difficult to determine during the tests and hence the resistances of the ball, stainless sheet and the contact area regarded as variables. Since the resistances of the ball and sheet are constant, the resistance change can be considered to be caused by the contact area. And the change of resistance in the friction process was reflected by the change of real-time current. Ohm's law was used to calculate the change of resistance. The steel ball with a diameter of 4 mm slides reciprocally against the lower steel sheet (20 mm \times 20 mm; 304 stainless steel polished to mirror) at an amplitude of 5 mm, a frequency of 2 Hz and a load of 5/15 N at the applied voltage of 0, 0.5, 1.5 and 3 V. The balls and sheets were ultrasonically washed with ethanol for 10 min before each test, and then, about 100 μL lubricant was introduced into the friction contact area.

2.4 Analysis of Wear Surface

After friction tests, each sheet was ultrasonically washed in ethanol for 10 min. The wear volume was observed by MicroXAM 3D surface mapping microscopy profile meter. The morphology of wear area was characterized by SEM, and the chemical states of the characteristic elements on the worn surfaces were analyzed by the x-ray photoelectron spectroscopy (XPS; K-Alpha; Thermo Fisher Scientific Inc.). Monochromatic Al-K α radiation (1486.6 eV) was used as the x-ray source. The spectra were calibrated by setting the measured

Table 1 Physical properties of IL (Ref 27)

	Melting point, °C	Viscosity, mPa s ⁻¹	Density, g cm ⁻³	Conductivity, mS cm ⁻¹	Electrochemical window, V	Decomposition temperature, °C
[BMIM] [ClO ₄]	- 78	47.5	1.26	1.8	3.6	320

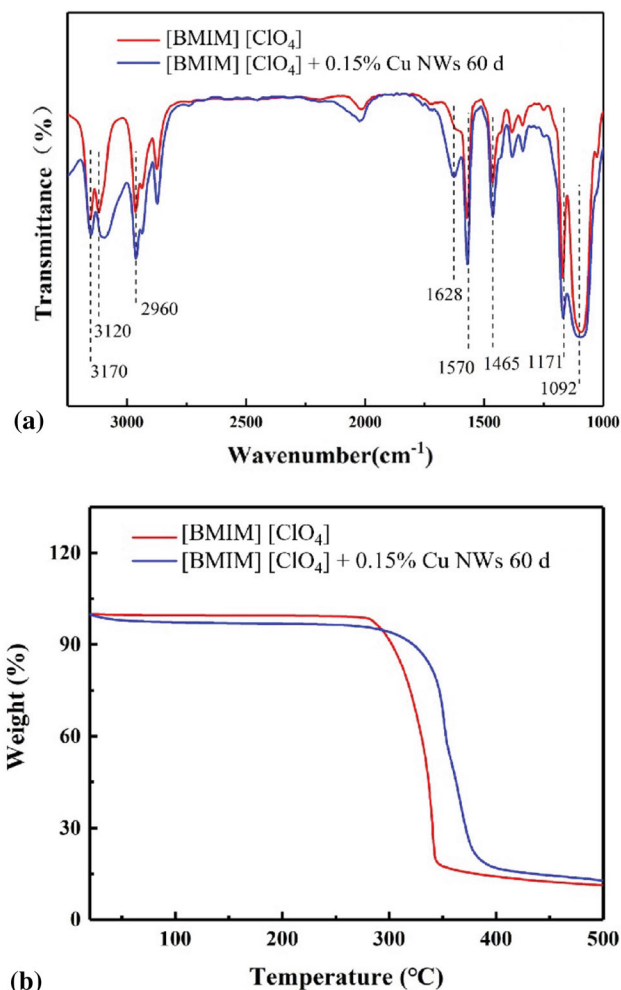
**Fig. 2** Schematic diagram of experimental device

binding energy of the C1s peak of adventitious carbon accumulated in the analysis chamber of the spectrometer to 284.6 eV.

