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STRUCTURE  
AND PROPERTIES

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## Influence of Humidity on the Complex Structure of PEO-Lithium Salt Polymer Electrolyte<sup>1</sup>

Xiaocan Zhang\*, Lu Zhou, Yufeng Wang, and Qiong Zhou

College of Science, State Key Laboratory of Heavy Oil Processing,  
China University of Petroleum-Beijing, Beijing, 102249, China

\*e-mail: xiaocan.zhang@cup.edu.cn

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**Abstract**—Solid polymer electrolytes of PEO/LiClO<sub>4</sub> and PEO/LiTFSI solution casting films were prepared with the EO/Li molar ratio of 3 : 1, and the effect of relative humidity (RH) on their complex structures were characterized. It is shown that the complex structures were barely changed at RH ≤ 10% while severe differences were shown at RH ≥ 20%. The reason was attributed to the interactions of water with lithium salt, and the formation of PEO–Li<sup>+</sup>–H<sub>2</sub>O decreased the interactions between PEO and lithium ions. Furthermore, it was shown that the hydrated samples after heat treatment were still strikingly different in characters from their anhydrous precursors, and the type of lithium salt affected the final structures. It was found that the structure of (PEO)<sub>3</sub>LiClO<sub>4</sub> (30% RH) was hardly changed after heating; however, an irreversible compositional transition was discovered in (PEO)<sub>3</sub>LiTFSI (30% RH) in which case (PEO)<sub>2</sub>LiTFSI was formed.

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### INTRODUCTION

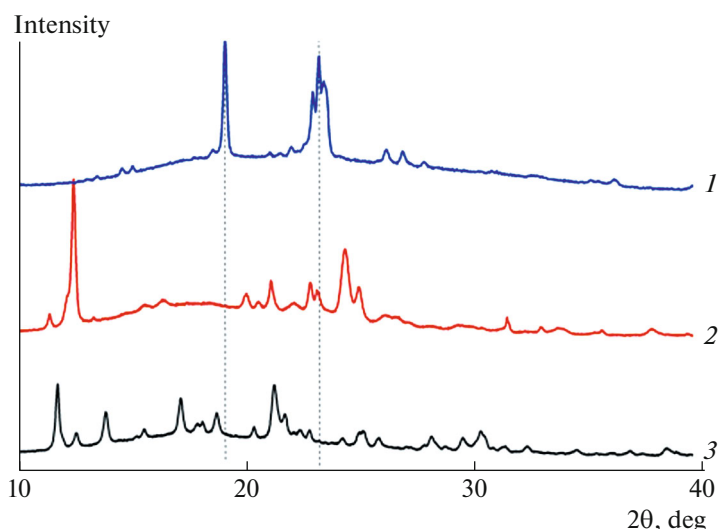
Polymer lithium ion battery has the advantages of high energy density, diverse processing shape, as well as reliable performance, and is a new generation of lithium ion battery with great development prospects. Polyethylene oxide (PEO) based electrolytes have the potential to replace the liquid electrolyte in the traditional lithium ion batteries and therefore received much attention.

Lithium ion batteries are susceptible to moisture from all stages in the production line, nevertheless, manufacturers had no uniform moisture control standards. Typical production of lithium ion batteries includes batching, coating, flaking, winding and other processes, and the moisture control in each workshop can vary from 1 to 30%, but only baking before the key processes. Therefore, components in the batteries would contact with water during the manufacture process and potentially affect their properties. In 1982, Weston and Steele [1] first reported the effect of aqueous solution to the conductivity of PEO based electrolyte. Other research groups [2–6] also published a few reports on the conductivity change caused by a small amount of water. As the composition, concentration and water content of the salt differ, the corresponding conductivity can vary up to several orders of magnitude. Although the presence of trace water is able to

improve the migration of lithium ions so as to improve the ionic conductivity, the water control is very difficult in the battery processing process. As soon as excessive water appeared, loads of negative effects would occur. The chemicals in batteries interact with water and release gas, leading to cell expansion. The produced HF destroys the integrity of the solid electrolyte interphase (SEI) film, affecting the battery performance [7–10].

