



Binary room-temperature complex electrolytes based on LiClO_4 and organic compounds with acylamino group and its characterization for electric double layer capacitors

Feng Wu^{a,b}, Renjie Chen^{a,b,*}, Fan Wu^c, Li Li^{a,b}, Bin Xu^a, Shi Chen^{a,b}, Guoqing Wang^{a,b}

^a School of Chemical Engineering and the Environment, Beijing Institute of Technology, Beijing 100081, China

^b National Development Center of High Technology Green Materials, Beijing 100081, China

^c School of Chemistry and Chemical Engineering, Queen's University, Belfast BT9 5AG, UK

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ABSTRACT

Binary room-temperature complex electrolytes have been synthesized based on lithium perchlorate (LiClO_4) and organic molecules with acylamino groups, including acetamide, ethyleneurea, 2-oxazolidinone (OZO), urea, methylurea (NMU) and 1,3-dimethylurea (DMU). Both LiClO_4 and all organic molecules with acylamino groups are solid at room-temperature, but their mixtures at the proper molar ratio are liquid with a liquidus temperature about below 25°C characterized by differential scanning calorimetry (DSC). Infrared spectroscopic studies show that the organic molecules can coordinate with the Li^+ cation and the ClO_4^- anion via their polar groups (the $\text{C}=\text{O}$ and NH groups). Such strong interactions lead to the dissociation of LiClO_4 and the breakage of the hydrogen bonds among the organic molecules, resulting in the formation of the complex systems. Electrochemical performances of the complex electrolytes are evaluated with ac impedance spectroscopy, cyclic voltammetry (CV), and in a test electric double layer capacitor (EDLC), respectively. The LiClO_4 -acetamide electrolyte at molar ratio 1:5.5 exhibits the highest ionic conductivity, $1.25 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C and $11.5 \times 10^{-3} \text{ S cm}^{-1}$ at 80°C . The analysis for the CV behavior indicates that the electrochemical stability window of these electrolytes is above 3 V. The results demonstrate that these complex systems are promising electrolyte candidates for supercapacitor and probably other electrochemical devices.

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1. Introduction

Room-temperature molten salts (RTMSs) are also known as ionic liquids because they are liquid at ambient or even lower temperatures and are composed entirely of ions [1,2]. RTMSs have attracted much attention as potentially safe electrolytes for a variety of electrochemical devices (e.g. high-energy density batteries, supercapacitors), because of their unusual properties, wide liquid phase range, high thermal stability, very low vapor pressure and nonflammability [3–14]. Most of the reported RTMS systems typically contain organic cations represented by the alkyl-substituted nitrogen-containing cations combined with a variety of anions [15,16]. Due to synthetic difficulties and cost of many cation precursors, it would be useful to find a simple and cheap RTMS system.

Some complex systems formed with amide and alkali metal nitrates or ammonium nitrates were studied as ion or proton-transfer media [17–19].

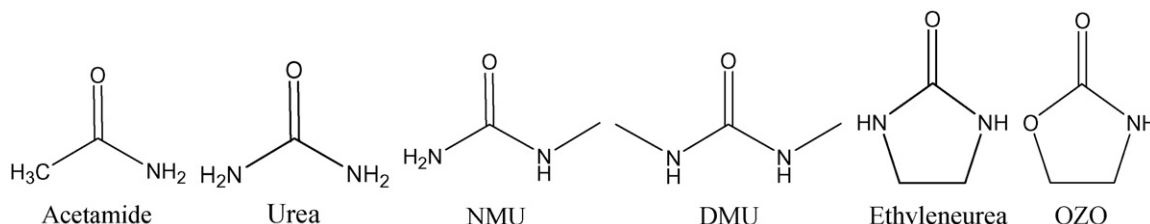
Previously, we reported a class of complex system based on lithium bis(trifluoromethane sulfonyl)imide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiTFSI) and solid organic compounds with acylamino group [20–22]. These complex systems are very easy to prepare and some samples possess favorable physical and electrochemical properties. In this paper, the binary complex system based on LiClO_4 and organic molecules with acylamino groups, such as acetamide, ethyleneurea, 2-oxazolidinone (OZO), urea, methylurea (NMU) and 1,3-dimethylurea (DMU) (see Scheme 1) are prepared and the thermal and electrochemical performances are evaluated. In order to make a comprehensive study on the formation of the complex electrolytes, Fourier transform infrared (FT-IR) are applied.