3. Results and Discussion

3.1 Physicochemical Properties of the Lubricants

Figure 3(a) shows the FTIR curves of the lubricants. The peaks at 1092 cm⁻¹ are originated from C-H bands, and the peaks at 1171 cm⁻¹ are due to the bending vibration of imidazole ring. The transmittance bands at 1465 and 1570 cm⁻¹ represent the C-N bands of imidazole ring. The peaks at 2960 cm⁻¹ correspond to the N=C stretch vibrations, and peaks at 3170 cm⁻¹ belong to the H-C-C-H asymmetric stretch vibrations (Ref 28, 29). However, the extra peak at 1628 cm⁻¹ of [BMIM] [ClO₄] + 0.15 wt.% Cu NWs after 60 days and the peak at 3120 cm⁻¹ of [BMIM] [ClO₄] were redshifted, which might be attributed to the hydrogen bond vibrations caused by cupric ion in the lubricant. Figure 3(b) presents the TGA curves of the lubricants. The decomposition temperature of the lubricants is all higher than 250 °C, demonstrating that the lubricants have excellent thermal stability. Table 2 shows the conductivity of the lubricants under 24 °C. Among the fresh mixtures, the conductivity improved with the increase in Cu NWs. However, compared with other mixtures after 60 days, the conductivity of IL mixed with 0.3 wt.% Cu NWs was the lowest. It is because the excellent conductivity of Cu promoted the conductivity of fresh lubricants. As time goes on, a small amount of Cu NWs was converted into Cu²⁺ by electrochemical reaction, which is stable in solution, improved the electrical

**Fig. 3** FTIR and TGA curves of [BMIM] [ClO₄] and [BMIM] [ClO₄] + 0.45 wt.% Cu NWs after 60 days

conductivity of the lubricants. However, with the increase in Cu NWs in IL, also a part of Cu was oxidized to CuO, leading to the decrease in conductivity. The lubricant of IL + 0.15 wt.% Cu NWs appeared to be light green and there was no precipitation, which inferred that Cu²⁺ was formed. Cu²⁺ has significantly improved electrical conductivity in the solution. Meanwhile, dark green deposits were observed in the IL + 0.45 wt.% Cu NWs after 60 days, for it is a mixture of cupric ion and copper oxide, and the IL + 0.3 wt.% Cu NWs after 60 days showed black and red with visible deposits, meaning most of the copper has been converted to copper oxide. Because of the poor conductivity of copper oxide, the above two exhibited lower conductivity than before.

Table 2 Conductivity of the lubricants under 24 °C

Sample	[BMIM] [ClO ₄]	IL + 0.15 wt.% Cu NWs	IL + 0.3 wt.% Cu NWs	IL + 0.45 wt.% Cu NWs	IL + 0.15 wt.% Cu NWs after 60d	IL + 0.3 wt.% Cu NWs after 60d	IL + 0.45 wt.% Cu NWs after 60d
Conductivity, mS cm ⁻¹	1.83	7.34	9.36	15.54	18.62	5.73	8.56

3.2 Tribological and Electrical Properties of the Lubricants under External Voltages

In this work, the effect of changing load and current direction was also investigated. Larger loads reduce current fluctuations, which lead to different current flow and wear from lower loads. Also, different current directions can cause complex changes of lubricant film (Ref 30, 31). Based on the reasons above, the tribology performance was tested under the condition of 15 N load or the opposite current direction. In the tests, set the ball as positive electrode and the sheet as negative electrode.

Figure 4(a) shows the average COFs of the lubricants under a load of 5 N and voltages varying from 0.5 V to 3.0 V. It can be seen that Cu NWs as additives can reduce the COF efficiently. But at a low voltage intensity (0.5 V), all lubricants presented the most excellent reduced friction performance, and [BMIM] [ClO₄] without additives had the lowest COF of 0.097. With increase in voltage, COFs also increased gradually. Under the same condition of high voltage, [BMIM] [ClO₄] + 0.3 wt.% Cu NWs exhibited the lowest friction coefficient compared with other lubricants. Herein, choose the situation at 0.5 V and 5 N as typical object. The average corresponding contact resistances of the lubricants during the friction process are shown in Fig. 4(b). It is clear that the values of contact resistances have little differences, which might be attributed to the low voltage and various electrical losses caused by incomplete contact in the process of friction, so that the conductivity of the Cu NWs has not been brought into play adequately. Figure 4(c) shows the average wear volumes of the stainless steel sheets, illustrating 0.3 wt.% Cu NWs could lower wear volume significantly, performing a better anti-wear ability. This might be attributed to the increase in Cu NWs in the IL; the sliding of copper at the friction interface reduced the friction and wear. While when the copper content increased to some value (0.45 wt.% Cu NWs addition), the Cu NWs began to agglomerate on the worn surface and a path was formed under external voltage, pits formed on the surface due to electrochemical corrosion, leading to the increase in wear.

Figure 4(d) presents the average COFs of the lubricants under a load of 5 N and voltages varying from 0.5 to 3.0 V after 60 days. By a sharp contrast with the initial mixture, the ionic liquid with 0.15 wt.% Cu NWs after 60 days performs very low COF at all voltages, and it keeps relatively stable, while voltage changes. Instead, [BMIM] [ClO₄] + 0.3 wt.% Cu NWs always exhibited the highest COF, which is totally different from the COF before. According to the average value of all COF curves, it can be seen that when the voltage increases, the tendency of COF curves will not change over time. Figure 4(e) shows the average resistance of the lubricants at 0.5 V and a load of 5 N. Different from Fig. 4(b), there is a significant difference in resistances, and the highest resistance is obtained by the ionic liquid with a Cu NWs content of 0.3 wt.%.

