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PAPER

Dramatically improved friction reduction and wear resistance by *in situ* formed ionic liquids

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A new concept of *in situ* preparing ionic liquid (IL) lubricant additives is described in the present work. It was found that IL additives, [Li(PEG)]X, could be obtained simply by adding lithium salts (LiX) to the base oil (PEG). The *in situ* formed ILs have extremely good solubility in PEG and exhibit excellent friction-reducing and anti-wear properties for the lubrication of steel/steel contacts. The tribological properties are even more effective than those of conventional ILs such as 1-ethyl-3-methyl imidazolium tetrafluoroborate (L-B102), 1-methyl-3-hexylimidazolium hexafluorophosphate (L-P106) and 1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide (L-F102). The easy preparation, extremely good solubility and excellent tribological properties of [Li(PEG)]X have great advantages as compared with conventional ILs, which will undoubtedly lower the cost of IL preparation and provide a completely new strategy of industrial application of ILs.

Introduction

Friction consumes a large portion of energy. Lubrication is employed in order to improve fuel efficiency and prevent wear of components in motion, and plays an important role in energy saving and low carbon emissions. Ionic liquids (ILs) have been long established as versatile lubricants, in addition to their widespread applications in various areas.[1–10] A variety of ILs have been synthesized and tested for tribological uses.[11–15] Normally, the preparation of ILs needs comparatively complex synthetic, metathesis and separation procedures, which adds more cost for their practical application. It is of vital importance, especially after ten years' extensive studies on ILs lubricants, to find simpler and cheaper ways to put them into real applications. It is already known that Li^+ can form complexes with oligoethers, such as crown ether, triglyme (G3), and tetraglyme (G4),[16–20] generating (by the donation of the lone pairs on the oxygen of an oligoether molecule to Li^+) a weakly Lewis acidic complex cation $[Li(oligoether)]^+$, which can form ILs ([Li(oligoether)]TFSI) with the weakly Lewis-basic anion ($TFSI^-$) of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and exhibit similar physicochemical properties to those of conventional ILs.[21] These ILs are extremely easy to prepare and even can be formed *in situ* only by dissolving LiTFSI in oligoethers, so that they can compete with conventional ILs as potential lubricants.[22–25] However, the concept of using *in situ* formed ILs as lubricants has not been proposed to date. In our experiment, a series of lithium salts were found to be excellent lubricant additives for polyethylene glycol (PEG) *via* the *in situ* formation of ILs ([Li(PEG)]X). The friction-reducing and anti-wear properties of these salts are even better than those of conventional ILs such as 1-ethyl-3-methyl imidazolium tetrafluoroborate (L-B102), 1-methyl-3-hexylimidazolium hexafluorophosphate (L-P106) and 1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide (L-F102). In addition, the *in situ* formed ILs dramatically enhanced the thermal stability of PEG, making the strategy attractive for practical applications.

Experimental

Chemicals. The following reagents and materials were used as received: LiTFSI, $LiBF_4$, $NaBF_4$, KBF_4, $LiPF_6$, $NaPF_6$, KPF_6, $LiSO_3CF_3$, $NaSO_3CF_3$, KSO_3CF_3, $LiSO_3(CF_2)_7CF_3$, (J&K Scientific LTD.), PEG (Sinopharm Chemical reagent Co. Ltd, the average molecular weight is 190–210 g mol^{-1}). The lubricants were prepared by stirring special amount of salts in PEG at room temperature (RT) until it was totally dissolved. L-B102, L-P106 and L-F102 were synthesized according to the literature.[26] All the other chemicals used in the synthesis were of AR grade.

Viscosity and copper strip test. The kinematic viscosity of the lubricants was carried out on a SYP1003-III viscometer at 40 °C and 100 °C, respectively. The copper strip test was performed using the GB-T5096-1985 (91) procedure. A piece of bright-finish copper was immersed within a certain amount of specimen. This was heated at 100 °C for 3 h. At the end of the test, the copper was taken out and washed for comparison with the corrosion standard tint board.