2. Experimental

LiClO_4 (Acros Inc., AP) and organic compounds, acetamide (Acros Inc., AP), urea (Beijing Chemical Reagents Inc., 99%), NMU (Acros

* Corresponding author at: School of Chemical Engineering and the Environment, Beijing Institute of Technology, 5 Zhongguancun South Road, Haidian, Beijing 100081, China. Tel.: +86 10 68912508; fax: +86 10 68451429.

E-mail address: chenrj@bit.edu.cn (R. Chen).



Scheme 1. Structure of organic compounds with acylamino group.

Inc., 97%), DMU (Acros Inc., 98%), ethyleneurea (Tokyo Kasei Kogyo Co. Inc., $W > 97\%$) and OZO (Acros Inc., 99%), were dried at 140°C and 55°C for 12 h in vacuum, respectively.

All the complex systems were prepared by simply mixing LiClO_4 and the organic compound with an acylamino group at various molar ratios in an argon-filled MBraun LabMaster 130 glovebox ($\text{H}_2\text{O} < 5$ ppm). The water content in the complex electrolyte was determined to be less than 42 ppm by Karl–Fischer titration method on DL37KF Coulometer, Mettler Toledo.

The melting points of the complex systems were determined on a DSC 2010 differential scanning calorimeter (TA Inc.) by sealing ca. 10 mg of the complex system in an aluminum pan. The pan and the electrolyte were first cooled to about -100°C with liquid nitrogen and then heated to 100°C at a rate of 5°C min^{-1} . Special attention was paid to avoid exposing the hygroscopic samples to moisture by continuous nitrogen flowing around the sample during measurement.

The IR spectra of the samples were recorded on a Nicolet Magna 750 FT-IR spectrometer between 4000 and 400 cm^{-1} with the resolution set at 4 cm^{-1} . The solid sample was mixed with dry KBr and pressed into pellet while a droplet of the liquid sample was spread on a dry KBr pellet for the IR spectroscopic measurements. The IR spectra shown here were the average results of 50 scans.

Ionic conductivity measurements were carried out with an electrochemical cell with Pt electrode. The cell constant was determined with standard KCl solution (0.01 M) at 25°C . The alternating current impedance of the samples was measured on a CHI660a electrochemical workstation (1 Hz to 100 KHz, 0 – 80°C). The electrochemical window of the complex electrolyte was measured with cyclic voltammetry (CV) on the electrochemical workstation. The samples were sealed in glass cells with Li foil (99.9%) as the reference and counter electrodes but different working electrodes depending on the studied potential range. All the cells were assembled in the glovebox.

Carbon electrodes were prepared by mixing 87 wt% activated carbon (specific surface area $1200\text{ m}^2\text{ g}^{-1}$), 10 wt% acetylene black and 3 wt% PTFE binder and pressing the mixture onto foamed nickel. A coin-like electric double layer capacitor (EDLC) was built with two carbon electrodes, separated with polypropylene film, soaked in LiClO_4 –acetamide complex electrolyte and locked in a test cell. All the operations were done in the glovebox. The galvanostatic charge–discharge was carried out on a Land cell tester. The cyclic voltammetry measurements of capacitors were performed on an IM6e electrochemical workstation.

3. Results and discussion

3.1. Thermal analysis

For the complex systems with LiClO_4 –acetamide molar ratios between 1:3.0 and 1:6.0, LiClO_4 –NMU molar ratios between 1:2.0 and 1:5.0, and LiClO_4 –OZO molar ratios between 1:2.0 and 1:6.0, the salt and the organic molecule become wet immediately after

contact with each other and liquid drops can be observed on the wall of the container. Thoroughly stirring the mixture leads to the formation of a homogeneous, transparent and stable liquid at room-temperature. The melting points of ethyleneurea with a five-membered ring (132°C), urea (132.7°C) and DMU (105°C) are higher than that of acetamide (81°C). The homogenous liquids are not available at room-temperature without heating. The LiClO_4 –ethyleneurea, LiClO_4 –urea and LiClO_4 –DMU composites with proper molar ratios remain liquid after cooled down to room-temperature. However, they are supercooled and have to be stored in a sealed container. Out of the above range of molar ratios, the liquid becomes waxy at room-temperature.