Figure 4(f) shows the wear volumes of the sheets, which illustrated that after 60 days, 0.3 wt.% Cu NWs in [BMIM] [ClO₄] could lead to a worse lubrication effect, while both the pure [BMIM] [ClO₄] and [BMIM] [ClO₄] with 0.15 wt.% Cu NWs possess a very low wear volume loss.

In order to further explore the effect of different loads on friction, tests under a load of 15 N were also investigated. Figure 5(a) and (b) presents the COF curves of [BMIM] [ClO₄] with 0.15 wt.% Cu NWs after 60 days at voltages of 0 and 0.5 V and loads of 5 and 15 N. It can be seen clearly that there is a COF-fluctuation during the wear process at 0.5 V voltage condition, and the range of COF-fluctuation was reduced with the increase in applied load. Moreover, there is a slight reduction of COF under larger load. It is noted that even if load increased in a sudden, the contact area would not increase dramatically, as there exists a proportional increase relationship between the contact area and the cube root of the load. But friction force is proportional to the contact area, which means that friction force would not increase with a sudden augment in load (Ref 32). According to the formula of COF, $\mu = f/F$ (μ refers to COF, f refers to the frictional force, and F refers to the load), it can be easily proved that under the same external voltage, a larger load tends to cause rise to a lower COF.

The friction phenomena of exchanging voltage directions were also investigated. It can be seen in Fig. 5(c) that negative voltage (current flows from the sheet to the ball) could cause a fluctuation of the COF curve, proving that it was not stable during the friction process. Besides, the COF at negative voltage is higher than that at positive, as one of the average COFs is 0.113 and the other is 0.096. The main reason for the COF difference relates to different electrocorrosion that occurred on the friction pairs. When applying negative voltages, lots of positive charges concentrated on the stainless steel sheet. With the electrochemical reaction between lubricant and the sheet, the constant anodic dissolution could aggravate corrosion on the worn surface (Ref 26).

3.3 Analysis of the Worn Surface

Figure 6 shows the SEM images of the worn surfaces on the stainless sheets to further explore the tribological properties of [BMIM] [ClO₄] with different Cu NWs contents and after different days. As shown in Fig. 6(a) and (b), the worn surfaces lubricated by pure [BMIM] [ClO₄] and [BMIM] [ClO₄] with 0.15 wt.% Cu NWs acquired a few wide furrows and shallow denudation. Because of the agglomeration of a small amount of Cu NWs, in Fig. 6(b) delamination can be also seen, and the furrows are clearer than that in Fig. 6(a). The worn surface lubricated by [BMIM] [ClO₄] with 0.3 wt.% Cu NWs in Fig. 6(c) is quite smooth with narrow scratch lines parallel to the sliding direction, but there still exists a spot of delamination and pitting corrosion pits. When lubricated by [BMIM] [ClO₄] with 0.45 wt.% Cu NWs (Fig. 6d), some furrows remain on the