Thermal analysis. The thermal behavior of the samples was carried out on an STA 449 C Jupiter simultaneous TGDSC. The temperature was programmed to increase from the initial

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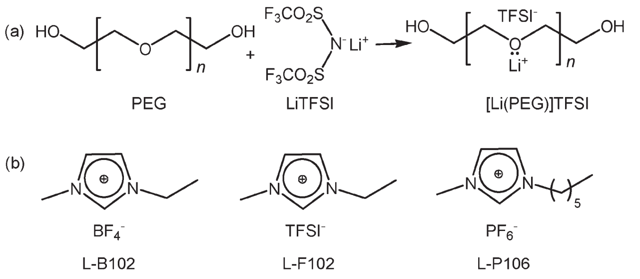

Fig. 1 The formation of [Li(PEG)]TFSI (a) and the chemical structures of L-B102, L-P106 and L-F102 (b).

temperature of 20 °C to approximately 500 °C, at a rate of 10 °C min^{-1} in air. The weight loss and heat flow values were monitored in the TG-DSC analysis.

Friction and wear test. The friction and wear tests were carried out on an Optimol SRV-IV oscillating reciprocating friction and wear tester. The contact between the frictional pair was achieved by pressing the upper running ball against the lower stationary disk which was driven to reciprocate at a given frequency and displacement. The upper ball is AISI 52100 steel with 10 mm diameter and approximately 61–64HRC hardness. The lower stationary disk is AISI52100 steel with Φ24 mm × 7.9 mm and hardness of approximately 61–64HRC hardness. The friction and wear tests in this work were conducted at an amplitude of 1 mm and a frequency of 25 Hz. The relative humidity was 20–50%. The wear volume of the lower disk was measured by a MicroXAM 3D noncontact surface mapping profiler.

The morphology of the worn surfaces was analyzed by a JSM-5600LV scanning electron microscope (SEM). The X-ray photoelectron spectrometer (XPS) analysis was carried out on a PHI-5702 multifunctional XPS using Al Ka radiation as the exciting source. The samples were ultrasonically rinsed three times with in ethanol before use. The binding energy of the target elements was determined at a pass energy of 29.35 eV with a resolution of about ± 0.3 eV. The binding energy of contaminated carbon (C1s: 284.6 eV) was used as the reference.

Results and discussion

Firstly, LiTFSI was used as an example compound to investigate the *in situ* formation of the ILs. The proposed chemical structure of [Li(PEG)]TFSI and structures of L-B102, L-P106, L-F102 are listed in Fig. 1. LiTFSI was found to have extremely good solubility in PEG (>50 wt%, concentrations higher than 50 wt% were not tested). Even when stored below −20 °C for several days, no LiTFSI salt would precipitate from the mixture of 50 wt% LiTFSI in PEG. The two important parameters of the lubricants, kinematic viscosity and viscosity index, are shown in Table 1. The viscosity of PEG increases slightly both at 40 °C and at 100 °C with the addition of LiTFSI. This can be explained by the *in situ* formation of [Li(PEG)]TFSI and that some of the free PEG molecules are sluggish or hindered altogether, resulting in the viscosity increase.[27] The increase in viscosity index indicates the enhancement of the viscosity–temperature characteristics of the base oil. In addition, it will not change the corrosion grade of the base oil according to the copper strip corrosion test (Table 1). Moreover, thermal analysis (DSC) verifies that addition of LiTFSI significantly increases the decomposition temperature of PEG as shown in Fig. 2 and Table 2, indicating the enhancement of the thermal oxidation stability of the base lubricating oil.[28] For example, the temperature for 50 wt% weight loss of PEG increases dramatically from 208.3 °C to 367.6 °C for 50 wt% LiTFSI-added PEG. Besides, the thermal stability curve of 50 wt% LiTFSI-added PEG can be divided into three steps. The first step (between about 200–250 °C) is the evaporation of free PEG molecules from the mixture and the second step (between about 250–400 °C) is the removal of PEG molecules from [Li(PEG)]TFSI. At temperatures higher than 400 °C, the decomposition of LiTFSI takes place. This thermal stability test further confirms the formation of ILs ([Li(PEG)]TFSI) in the mixture of PEG and LiTFSI.[21]