Fig. 1 shows the typical DSC trace of the phase transitions for LiClO_4 -based composite. It reveals that the eutectic temperature of every complex system is lower than the melting point of LiClO_4 (234°C) or organic compounds. Experimental results for the eutectic temperature, melting point and range of liquid phase are summarized in Table 1. The eutectic temperatures of the LiClO_4 –acetamide composites decrease with increasing acetamide concentration. This indicates that the thermal properties of the complex system depend on its salt content.

The eutectic temperature of LiClO_4 –urea at molar ratio 1:4.0 occurs at 46.4°C . It is worth noticing that only one endothermic peak related to the glass transition temperature is observed in the DSC trace of the LiClO_4 –NMU composites. In comparison, the eutectic temperature of the LiClO_4 –NMU complex system is lower and their range of liquid phase is wider than that of the LiClO_4 –urea system. This means that this type of complex systems possess higher thermal stability in the studied temperature range. The formation of the LiClO_4 –DMU complex system is very slow at

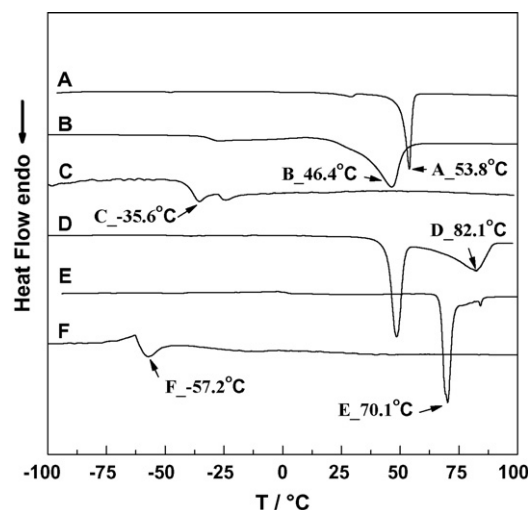


Fig. 1. Typical DSC diagram of complex systems A: LiClO_4 :acetamide = 1:4.5; B: LiClO_4 :urea = 1:4.0; C: LiClO_4 :NMU = 1:4.0; D: LiClO_4 :DMU = 1:4.0; E: LiClO_4 :ethyleneurea = 1:4.5; F: LiClO_4 :OZO = 1:4.5.

Table 1
Thermal properties of some room-temperature complex systems

Composition	Eutectic temperature at various molar ratios T_e ($^{\circ}\text{C}$)						Melting point of organic compounds T_m ($^{\circ}\text{C}$)	Range of liquid phase ^a
	1:2.5	1:3.0	1:3.3	1:4.0	1:4.5	1:5.5		
LiClO ₄ -acetamide	–	–	50.3	52.4	53.8	58.0	81	1:3.0–1:6.0
LiClO ₄ -urea	–	63.5	–	46.4	–	–	132.7	1:3.0–1:4.0 ^b
LiClO ₄ -NMU	–	–33.0	–	–35.5	–	–	102	1:3.0–1:5.0
LiClO ₄ -DMU	–	–	–	82.1	–	–	105	1:4.0 ^b
LiClO ₄ -ethyleneurea	–	–	119.2	85.5	70.1	69.6	132	1:4.0–1:6.0 ^b
LiClO ₄ -OZO	–47.4	–	–	–	–57.2	–	88	1:2.0–1:6.0

^a At room-temperature.

^b Supercooled liquid.