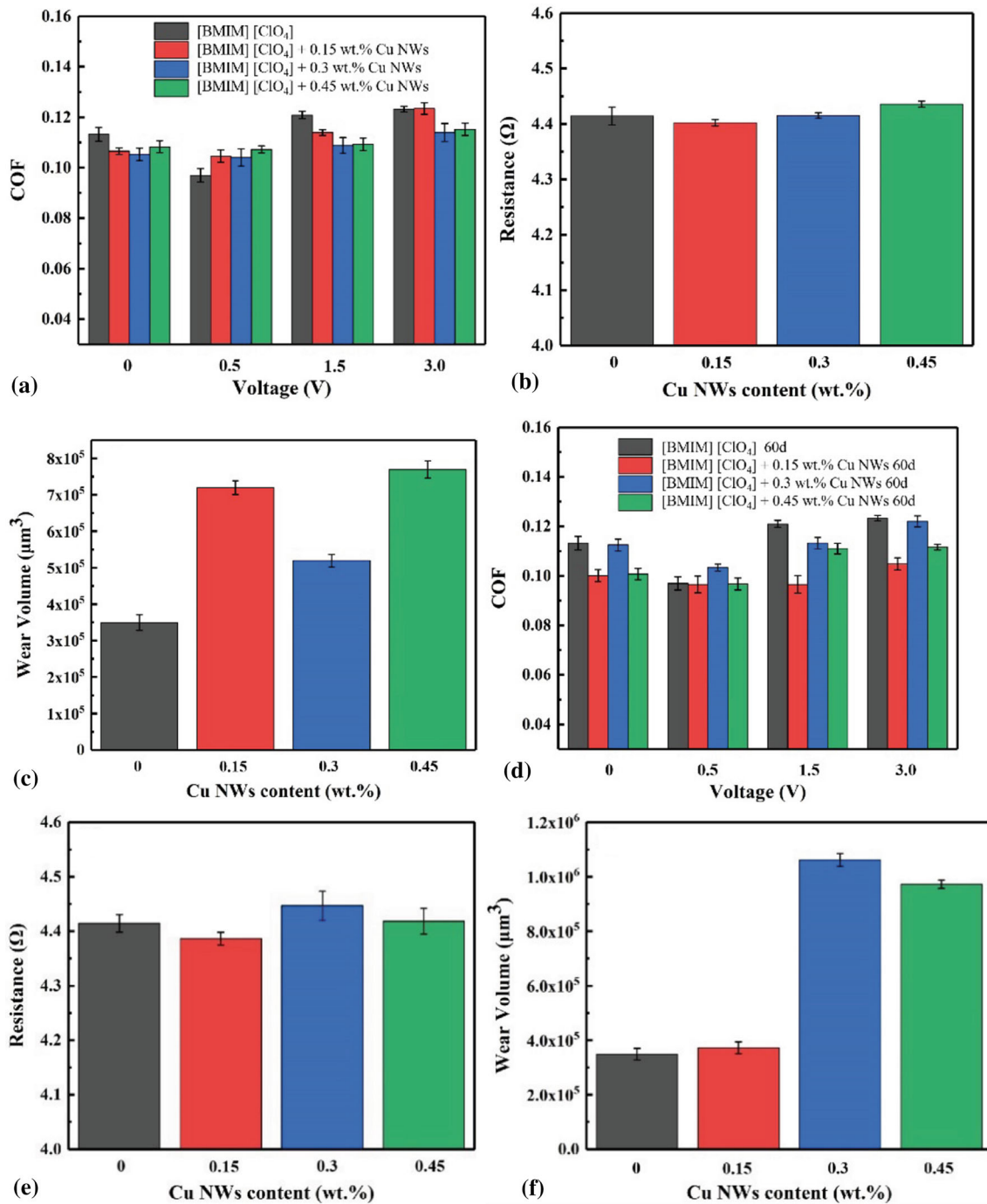


Fig. 4 The tribological properties of ionic liquid with different contents of Cu NWs and conductivity behaviors under a load of 5 N, (a), (b), (c): the initial mixed lubricants; (d), (e), (f): the lubricants after 60 days. (a), (d): the average COFs; (b), (e): the average resistances at 0.5 V; (c), (f): the average wear volumes at 0.5 V

worn surface and even deep cracks appeared on the worn surface due to the high content of Cu NWs; meanwhile, a lot of pitting corrosion pits appeared. The Cu NWs under current condition and IL environment caused electrochemical corrosion on the stainless steel sheets, which can explain the emergence of pitting corrosion pits. Compared with others, the worn surface lubricated by [BMIM] [ClO₄] with 0.15 wt.% Cu NWs after 60 days in Fig. 6(e) behaves smoother and the wear width was reduced, suggesting an outstanding anti-wear ability. On the contrary, when lubricated by [BMIM] [ClO₄] with 0.3 wt.%

Cu NWs after 60 days (Fig. 6f), the worn surface appeared more wide furrows; in addition, delamination can be observed at the edge of furrows. The characteristics prove that large particles once were generated at the surface and contributed to more serious wear, which is corresponding to the wear volume in Fig. 4(f). In Fig. 6(g), which was lubricated by [BMIM] [ClO₄] with 0.45 wt.% Cu NWs after 60 days, the edges of the abrasions are uneven, because a small amount of Cu₂O in the lubricant, and denudation also exists on the surface. Besides, deep spots can be observed on the worn surfaces as shown in