The tribological properties of PEG with different concentrations of LiTFSI were firstly tested. The coefficient of friction (COF) evolution and wear volume of sliding discs are shown in Fig. 3. It is seen that pure PEG has a relatively long running-in time with a large COF, while the addition of 1 wt% LiTFSI can

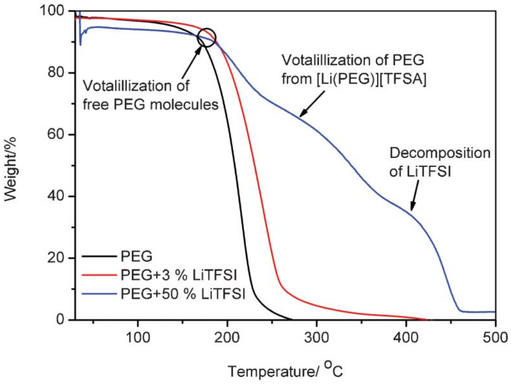

Fig. 2 TGA curves of PEG with different concentrations of LiTFSI in an air atmosphere.

Table 1 The kinematic viscosity, viscosity index and corrosion grade of the lubricants

	Kinematic viscosity/mm^2 s^{-1}			
Lubricants	40 °C	100 °C	Viscosity index	Copper strip test/corrosion grade
PEG	23.68	4.27	72.46	1a
PEG+1% LiTFSI	24.61	4.38	74.97	–
PEG+2% LiTFSI	25.32	4.45	75.14	–
PEG+3% LiTFSI	26.17	4.59	82.44	1a
PEG+4% LiTFSI	27.03	4.68	83.29	–
PEG+5% LiTFSI	27.77	4.75	83.25	–

Table 2 Performance parameters for PEG with different concentrations of LiTFSI

Lubricants	Decomposition *T*/°C	TG *T*/°C per weight loss		
		10%	20%	50%
PEG	185.1	172.1	187.1	208.3
PEG+3% LiTFSI	192.8	188.0	204.5	230.5
PEG+50% LiTFSI	190.5	204.1	232.3	367.6

dramatically reduce the COF (Fig. 3). When the concentration increases to 2 wt%, the running-in time is greatly shortened and the COF decreases to a comparatively low level. No significant improvement can be observed after 3 wt% concentration. The wear volumes of the lower discs reduce by about 28 times as compared with that lubricated with pure PEG and are very similar when lubricated with PEG containing different concentrations of LiTFSI (Fig. 3). Moreover, the friction-reducing and anti-wear properties of LiTFSI are better than those of conventional ILs such as L-B102, L-P106 and L-F102 at RT and are even more prominent at high temperature (Fig. 4 and 5). It is worth noting that L-F102, an IL synthesized from LiTFSI, has the same anion as [Li(PEG)]TFSI, but its friction-reducing and anti-wear properties are worse than [Li(PEG)]TFSI. The inset in Fig. 5 shows the appearance of pure PEG and added PEG lubricating oil after the friction tests. It is seen that pure PEG turns to a dark black color and the added PEG has almost no color change and is still very clear. The deep color of pure PEG is caused by the thermal oxidation and wear debris, therefore oxidation and wear are greatly alleviated by the addition of LiTFSI salt.

Fig. 6 displays the SEM micrographs of the worn surfaces of steel discs lubricated by different lubricants. It is clearly seen that the worn surfaces of steel discs lubricated by pure PEG exhibit considerably wider and deeper wear scars, with a number of deep and narrow grooves (Fig. 6a, 6c). Thus, severe scuffing occurs in these cases. However, the wear scars of the steel disc lubricated by 3 wt% LiTFSI in PEG are much narrower and shallower, and scuffing is greatly alleviated, indicating a significantly improved antiwear behavior by simple addition of LiTFSI (6b, 6d). These results are consistent with previously measured wear volume results and indicate undoubtedly the excellent anti-wear properties of LiTFSI as an additive for PEG.