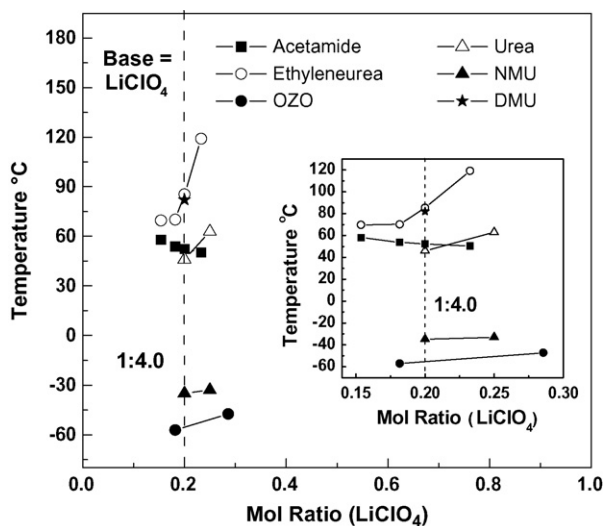


Fig. 2. The molar ratio dependence of the eutectic temperatures of LiClO₄-based complex systems. Inset: a selected part (molar ratio range of 0.14–0.30).

room-temperature. However, slight heating leads to the quick formation of a homogeneous liquid. The eutectic temperature (82.1 $^{\circ}\text{C}$) is reached at LiClO₄:DMU = 1:4.0.

Clearly the eutectic temperatures of the LiClO₄-ethyleneurea composites are higher than that of the LiClO₄-acetamide system, suggesting that the structure of the organic molecule affects the thermal properties of the composite. OZO organic molecular possess the stable five-membered rings structure also. However, owing

to the electronegative differences among various atoms, the symmetry of molecular structure debases and the area of the charge delocalization extend. As a result, it can form a liquid system with a number of organic and inorganic compounds due to its 'water-like' physical properties [23]. Only one endothermic peak related to the eutectic temperature (-57.2°C) is observed in the DSC trace of the LiClO₄-OZO complex at molar ratio 1:4.5 in the measurement temperature range in Fig. 1.

Fig. 2 shows the eutectic temperatures of some binary complex systems. In comparison, the LiClO₄-ethyleneurea complex system has higher eutectic temperature than the other complex systems. Only the eutectic temperature of the LiClO₄-NMU and LiClO₄-OZO complex systems are below 0°C . The phenomena observed during sample preparation and the DSC results indicate that a eutectic system can be formed by mixing some organic compounds with LiClO₄.

3.2. Spectroscopic characterization

The vibration spectrum of acetamide has been extensively studied and the assignments of Ganeshsrinivas et al. based on experimental measurements and theoretical study are more reasonable and generally accepted [24]. The X-ray diffraction (XRD) analysis for OZO and the IR spectra of the hydrogen bond in OZO crystals have been reported [23,25,26] and applied in the recognition to the vibration spectra of OZO in this work.

Fig. 3A shows the IR spectra of the LiClO₄-acetamide complex with different molar ratios between 1530 and 1730 cm^{-1} . The band at 1682 and 1643 cm^{-1} is assigned to the C=O stretching mode and NH bending mode of acetamide, respectively. The C=O stretch-

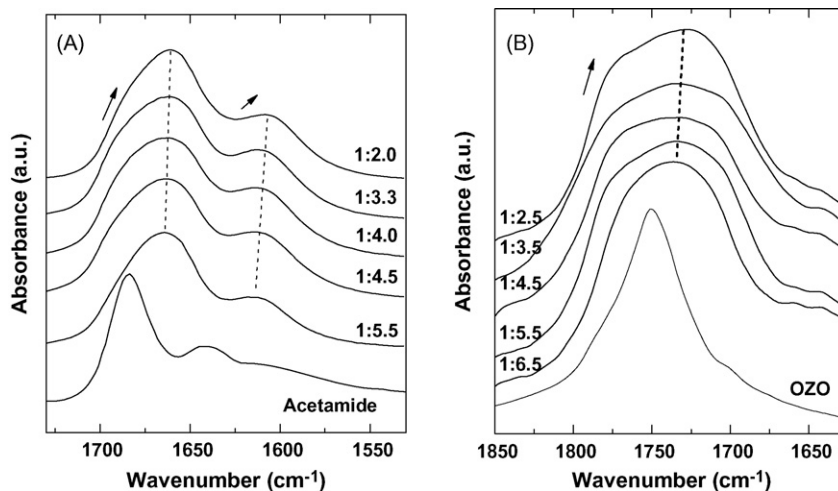
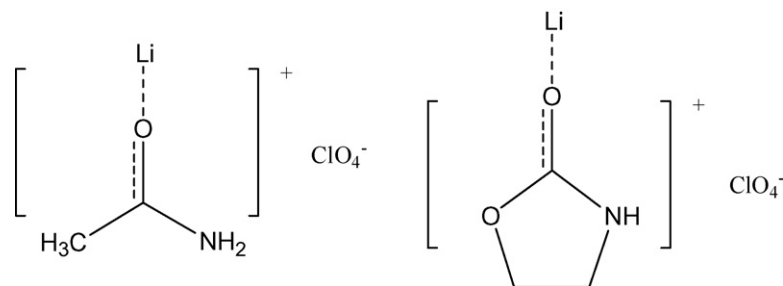