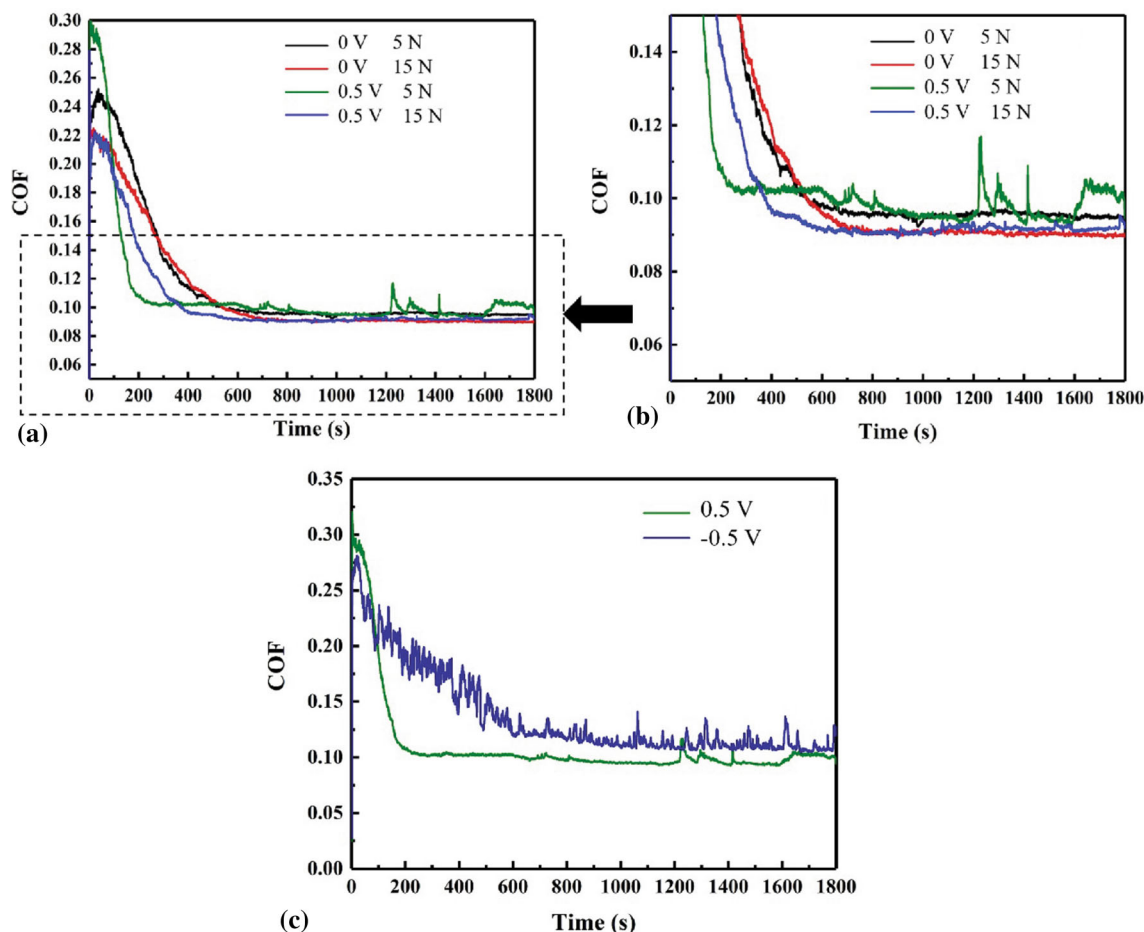


Fig. 5 The COF curves of [BMIM] [ClO₄] with 0.15 wt.% Cu NWs after 60 days under different conditions. (a): under 5/15 N and 0/0.5 V; (b): partial enlarged view of (a); (c): under 5 N and different voltage directions

Fig. 6(e), (f) and (g), which might be caused by a weak electrochemical corrosion.

Because the [BMIM] [ClO₄] with contents of 0.15 wt.% Cu NWs and 0.3 wt.% Cu NWs after 60 days obtained the lowest and highest COF, XPS measurements were taken to detect the chemical states of the characteristics elements including C1s, Cl2p, Cu2p3, Fe2p3, O1s and N1s on the worn surfaces lubricated by them and pure [BMIM] [ClO₄]. Figure 7(a) shows the photoelectron peaks of element C. The corresponding binding energy is 284.6 eV, which is identified as the carbon in air and is used as the reference. Figure 7(b) presents the XPS spectra of Cl2p on the worn surfaces and the peaks are at 198.7 eV, which is attributable to metal chloride. As shown in Fig. 7(c) and (d), the XPS of Cu2p3 has a strong and symmetrical peak at 932.6 eV when lubricated by [BMIM] [ClO₄] with 0.3 wt.% Cu NWs after 60 days, illustrating that Cu₂O occurred on the worn surface (Ref 33). But there is no obvious peak of Cu on the worn surfaces when lubricated by [BMIM] [ClO₄] and [BMIM] [ClO₄] with 0.15 wt.% Cu NWs after 60 days. This can be attributed to that no Cu was introduced when [BMIM] [ClO₄] was used as lubrication. As for the one lubricated by [BMIM] [ClO₄] with 0.15 wt.% Cu NWs after 60 days, the result indicates that Cu ion did not react with the elements on the stainless sheet during the friction process. There are two main peaks in the spectra shown in Fig. 7(e), the peaks at 706.7 eV are attributed to the metallic

iron in the stainless sheets, and the strong peaks at 710.8 eV are from Fe₂O₃ and FeCl₃ (Ref 22). The binding energies of N1s appeared at 398.4 eV may belong to carbon–nitrogen bond compounds (Ref 34), as shown in Fig. 7(f). In Fig. 7(g), O1s possesses two peaks in the spectra: the one at 529.6 eV is assigned to iron oxides, and the other one at 531.3 eV can be assigned to C–O bonding (Ref 22, 31). The XPS analysis indicated that complex tribochemical reactions and physical adsorption produced films between the sliding surfaces, which plays a role in promoting or inhibiting lubrication properties and conductivity.