Solid polymer electrolytes are sensitive to water because both salt and PEO can absorb water from surroundings. When water diffuses into the polymer electrolyte, the property of polymer electrolyte may change [1–6, 11–16]. Techniques such as differential scanning calorimetry (DSC) [1, 13, 16], infrared spectroscopy (IR Spectroscopy) [1, 11–13], UV–Vis spectroscopy [14], nuclear magnetic resonance (NMR) [2, 5, 15, 16], electron spinning resonance (ESR) [12] and X-ray diffraction (XRD) [3, 14] had been used to understand the details of water influence and had shown that water either lessened or damaged the complexation of ethylene oxide (EO) and metal ions. However, whether the effect is reversible upon the removal of water is unclear. Kovač et al. reported that effect of water on polymer was a reversible process when the hydration sample was put back to dry environment [4]. In contrast, dehydrated PEO<sub>8</sub>NiBr<sub>2</sub> presented a big difference when compared to its anhydrous precursor even with similar water content [14].

<sup>1</sup> The article is published in the original.



**Fig. 1.** (Color online) WAXD patterns of pure (1) PEO, (2)  $(\text{PEO})_3\text{LiClO}_4$ , and (3)  $(\text{PEO})_3\text{LiTFSI}$  at room temperature. All samples “as cast” were prepared and stored in glove box before experiments.

The irreversible phenomenon was analyzed by reason of compositional transition. In the present work, two kinds of lithium salts, lithium perchlorate  $\text{LiClO}_4$  and lithium bis(trifluoromethanesulfonyl)imide  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  ( $\text{LiTFSI}$ ), were used individually to form complex with PEO. The effect of humidity on structural change and reversibility were characterized and discussed.

## EXPERIMENTAL

### Preparation of Hybrid Membrane

Polymer films were prepared in a  $\text{N}_2$  filled glove-box. Lithium salt was dried under vacuum and added to PEO ( $M_v = 4 \times 10^5$  g/mol, Sigma Aldrich) in anhydrous acetonitrile. The obtained solution was poured onto a Teflon dish and thin film was formed upon evaporation. Both  $\text{PEO}/\text{LiClO}_4$  (Shanghai China Lithium Industrial Co., Ltd) and  $\text{PEO}/\text{LiTFSI}$  (Aladdin) polymer electrolytes were prepared with  $\text{EO}/\text{Li}$  molar ratio of 3 : 1 in the same fashion. Similar procedure was followed for the preparation of pure PEO. For humidity study, sample films were exposed to various relative humidity (RH) for 72 h before testing. Different RH values were achieved by the evaporation of selected saturated salt solutions and monitored by a digital hygrometer. In this way, 10, 20, 30, 40, and 55% RH were prepared.

### Membrane Characterization

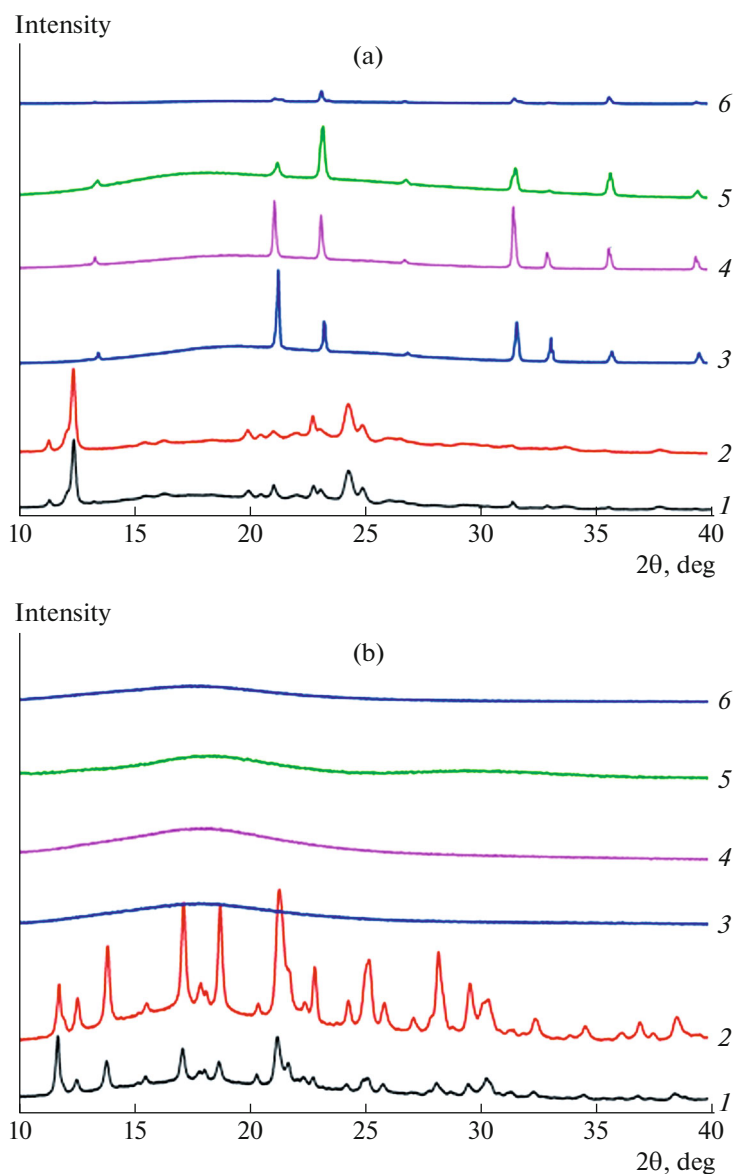
Thermal study was performed on a NETZSCH 204F1 differential scanning calorimeter equipped with intercooler as cooling system under an argon atmosphere. Measurements were carried out from 20 to