Fig. 3. Comparison of the FT-IR spectra of the $\nu(\text{C}=\text{O})$ and δNH mode of acetamide at various molar ratios of LiClO₄-acetamide (A) and the $\nu(\text{C}=\text{O})$ mode of OZO at various molar ratios of LiClO₄-OZO (B).



Scheme 2. Possible structure of complex electrolyte LiClO₄-acetamide and LiClO₄-OZO.

ing band changes significantly and located at 1666 cm⁻¹ upon introducing lithium perchlorate into the acetamide. The band at 1682 cm⁻¹ is broadened and red-shifted to 1666 cm⁻¹. The Li ions have a tendency to coordinate with the O atoms in the C=O group because these O atoms are negatively charged in the present complex system. This interaction results in the red-shifting of the C=O stretching mode. Fig. 3B shows the IR spectra of the LiClO₄-OZO complex with different molar ratios between 1620 and 1900 cm⁻¹. The strong band at 1751 cm⁻¹ in the IR spectrum of solid OZO is attributed to its C=O stretching, which is mainly affected with the neighboring nitrogen atom and oxygen atom. The nitrogen atom with free electrons pairs is very prone to be polarized and form p-π conjugation with the carbonyl group due to its (sp² + p) configuration in the solid state. Moreover, the strong electron-drawing oxygen possesses induction effect. Consequently, the frequency of this band is higher than that of the chain-structured acetamide and urea due to the tension effect of the five-membered rings of solid OZO [27]. The position of the C=O stretching band shift from 1751 to 1740 cm⁻¹ and are broadened with increasing LiClO₄ content in the complex owing to the influences of the Li⁺-oxygen coordination (see Scheme 2).

The molecules of solid acetamide or OZO are all associated with hydrogen bonding due to the coordination between the O atom on the C=O group and the H atom on the NH group (N-H...O). Obvious spectral changes are also observed throughout the spectra when solid acetamide or OZO is mixed with solid LiClO₄ and a homogeneous liquid is obtained. Table 2 lists the IR spectra of the symmetric (3170 cm⁻¹) and asymmetric (3330 cm⁻¹) stretching of NH of acetamide. Both bands blue-shift gradually with increasing LiClO₄ content and reach 3376 and 3455 cm⁻¹ for LiClO₄-acetamide = 1:2.0, respectively. These demonstrate the breaking of the hydrogen bonds among the acetamide molecules and the coexistence of the associated and non-associated (free) NH groups in the complex system. Similarly, the ν_{as}NH and ν_sNH of LiClO₄-OZO all shifted to higher frequency. These results suggest that the hydrogen bonding in OZO is weakened and even broken down due to the competitive Li⁺-oxygen interaction in concentrated complex. As a lactam, OZO does not have NH bending mode. The bands at 1643 in the IR spectrum are attributed to the NH bend-

ing of chain-structured acetamide, respectively. The NH bending band, be different from the NH stretching band, red-shifts due to the breaking of the hydrogen bonding among the acetamide molecules. All the bands shift to lower frequencies with the addition of lithium salt into the organic compounds. The red-shifting of the NH bending band is also originated from the destruction of the hydrogen bonding induced by the addition of LiClO₄.