As shown in Fig. 4(a) and (d), when voltage exceeds 1.0 V, a high voltage could lead to the deterioration of the lubricants and the poor worn behaviours. Therefore, the lower voltage could contribute to the decrease of COF value (Ref 35). At the same voltage of 0.5 V, [BMIM] [ClO₄] with 0.3 wt.% Cu NWs exhibited the similar COF with pure [BMIM] [ClO₄] initially. But the four kinds of lubricants presented the similar resistance, which is totally different from the measured value in Table 2. This is partly owing to the partial voltage in the circuit, and once a conductive lubrication film was formed, the rolling of Cu particles and abrasive dust on the worn surfaces would destroy it, made it hard to transport current. After 60 days, it can be inferred that 0.15 wt.% Cu NWs have totally dissolved in [BMIM] [ClO₄] because there is no sediment in the lubricant; thus, the grinding cracks are relatively smooth. At

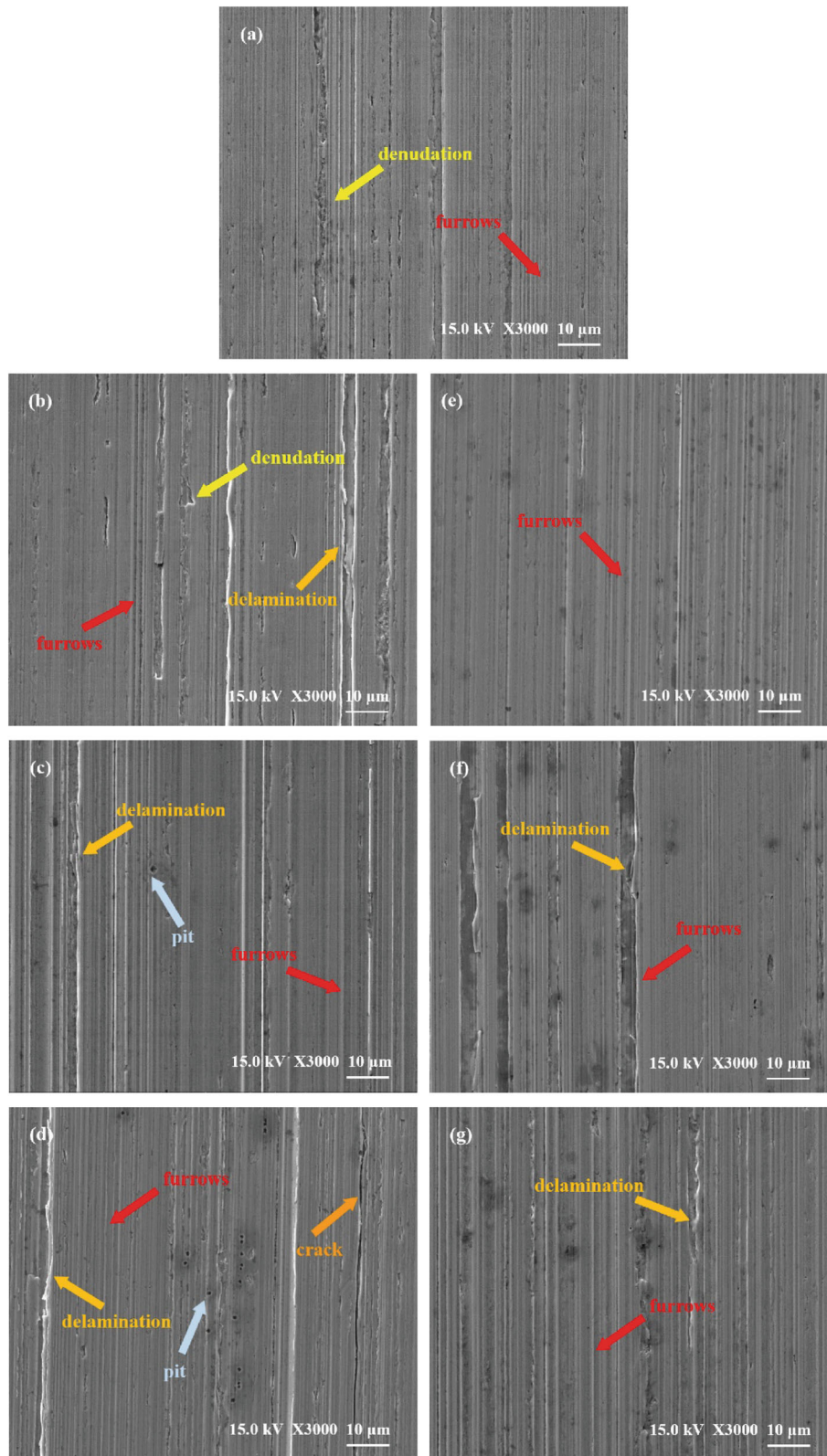


Fig. 6 SEM images of the worn surfaces on the stainless sheets lubricated by (a) [BMIM] [ClO₄], (b) [BMIM] [ClO₄] with 0.15 wt.% Cu NWs, (c) [BMIM] [ClO₄] with 0.3 wt.% Cu NWs, (d) [BMIM] [ClO₄] with 0.45 wt.% Cu NWs, (e) [BMIM] [ClO₄] with 0.15 wt.% Cu NWs after 60 days, (f) [BMIM] [ClO₄] with 0.3 wt.% Cu NWs after 60 days, (g) [BMIM] [ClO₄] with 0.45 wt.% Cu NWs after 60 days under a load of 5 N and a voltage of 0.5 V