280°C under argon with a heating/cooling rate of 10 deg/min. Wide angle X-ray diffraction (WAXD) measurement was carried out on a Bruker AXS D8 Advance powder diffractometer using  $\text{CuK}\alpha$  ( $\lambda = 0.154$  nm) radiation. The  $2\theta$  scanning was carried out from  $10^\circ$  to  $40^\circ$  with a scanning rate of 2 deg/min. Samples were covered with paraffin to prevent the absorption of water. The spherulitic morphology was taken with a DM2500P polarized optical microscope (Leica Company, Germany) equipped with a THMS-600 hot stage (Linkam Scientific Instrument Ltd, England) and a 590CU CCD camera (Micrometrics Company).  $(\text{PEO})_3:\text{LiClO}_4$  and  $(\text{PEO})_3:\text{LiTFSI}$  complexes were heated to 200°C, held for 10 min and then isothermally crystallized at 120 and 45°C, respectively. All samples from the glove box were covered with Teflon tape and only the observation areas were exposed for photos.

## RESULTS AND DISCUSSION

WAXD was employed to study the crystalline property of the electrolyte compared with that of pure PEO. As shown in Fig. 1, the characteristic peaks of PEO were at  $2\theta = 19.0^\circ$  and  $23.2^\circ$ . No diffraction from PEO was observed in either  $(\text{PEO})_3\text{LiClO}_4$  or  $(\text{PEO})_3\text{LiTFSI}$  electrolytes, indicating the complete formation of the electrolyte. All diffraction patterns in the electrolyte were consistent with what have been reported [17–19] for polymer electrolyte dry films.

The effect of relative humidity on the crystalline properties is illustrated in Fig. 2. It is shown that 10% RH did not change the WAXD patterns of dry  $(\text{PEO})_3\text{LiClO}_4$  or  $(\text{PEO})_3\text{LiTFSI}$  samples. However, at higher humidity levels, the characteristic peaks of