It is a common feature for the acylamino group to take an important role in the interaction between the organic compound and LiClO₄ and the formation of a complex system. The acylamino groups work as a complexing agent for both the cations and the anions due to their polarity (C=O and NH₂) capable of coordinating with cations and anions, respectively, weakening and even breaking down the bonding between the Li⁺ cation and ClO₄⁻ anion, and resulting in the formation of complex system.

4. Electrochemical evaluation

Fig. 4 shows the relationship between conductivity and temperature of LiClO₄-acetamide and LiClO₄-OZO at various molar ratios, respectively. As can be seen, ionic conductivity increases with increasing temperature over the entire salt concentration studied. Of all the LiClO₄-based complex samples, the LiClO₄-acetamide electrolyte at molar ratio of 1:5.5 shows the highest ionic conductivity (i.e., 1.25 × 10⁻³ S cm⁻¹ at 25 °C and 11.5 × 10⁻³ S cm⁻¹ at 80 °C). For some recipes, this difference can be as high as one order of magnitude as summarized in Table 3.

Fig. 5 shows the Arrhenius plots of different binary complex systems. The Arrhenius plots of the LiClO₄-acetamide complex electrolyte are linear due to its low viscosity. However, the conductivity of the LiClO₄-OZO complex with the molar ratio of [OZO]/[LiClO₄], *n*, decreases from 6.5 to 2.5, clearly changes at various temperatures. It is clearly shows that there are critical points of the ionic conductivity in the different temperature. This behavior is mainly attributed to the formation of effective dissociation of LiClO₄ at low salt contents and the dramatic ion association at high salt contents. The formation of large amounts of contact ion pairs does not contribute to the ionic conductivity in the complex system. Another important reason for the quick decrease of conductivity is

Table 2

Frequencies and vibration assignments of the IR spectra of some complex samples and pure acetamide and OZO

Assignment ^a	LiClO ₄ -acetamide					Acetamide	LiClO ₄ -OZO					OZO	Intensity ^b
	1:2.0	1:3.3	1:4.0	1:4.5	1:5.5		1:2.5	1:3.5	1:4.5	1:5.5	1:6.5		
ν _{as} NH	3455	3444	3442	3442	3438	3330	3400	3395	3395	3393	3370	3271	m
ν _s NH	3376	3371	3369	3369	3365	3170	3268	3260	3258	3254	3250	3142	m
νCO	1660	1662	1662	1664	1666	1682	1727	1732	1732	1734	1736	1751	s
δNH	1608	1612	1614	1616	1617	1643	-	-	-	-	-	- ^c	s

^a The symbols in the above table have their usual meanings: ν for stretching, δ for bending, as for asymmetry, and s for symmetry.

^b Classification of intensity: m for middle and s for strong.

^c As a lactam, OZO does not have NH bending mode.