In a further study, it was found that not only LiTFSI but also other lithium salts, such as $LiBF_4$, $LiPF_6$, $LiSO_3CF_3$ and $LiSO_3(CF_2)_7CF_3$), can form *in situ* ILs in PEG. These ILs are also effective lubricant additives and show excellent friction-reducing and anti-wear properties for the lubrication of steel/steel contacts (Fig. 7).

From a mechanistic point of view, the good lubricating behavior of ILs is attributed to the polarity of their molecules and so their ability to form ordered adsorbed layers, resulting in the formation of physical adsorption protective films and further tribochemical-reaction protective films on the sliding metallic surfaces.[29] A possible reason for the better friction-reducing and anti-wear properties of the above lithium salts than conventional ILs is that PEG is a good lubricant and the complexation between Li^+ and PEG helps the adsorption of PEG molecules on the metallic surface. The high thermal stabilities of [Li(PEG)]X prevent loss of these molecules. Moreover, because of the relatively big molecules of PEG, the *in situ* formed IL adsorbed layer is much thicker than the adsorption of conventional ILs and more difficult to be destroyed. This effective molecular absorption between sliding pairs and further tribochemical-reaction protective films on the metallic surface separates asperities and so friction reduction is achieved. To further prove this speculation, we have also investigated the tribological properties of a succession of alkali metal salts with the same anion, $SO_3CF_3^-$, as additives for PEG ($LiSO_3CF_3$, $NaSO_3CF_3$ and KSO_3CF_3). From the results, it is seen that $LiSO_3CF_3$ has better friction-reducing and antiwear properties than the other two salts, which is in accordance with the complexation ability order of $Li^+ > Na^+ > K^+$ (Fig. 8).[30] The same tribological property change trend was also observed in $LiBF_4$ and $NaBF_4$ (KBF_4 can't be dissolved in PEG). Moreover, obvious electrical contact resistance was also measured when the surface was lubricated by 3 wt% $LiSO_3CF_3$-added PEG at RT, whereas almost no resistance could be observed during the lubrication of $NaSO_3CF_3$ and KSO_3CF_3-added PEG (Fig. 9). This indicates that more effective molecular absorption between sliding pairs was formed during the lubrication of $LiSO_3CF_3$ than the other two salts (due to the stronger complexation ability of Li^+ with PEG than Na^+ and K^+), so that separation of asperities and more effective friction reduction was achieved. These results confirm our speculation that the excellent tribological properties of lithium salts are attributed to the *in situ* formation of ILs as

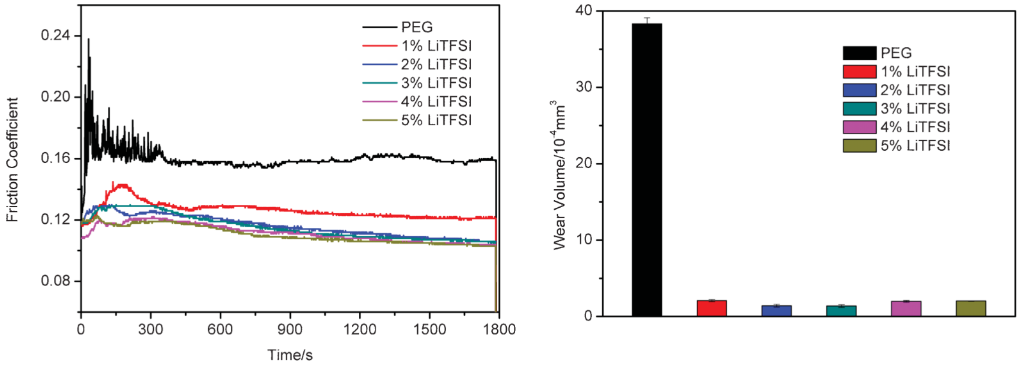

Fig. 3 The evolution of friction coefficient/time and wear volume of the lower disks lubricated by different concentrations of LiTFSI in PEG at RT (with of load 200 N and frequency of 25 Hz).