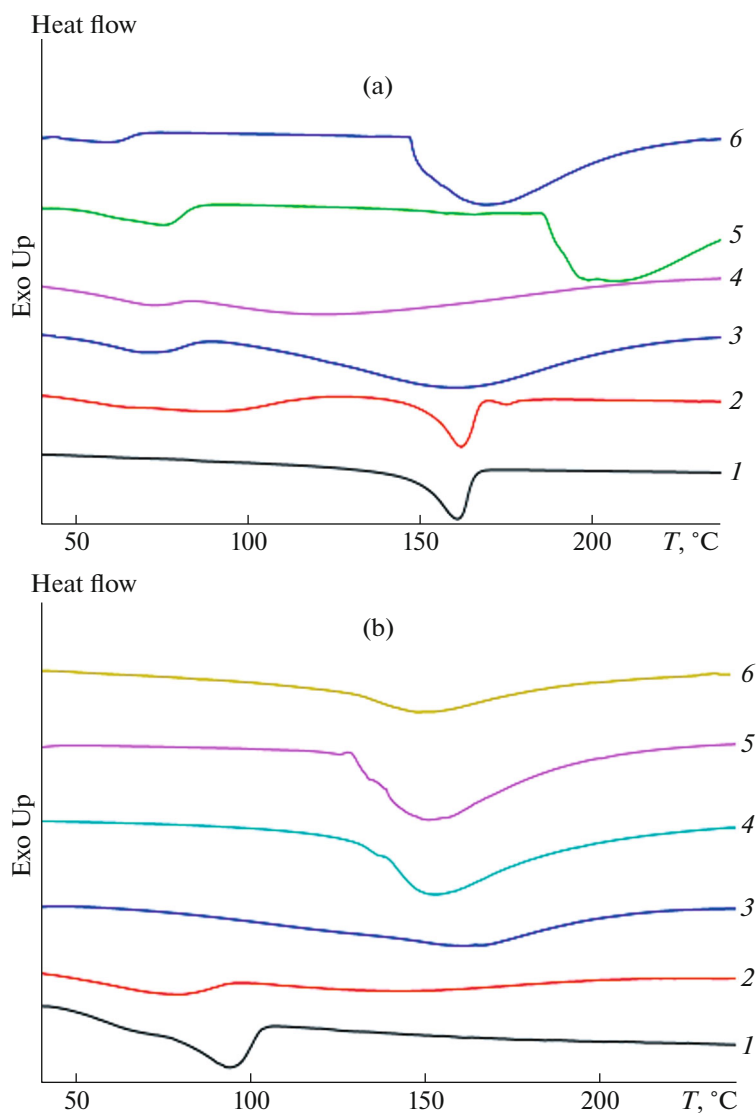
**Fig. 2.** (Color online) WAXD diffractograms of polymer electrolytes (a)  $(\text{PEO})_3\text{LiClO}_4$  and (b)  $(\text{PEO})_3\text{LiTFSI}$  at room temperature under various RH: (1) 0, (2) 10, (3) 20, (4) 30, (5) 40, and (6) 55%.

both PEO-salt complexes disappeared and new peaks appeared for  $(\text{PEO})_3\text{LiClO}_4$  yet none for  $(\text{PEO})_3\text{LiTFSI}$ . It was reported that the cations in aqueous polymer electrolytes tend to combine with water, weakening its interactions with PEO chains [2, 12]. In addition, new peaks in  $(\text{PEO})_3\text{LiClO}_4$  ( $\geq 20\%$  RH) were not correspondence to the characteristic peaks of PEO or  $\text{LiClO}_4$  (WAXD not shown), thus  $\text{PEO-Li}^+-\text{H}_2\text{O}$  complex might have formed.

The effect of humidity on DSC thermograms is shown in Fig. 3. As RH increased, the DSC thermograms deviated more from that of dry samples, whose  $T_m$  is around  $160^\circ\text{C}$  for  $(\text{PEO})_3\text{LiClO}_4$  and  $95^\circ\text{C}$  for  $(\text{PEO})_3\text{LiTFSI}$ . Both values are consistent with what

have been reported [17, 18]. At 10% RH,  $T_m$  and  $\Delta H$  decreased slightly for  $(\text{PEO})_3\text{LiClO}_4$  but more for  $(\text{PEO})_3\text{LiTFSI}$ ; yet, both thermograms remained similar feature as those for the dry samples. On the other hand, higher humidity ( $\geq 20\%$  RH) greatly deteriorated the DSC traces for both complexes, and the flattened peaks had been suggested to be the vaporization of water in hydrated samples [13, 16].

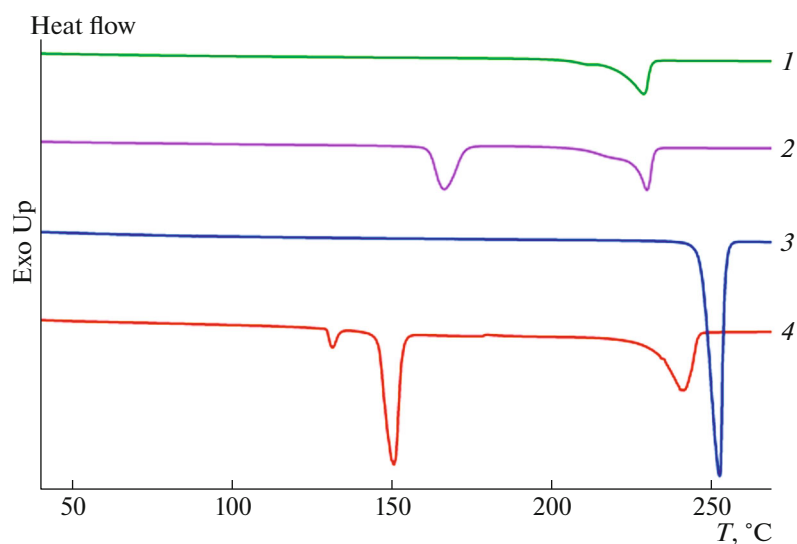
In order to further discuss the state of water in PEO-lithium salt complex, the DSC thermograms of dry (RH = 0%) and hydrated salts (RH  $\geq 20\%$ ) were compared. Figure 4 shows that  $T_m$  values of both dry salts were greater than  $200^\circ\text{C}$ . At RH  $\geq 20\%$ , multiple peaks appeared, suggesting the loss of moisture during