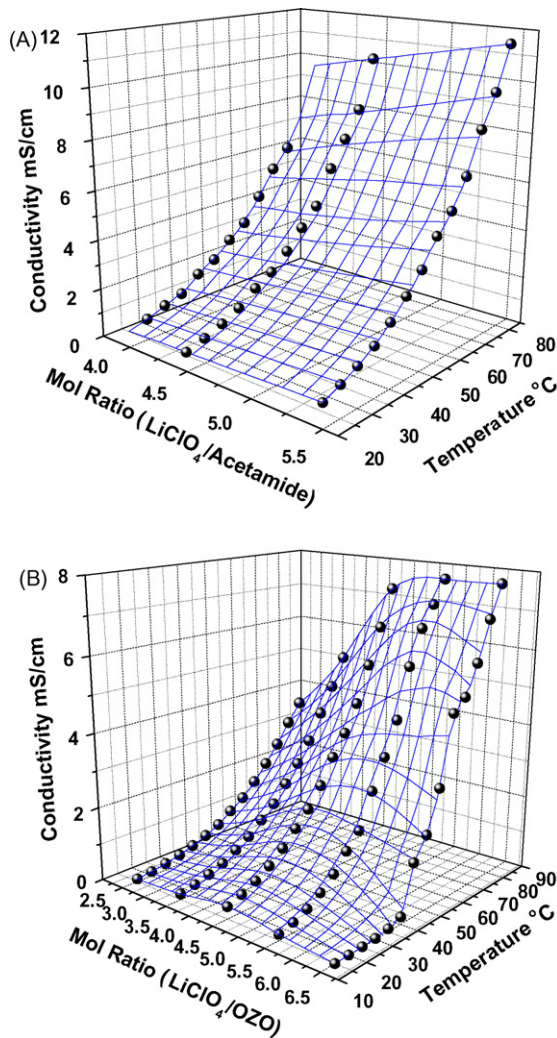


Fig. 4. Conductivity vs. temperature diagrams of LiClO_4 -acetamide (A) and LiClO_4 -OZO (B) at various molar ratios.

Table 3

Ionic conductivities for LiClO_4 -based complex samples with various molar ratios at different temperature (10^{-3} Scm^{-1})

Complex samples	25 °C	40 °C	60 °C
LiClO_4 -acetamide (1:4.0)	0.87	1.96	4.45
LiClO_4 -acetamide (1:4.5)	1.00	2.17	4.67
LiClO_4 -acetamide (1:5.5)	1.25	2.58	5.76
LiClO_4 -urea (1:2.0)	0.0002	0.001	0.01
LiClO_4 -urea (1:3.0)	0.25	0.80	3.18
LiClO_4 -urea (1:4.0)	0.07	0.63	4.61
LiClO_4 -NMU (1:2.0)	0.05	0.26	1.13
LiClO_4 -NMU (1:3.0)	0.07	0.33	1.28
LiClO_4 -NMU (1:4.0)	0.12	0.48	1.78
LiClO_4 -DMU (1:3.0)	- ^a	0.001	0.06
LiClO_4 -DMU (1:4.0)	- ^a	0.0005	0.23
LiClO_4 -ethyleneurea (1:4.0)	- ^a	0.06	0.30
LiClO_4 -OZO (1:2.5)	0.18	0.54	1.61
LiClO_4 -OZO (1:3.5)	0.35	0.94	2.51
LiClO_4 -OZO (1:4.5)	0.66	1.60	3.71
LiClO_4 -OZO (1:5.5)	0.43	1.43	4.37
LiClO_4 -OZO (1:6.5)	0.01	0.19	4.83

^a Ionic conductivity of the sample cannot be measured because it has been crystallized at 0 °C.

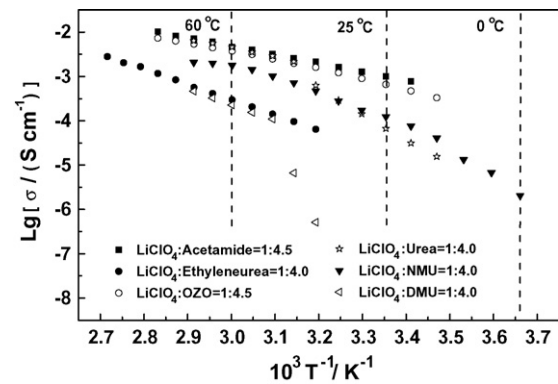


Fig. 5. The Arrhenius plots of different LiClO_4 -based binary complex systems.

the increasing viscosity of the complex system with increasing salt content.

Electrochemical stability windows of some complex electrolytes are determined by cyclic voltammetry at 25 °C and summarized in Table 4. The cyclic voltammograms of LiClO_4 -acetamide with a molar ratio of 1:5.5 on stainless steel electrodes are recorded. Reduction and oxidation peaks are observed at 1.5 and 4.35 V, respectively. Copper and aluminum foil are used as the working electrodes for electrochemical cells cycled between 0.0 and 3.0 V and between 3.0 and 5.0 V, respectively, to evaluate the electrochemical performance of the LiClO_4 -urea complex system with a molar ratio of 1:4.0. As for LiClO_4 -OZO complex electrolyte with a molar ratio of 1:4.5, an irreversible oxidation peak starts at 5.0 V and a reduction peak is observed at 1.5 V. Therefore, the electrochemical stability window of the molten salt is about 3.5 V.