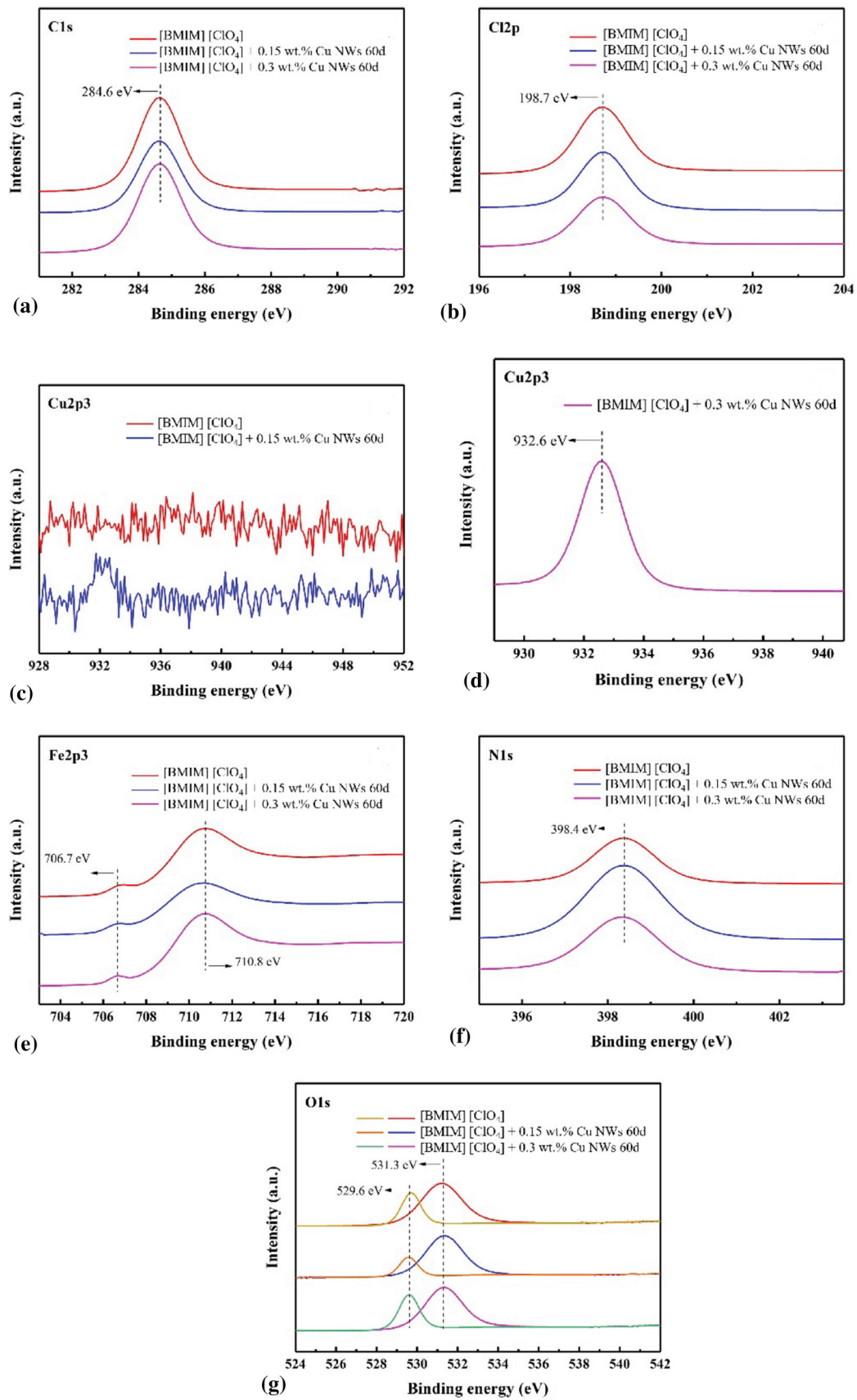


Fig. 7 X-ray photoelectron spectra of the elements (C1s, Cl2p, Cu2p₃, Fe2p₃, N1s and O1s) on the worn surfaces under a load of 5 N and a voltage of 0.5 V

this point, the lubrication film formed on the friction surface was mainly produced by FeCl_3 and Fe_2O_3 , which decreased COF and wear volume. As far as the conductive ability is concerned, based on the excellent conductivity of [BMIM] $[\text{ClO}_4]$ itself, Cu^{2+} produced by the reaction of copper with IL and Fe^{3+} produced on the worn surface, all play an important role in improving the conductivity in the friction process, leading to a lower resistance ultimately. The opposite is the [BMIM] $[\text{ClO}_4]$ with 0.3 wt.% Cu NWs after 60 days, Cu NWs were oxidized to CuO, and CuO converted to Cu_2O under the high temperature during the friction process, Cu_2O particles and abrasive dust assembled at the frictional contact area caused severe abrasive wear, leading to the high COF and wear volumes. Besides, Cu_2O conducts electricity poorly; thus, the resistance is higher than that of other lubricants, as shown in Fig. 4(e). Thermal energy caused by high resistance resulted in the fusion and gasification, which caused erosion pits and massive spalling on the worn surface, basically consistent with the results in Fig. 6(f) and 7(d) (Ref 36).

The experimental characterizations suggest that the lubricants presented different lubricity and conductivity, which is attributed to the contents and forms of Cu NWs in the lubricants. Herein, the conductive and lubrication mechanisms was further discussed. As shown in Fig. 4, when no electric current passed through, the sliding of copper at the friction interface reduced the friction and wear. When voltage was applied, the polarities on the friction pairs were different, leading to the result that different kinds of ion were absorbed. The anions and cations can arrange into ion adsorption layer near the interface, which could avoid the direct contact of rough surfaces and improve the tribological properties efficiently (Ref 37-41). When Cu NWs were introduced in the IL, the adsorption film formed under low voltage was vulnerable and easily damaged due to the rolling of Cu NWs, resulted in the COFs higher than that of pure IL lubricated. As the voltage further increased, the formed oil film was broken by the high voltages, leading to the COF increase of IL and IL with low content of Cu NWs. For the IL reacted completely with 0.15 wt.