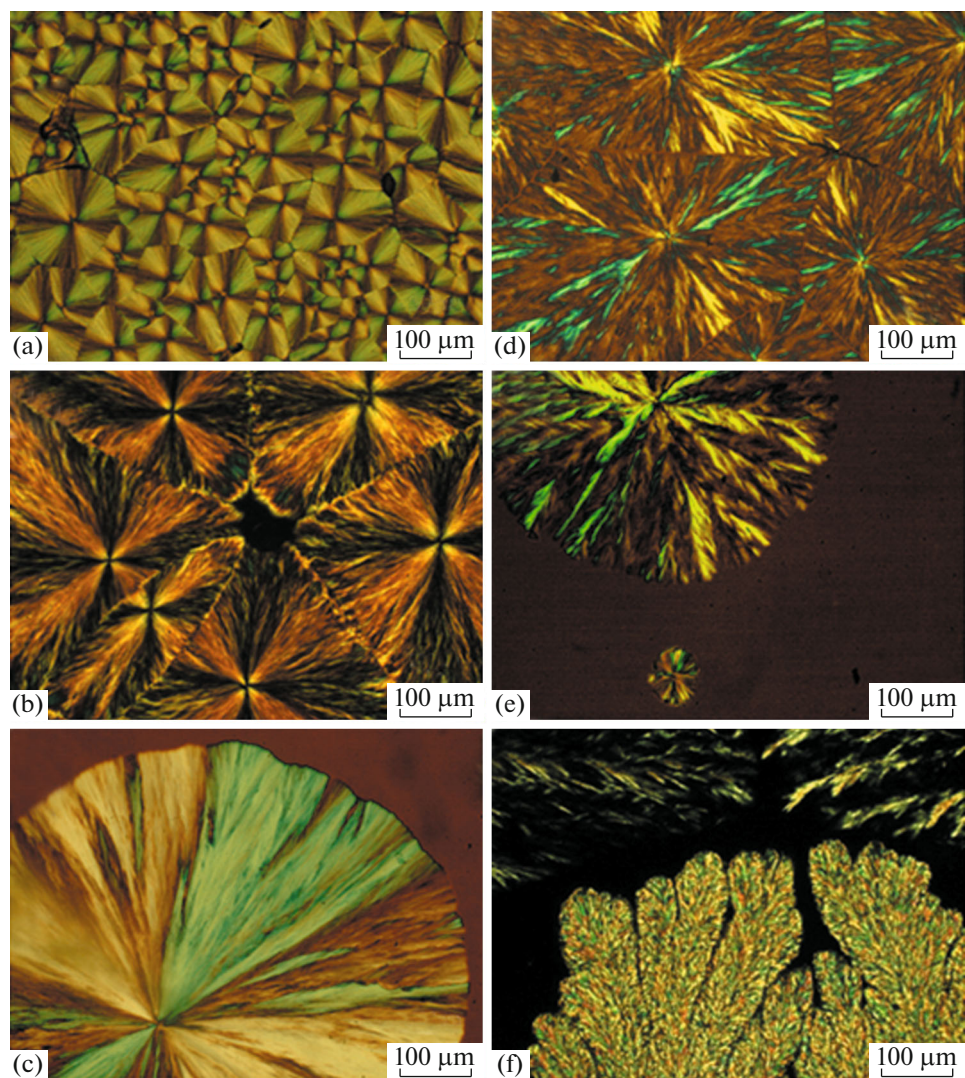
**Fig. 3.** (Color online) DSC thermograms of (a)  $(\text{PEO})_3\text{LiClO}_4$  and (b)  $(\text{PEO})_3\text{LiTFSI}$  under various RH: (1) 0, (2) 10, (3) 20, (4) 30, (5) 40, and (6) 55%, and the scanning rate was 10 deg/min.