In order to evaluate the performance of the complex system in practical electrochemical devices, an EDLC is assembled with LiClO_4 -acetamide complex system as the electrolyte. The voltammetry curves are roughly rectangular at a scan rate of 5 mV s^{-1} as shown in Fig. 6. A high specific capacitance of 84.2 F g^{-1} obtained by galvanostatic discharge (see Fig. 7) is higher than that of the LiTFSI -acetamide reported [27]. These performances are much better than those with aqueous electrolyte although not as good as that of the EDLCs with normal nonaqueous electrolytes at the moment. Coupled to their excellent properties such as high thermal stability and negligible vapor pressure, the complex systems are promising electrolyte candidates for the EDLCs and, probably, other electrochemical devices with high safety and stability.

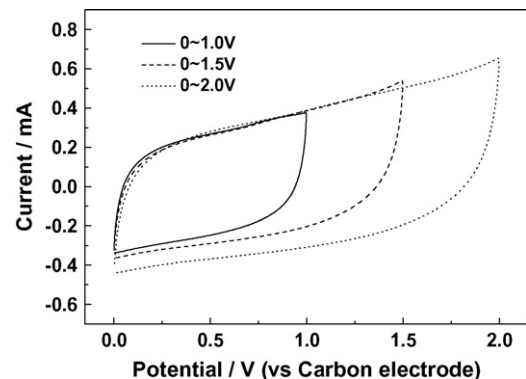


Fig. 6. Cyclic voltammetry curves at different potential range of EDLCs with LiClO_4 -acetamide (1:5.5) electrolyte (scan rate: 5 mV s^{-1}).

Table 4
Electrochemical stability window of some room-temperature complex samples

Complex samples	Stability window (V) (working electrode) ^a		Scan rate (mV s ⁻¹)
	φ_{red}	φ_{ox}	
LiClO ₄ -acetamide (1:5.5)	1.5 (stainless steel)	4.35 (stainless steel)	0.1
LiClO ₄ -urea (1:4.0)	0.8 (Cu foil)	3.8 (Al foil)	0.2
LiClO ₄ -OZO (1:4.5)	1.5 (platinum foil)	5.0 (platinum foil)	2

^a Measured at 25 °C with Li foil as reference and counter electrodes.

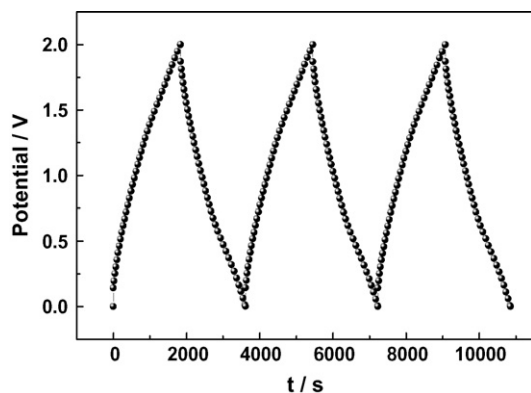


Fig. 7. Galvanostatic charge-discharge curves of EDLCs with LiClO₄-acetamide (1:5.5) electrolyte (voltage range: 0–2 V, current, 0.36 mA).

5. Conclusions

A series of novel room-temperature complex electrolytes based on LiClO₄ and organic substances with acylamino groups have been prepared and characterized. Some of these complex electrolytes are stable liquids and some are supercooled liquids at room-temperature though both the salt and the organic compounds are solid. The formation mechanism of the complex systems are due to the strong interaction between the O atom of the C=O group in the organic compounds and the Li cations in addition to the interaction of the ClO₄⁻ anions with the NH group in the organic compounds via hydrogen bonding. Some complex systems exhibit favorable physicochemical properties as potential electrolytes. In comparison, the ionic conductivity of the LiClO₄-acetamide and LiClO₄-OZO composite is about one order higher than that of other complex systems. In addition, CV analysis shows that the electrochemical windows of these samples are all over 3 V. Finally, EDLC with the LiClO₄-acetamide complex system as the electrolyte shows a high specific capacity, indicating that the complex system is a promising candidate of electrolyte for the EDLCs.

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