% Cu NWs after 60 days, the increase in ions made it easier to form a denser adsorption film, resulting in the low COF and resistance. When the load increased, the friction pairs contact closer, and the attraction between the ions makes the resulting oil film less vulnerable to be destructed. In addition, when the direction of voltage was changed, the anodic dissolution on the sheet would be more serious, which accelerated the corrosion of the sheet, increased the COF and caused obvious fluctuation during the friction process (Ref 26).

4. Conclusions

In this study, [BMIM] $[\text{ClO}_4]$ mixed with Cu NWs was used as lubricant. The physical and chemical properties of the lubricants were characterized, and a series of tribology tests have been carried to investigate the tribological behaviors of the lubricants under external voltages. Due to the different forms of Cu in the lubricants, the tribology tests showed different results. According to the SEM and XPS results of the worn surfaces, the possible lubrication mechanism was proposed. The conclusions are summarized as follows:

1. Cu NWs would react with [BMIM] $[\text{ClO}_4]$, and different products would be produced depending on the reaction days. Due to that Cu^{2+} has come into the mixture, [BMIM] $[\text{ClO}_4]$ with 0.15 wt.% Cu NWs after 60 days showed the best tribology property and conductivity.
2. When low voltages or large loads were applied, the lubricants showed better lubricating properties.
3. [BMIM] $[\text{ClO}_4]$ mixed with 0.3 wt.% Cu NWs initially could present better tribology property than pure [BMIM] $[\text{ClO}_4]$, but because the reaction is incomplete after 60 days, the Cu_2O particles produced in the lubricant aggravated the wear of the materials.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 41872183, 51775044), the Pre-Research Program in National 13th Five-Year Plan (Grant No. 61409230603) and the Fundamental Research Funds for Central Universities (Grant No. 2652018095).

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