the course of heating. This is consistent with the flattened peaks for PEO salt complexes in the range of 80–200°C in Fig. 3. For  $(\text{PEO})_3\text{LiClO}_4$ , the widened endothermic peaks did not appear until 150°C at RH levels of 40 and 55%. This might be caused by the stable tetrahedral structure [20–24] formed by lithium salt and water, and the binding energy between water and  $\text{Li}^+$  was too high to be consumed at low temperatures. Since no  $(\text{PEO})_3\text{LiClO}_4$  crystals existed at these RH levels (Fig. 2), the endothermic peaks in Fig. 3 should be correspondence with the melting of  $\text{LiClO}_4 \cdot x\text{H}_2\text{O}$ . As the exact  $T_m$  value depends on the numbers of hydrate water [21], the peak values of the endothermic peaks were different at RH levels of 40 and 55%.

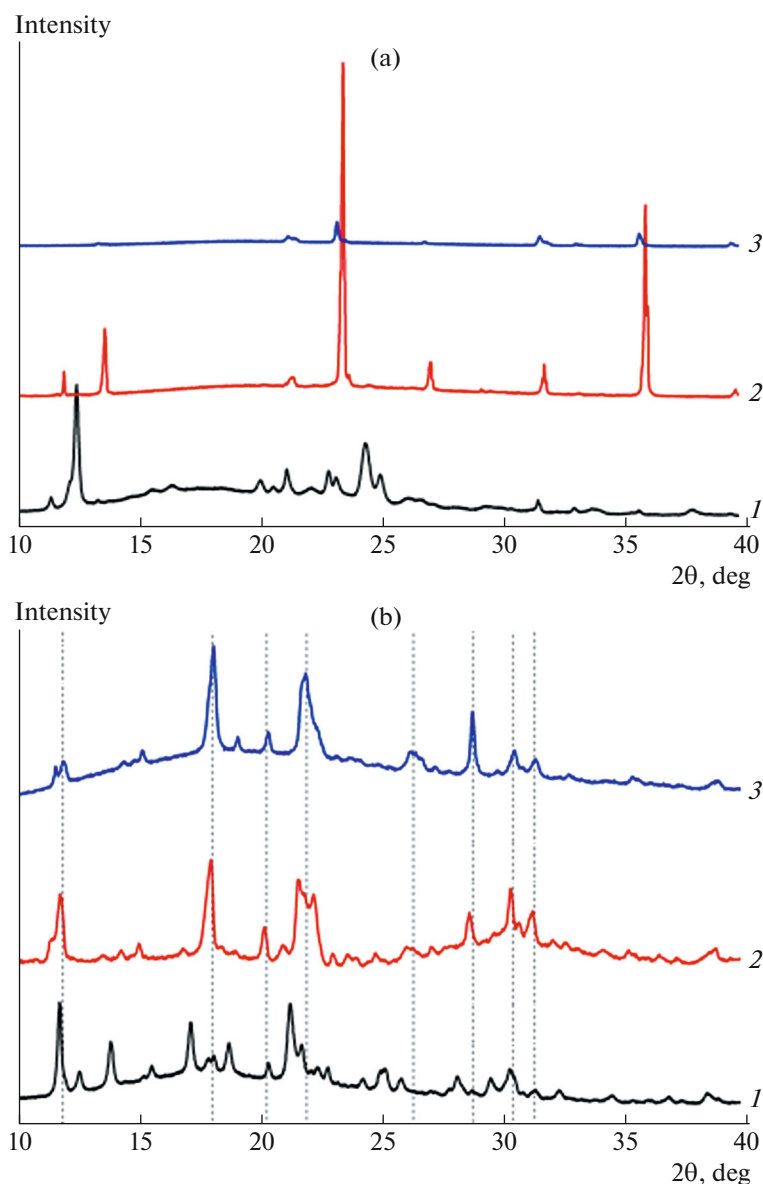
The effect of humidity on spherulitic morphology of  $(\text{PEO})_3\text{LiClO}_4$  and  $(\text{PEO})_3\text{LiTFSI}$  is illustrated in Fig. 5. It is obvious that the size of the formed spherulites were progressively larger with higher RH. WAXD and DSC have shown that the structures of  $(\text{PEO})_3\text{LiClO}_4$  and  $(\text{PEO})_3\text{LiTFSI}$  barely changed at RH lower than 10% while greatly changed at higher RH values ( $\geq 20\%$ ). It was suspected that high RH caused the precipitation of  $\text{LiClO}_4 \cdot x\text{H}_2\text{O}$  from the polymer–lithium salt complexes at elevated temperatures, and  $\text{PEO}-\text{Li}^+-\text{H}_2\text{O}$  complex might be therefore formed. The growth of spherulites was slower at RH levels  $\geq 20\%$ , and this might be due to the discrepancy in structures, which were in accordance with the above findings. Moreover, the change of morphology might be attributed to the transformation in crystal form derived from inho-