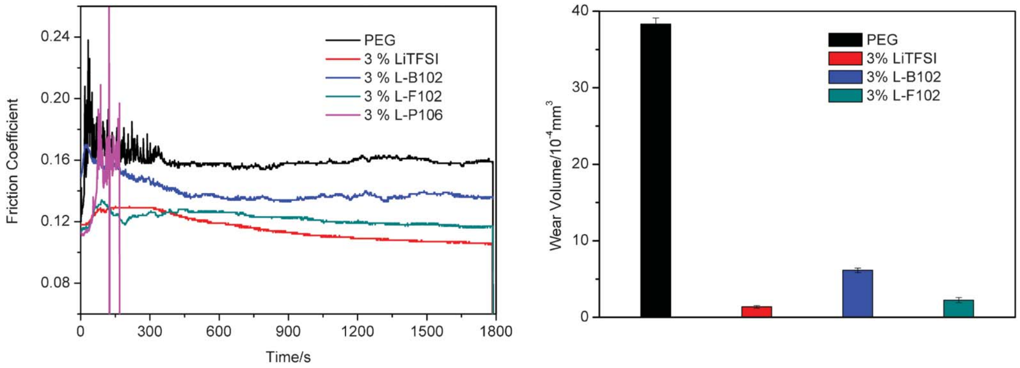

Fig. 4 The evolution of friction coefficient/time and wear volume of the lower disks lubricated by different ILs in PEG at RT (with of load 200 N and frequency of 25 Hz).

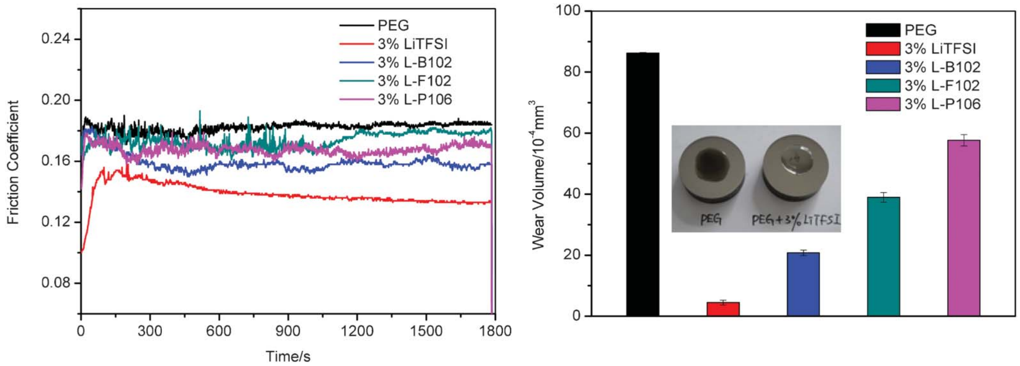

Fig. 5 The evolution of friction coefficient/time and wear volume of the lower disks lubricated by different ILs in PEG at 100 °C (with of load 200 N and frequency of 25 Hz).

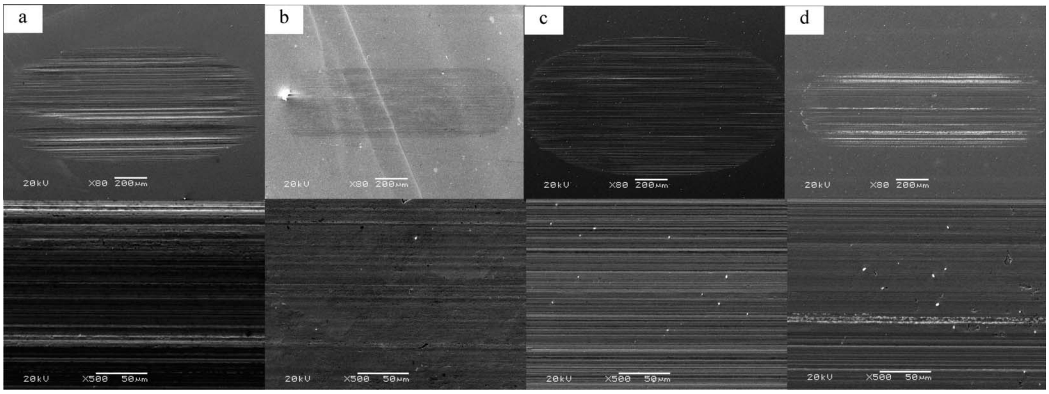

Fig. 6 The SEM micrographs of the worn surfaces lubricated by different lubricants: (a) PEG, RT; (b) 3 wt% LiTFSI in PEG, RT; (c) PEG, 100 °C; (d) 3 wt% LiTFSI in PEG, 100 °C.

further additives for the base oil. It is worth noting that the three salts have almost the same friction-reducing and antiwear abilities at high temperature as at 100 °C. This is probably due to the different lubrication mechanism of these salts at RT and high temperature. The excellent tribological properties of LiX at RT are more attributable to the formation of physical adsorption films than to tribochemical reaction films on the sliding metallic surfaces. However, under harsh friction conditions, especially at high temperatures, the excellent tribological properties are proposed to be attributed to polarity-induced physical adsorption of *in situ* formed ILs on the surfaces and, more importantly, further tribochemical reaction films of anions (X^-) with the sliding metallic surfaces. If the salts have same anions, similar tribochemical reactions occur at high temperatures resulting in similar friction-reducing and antiwear abilities during lubrication.

Finally, X-ray photoelectron spectrometry (XPS) analysis of the worn surfaces lubricated by different salts was performed to verify the above mechanism. The XPS spectra of the worn surfaces lubricated by LiTFSI are shown in Fig. 10 as an example. At the same time, the XPS data with possibly formed compounds on the worn surfaces is shown in Table 3.[31] It is seen

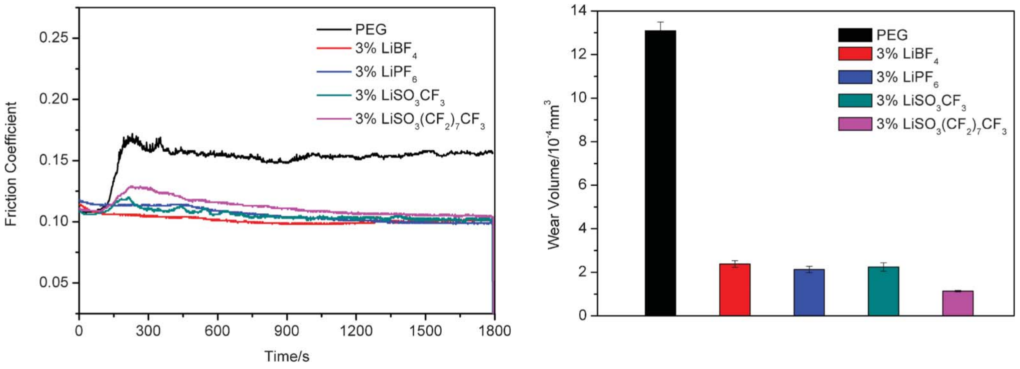

Fig. 7 The evolution of friction coefficient/time and wear volume of the lower disks lubricated by different lithium salts in PEG at RT (with of load 100 N and frequency of 25 Hz).