**Fig. 4.** (Color online) DSC thermograms of LiTFSI at RH of (1) 0 and (2)  $\geq 20\%$  and LiClO<sub>4</sub> at RH of (3) 0 and (4)  $\geq 20\%$ .



**Fig. 5.** (Color online) Polarized optical micrographs of spherulitic morphology of (PEO)<sub>3</sub>LiClO<sub>4</sub> (first column) and (PEO)<sub>3</sub>LiTFSI (second column) at  $T_c = 120$  and  $45^\circ\text{C}$ , respectively. The RH values and crystallization times are: (a) 0% RH, 2 min; (b) 10% RH, 23 h; (c) 30% RH, 74 h; (d) 0% RH, 4 h; (e) 10% RH, 27 h; (f) 30% RH, 27 h.



**Fig. 6.** (Color online) WAXD diffractograms of (a)  $(\text{PEO})_3\text{LiClO}_4$  and (b)  $(\text{PEO})_3\text{LiTFSI}$  polymer electrolytes at (1) 0, (2) 30, and (3) 55% RH. The conditioned samples had the same thermal history as that of shown in Fig. 5.

mogeneous melt, which was caused by humidity. This assumption was further discussed below by WAXD of samples under the same thermal history.

Figure 6 demonstrates the WAXD patterns of dry and wet polymer–lithium salt complexes. For  $(\text{PEO})_3\text{LiClO}_4$ , 30% RH greatly changed the crystalline form comparing to the dry sample while the conditioned sample did not change thereafter, and the unchanged WAXD diffractogram suggested that the heat treatment was ineffective in reversing the effect of humidity. In the case of  $(\text{PEO})_3\text{LiTFSI}$ , however, the conditioned sample superposed with that of  $(\text{PEO})_2\text{LiTFSI}$ , indicating the formation of a new crystalline form. It has been reported that comparing

to  $(\text{PEO})_3\text{LiTFSI}$ ,  $(\text{PEO})_2\text{LiTFSI}$  crystals display larger and less regular spherulites [25], therefore the morphology in Fig. 5f indicated the formation of  $(\text{PEO})_2\text{LiTFSI}$ . The correspondence leads to the conclusion that new crystalline form was developed at high RH (30%).

## CONCLUSIONS

It was found that the complex structures of  $(\text{PEO})_3\text{LiClO}_4$  and  $(\text{PEO})_3\text{LiTFSI}$  were greatly influenced by humidity in the environment. At  $\text{RH} \leq 10\%$ , the complex structures barely changed except that the corresponding  $T_m$  and  $\Delta H$  decreased. How-

ever, at RH  $\geq$  20%, both complex structures were severely altered. The reason was tentatively attributed to the interactions of water with lithium salt, and the formation of PEO–Li<sup>+</sup>–H<sub>2</sub>O decreased the interactions between PEO and lithium ions. In other words, the interactions between water and Li<sup>+</sup> were stronger than that of water and PEO chains under conditions applied. Moreover, the structural change could not be easily reversed by the subsequent heat treatment. Polarized optical micrographs and WAXD diffractograms showed that upon the removal of water the structure of (PEO)<sub>3</sub>LiClO<sub>4</sub> (30% RH) hardly changed while (PEO)<sub>3</sub>LiTFSI (30% RH) had developed the new crystals of (PEO)<sub>2</sub>LiTFSI. This irreversibility can be attributed to a different interaction between PEO and LiTFSI from that of LiClO<sub>4</sub>. These findings can be an effective guidance towards the establishment of humidity control under industrial production conditions.

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