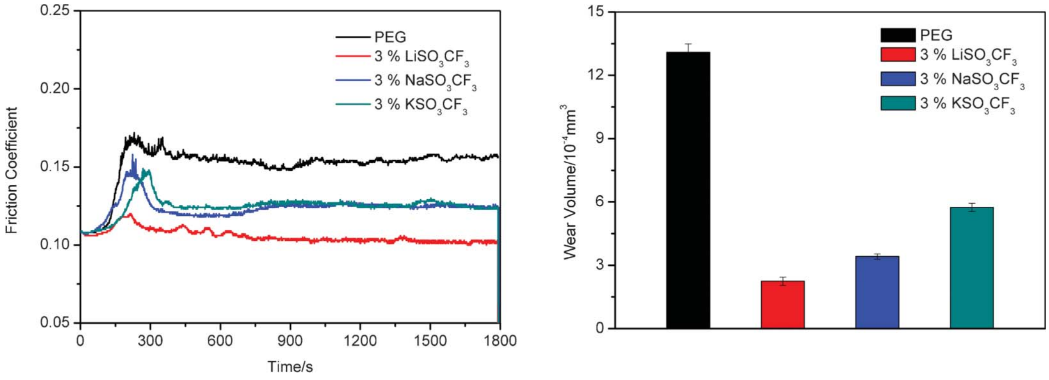

Fig. 8 The evolution of friction coefficient/time and wear volume of the lower disks lubricated by different alkali metal salts in PEG at RT (with of load 100 N and frequency of 25 Hz).

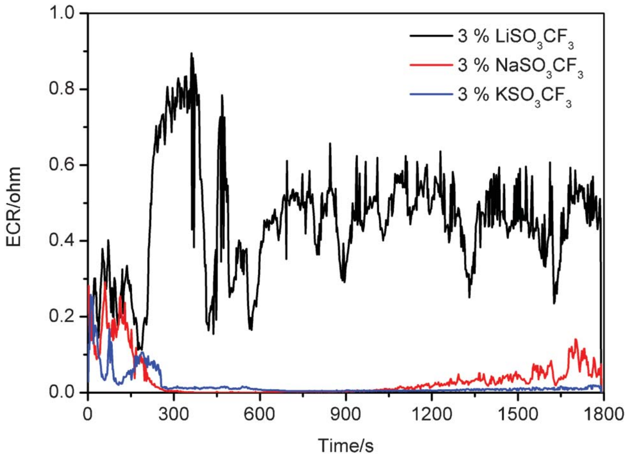

Fig. 9 The electrical contact resistance during the lubrication of different alkali metal salts in PEG at RT.

that no obvious difference is observed on the XPS spectra of Fe2p and O1s for worn steel surfaces lubricated by PEG and 3 wt% LiTFSI-added PEG at RT (a, b). Also no obvious characteristic peaks of S2p, F1s, N1s and Li1s were detected. So in this case, the excellent tribological properties of LiTFSI are more attributable to the formation of physical adsorption films (which were removed by ultrasonic rinsing during sample preparation before XPS tests) than tribochemical reaction films on the sliding metallic surfaces. On the contrary, in the XPS spectra of S2p, one peak appears at approximately 161.5 eV for a worn steel surface lubricated by 3 wt% LiTFSI-added PEG at 100 °C (c), which may correspond to FeS or FeS_2. A peak appears at a very wide range around 685.0 eV (c) in the XPS spectra of F1s, which indicates the presence of F^-, possibly due to the formation of FeF_2 or FeF_3. Thus, with the existing conditions, it is difficult to determine the exact tribological protective film species on the worn steel surfaces. However, on the basis of above data it can be concluded generally here that under a collective impact of high pressure, exoelectron emission, and frictional heating, complicated tribochemical reactions occur on the surfaces lubricated by LiTFSI in PEG at high temperature. Thus, some of the newly formed compounds, such as FeS, FeS_2, FeF_2, or FeF_3, coming from the reaction of the additive anions with fresh metal were observed and acted as a protective film to prevent cold-welding of fresh metal and to alleviate wear. So in this case, the excellent tribological properties are attributed to the polarity induced physical adsorption films of *in situ* formed ILs on the surfaces and, more importantly, further tribochemical reaction films of $TFSI^-$ with the sliding metallic surfaces.

Conclusion

In conclusion, lithium salts was used for the first time as lubricant additives for polyether lubricating oils. They were

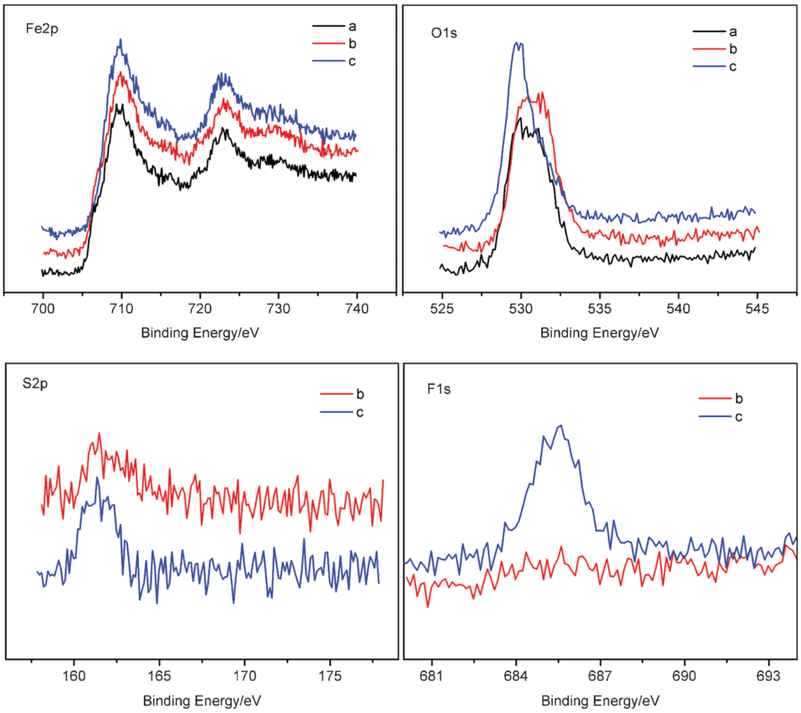

Fig. 10 The XPS spectra of the worn surfaces lubricated by different lubricants: (a) PEG, RT; (b) 3 wt% LiTFSI in PEG, RT; (c) 3 wt% LiTFSI in PEG, 100 °C.

Table 3 The XPS data and possibly formed compounds on the worn surfaces

Lubricant	T/°C	Peaks	Observed peaks value/eV	Possible compounds
PEG	25	Fe2p O1s	709.5, 723.5 529.0–532.5	FeO, Fe_2O_3, Fe_3O_4 or FeOOH
PEG+3% LiTFSI	25	Fe2p O1s	709.5, 723.5 529.0–532.5	FeO, Fe_2O_3, Fe_3O_4 or FeOOH
PEG+3% LiTFSI	100	Fe2p O1s S2p F1s	709.5, 723.5 529.7 161.5 685.0	FeO, Fe_2O_3, Fe_3O_4 or FeOOH FeS or FeS_2 FeF_2 or FeF_3

found to have excellent friction-reducing and anti-wear properties for the lubrication of steel/steel contacts. The excellent tribological properties are attributed to the *in situ* formation of ILs ([Li(PEG)]X) as further additives for the base oil. The key points of this work are: (1) It provides a completely new strategy for applying IL lubricants without the synthesis of ILs. The lubrication system can be easily prepared only by dissolving commercially available lithium salts in the base oil at RT. No synthetic or separation step is required in the whole process. This is a great advantage as compared with conventional ILs, which undoubtedly lowers the cost of IL application. (2) Lithium salts have good solubility in PEG, especially LiTFSI (> 50 wt%), while the solubility of conventional ILs is relatively low. (3) the tribological properties of this type of IL are better than those of conventional ILs. The easy preparation, low cost and extremely good solubility provide a convenient and potential access to industrial application of ILs in lubrication engineering. Further studies on the using of this concept, *in situ* formation of ILs, to other base oils, such as polyester and polyurea grease, are in progressing in our laboratory and delightedly found to be effective. The results will be reported as a following work.

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