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Electrical conductivity of REF_3-LiF (RE=La and Nd) molten salts☆

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ABSTRACT

The electrical conductivity of REF_3-LiF (RE = La and Nd) molten salts ($x$$REF_3$ = 5 mol%–40 mol%) was systematically measured over the temperature range from 1223 to 1423 K by using continuously varying cell constant (CVCC) method. Electrical conductivity values of LaF_3-LiF and NdF_3-LiF molten salts within the studied ranges are 4.11–9.39 and 3.62–9.51 S/cm, respectively. The composition and temperature dependences of electrical conductivity and the factor of RE_2O_3 on electrical conductivity were investigated. The electrical conductivity nonlinearly decreases with the increasing mole percent of REF_3 for the changing of structural ion in molten salts. A good linear relationship between the natural logarithm of electrical conductivity ($\ln\kappa$) and the reciprocal of the absolute temperature (T^{-1}) can be interpreted by the trend that electrical conductivity linearly increases with increasing temperature. Although it is an important factor of RE_2O_3 on electrical conductivity, the influence of RE_2O_3 on conductivity is small for the very limited solubility of RE_2O_3 in REF_3-LiF molten salts. The results of this work supplement the present electrical conductivity data of rare earth fluoride electrolyte.

1. Introduction

Electrolysis raw material of RE_2O_3 in REF_3-LiF molten electrolyte has an important role in producing rare earth metal and its alloys in modern industry.[1–3] Moreover, REF_3-LiF is not only the foundation system of developing novel and green electrolysis technology and equipment (submerged-liquid cathodic rare earth electrolysis process,[4–7] simulations of novel electrolytic cell[8–10]), but also very significant for its potential use in the extraction lanthanum (RE) components from molten salts in the general frame of reprocessing nuclear wastes.[11–13] However, its application has been restricted by unclear physicochemical properties, such as liquidus temperature, viscosity and electrical conductivity. Electrical conductivity of molten electrolyte is an essential knowledge for understanding molten structural and electromigration mechanism, which has been carefully investigated for its great significance in the application,[14] nevertheless the fundamental data are still not sufficient or unambiguous. The REF_3-LiF system is an especially obvious example. The previous references related are very limited.[15–18] So, study on the electrical conductivity of the REF_3-LiF system is of both scientific and practical interest.

The continuously varying cell constant (CVCC) is one type of advanced technique for measurements of electrical conductivity of high temperature molten salts with strong corrosion. The previous reports cover several electrolyte systems, such as molten salts based on cryolitic,[19–26] NdF_3-LiF-Nd_2O_3 system[15,17,27] and some others.[28–32] Its inventors Wang et al.[19] considered that the total resistance of the circuit was composed of molten salt resistance, electrode and wire resistance and polarization resistance in series. For a fixed frequency of the AC, the total resistance will change linearly with the conductivity cell constant. If the conductivity cell constant change is determined by the length of conductance cell, the linear coefficient is a constant. So, the molten salt conductivity can be obtained by the following formula:

$$\kappa = \frac{1}{A\left(\frac{dZ'}{dL}\right)} \tag{1}$$

where the κ is molten salt conductivity, S/cm; dZ'/dL, slope of the resistance of the measuring circuit versus the cell length; A, inner cross-sectional area of conductance cell, cm^2 (In practice, A is determined by the dZ'/dL of standard molten salt).

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In view of this, this work dedicated research on electrical conductivity of REF_3-LiF (RE = La and Nd) electrolyte system. By using AC impedance technology combining CVCC method, the temperature and composition dependences of electrical conductivity of REF_3-LiF molten salts were systematically investigated. By considering the significant influence of RE_2O_3 on physicochemical properties of the molten system, the electrical conductivity factor of RE_2O_3 was also investigated, so as to quest for suitable addition system in practical electrolysis production.

2. Experimental

2.1. Preparation

All of the chemicals were analytically pure (Table 1). Na_3AlF_6, REF_3, LiF and RE_2O_3 (RE = La and Nd) were dried at 393 K for over 24 h before being used. Because of strongly corrosive and high temperature of the molten salts, the crucible was made of high-purity graphite material, the conductivity cell was made of a pyrolytic boron nitride (BN) tube and the working electrode was made of platinum material. The experimental device (type CM-1 comprehensive testing device for high temperature molten salts) and its details of conductivity testing part are shown in Fig. 1, which is designed and developed by Northeastern University of China. The high-purity argon was needed to be put into the furnace to protect the equipment from oxidation. The AUTOLAB PGSTAT30 was used for testing the cell impedance. AC frequency signal and impedance numeration were controlled by a PC. The frequency was varied from 100 Hz to 100 kHz with voltage perturbation of 10 mV, and according to the previous work,[15,17] the frequency was set at 10 kHz.

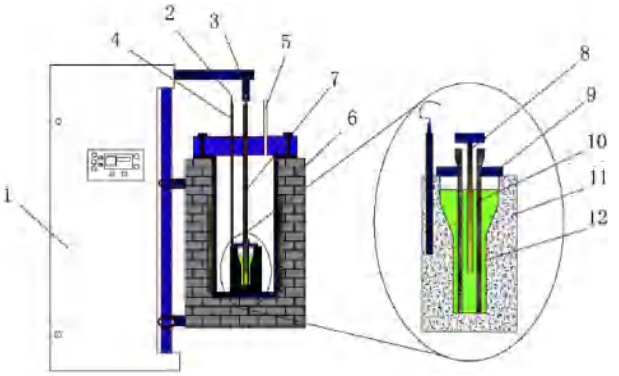

Fig. 1. Conductivity testing device. 1- CM-1 comprehensive test instrument for molten salts; 2- Thermocouple; 3- Electrode clamp; 4- reference electrode/counter electrode; 5- Argon inlet; 6- High temperature furnace; 7- Corundum tube for insulation protection; 8- Platinum electrode; 9- High purity graphite cover; 10- Pyrolytic boron nitride (BN) tube; 11- High purity graphite crucibles; 12- Molten salts.

2.2. Processes

The inner cross-sectional area A of conductance cell was calibrated by pure molten cryolitic (Na_3AlF_6) at 1273 K. By using the reference conductivity value 2.80 S/cm, area A of the designed conductance cell in this study was 16.24 mm^2. The total resistance of melt to be tested is related to the length of the cell. We can get the value of dZ'/dL by continuously varying the length of the cell. In this study, each step varying set at 5 mm and 5 steps for each test. REF_3-LiF samples by mass of 100 g in which the mole percent of REF_3 was in the range of 5 mol%–40 mol% were prepared, and the testing temperatures were 1223–1423 K which was specifically chosen for meeting the actual electrolysis temperature (about 1323 K). During the test on electrical conductivity factor of RE_2O_3, the variation of RE_2O_3 mass per 100 g REF_3-LiF melt were 0, 0.5, 1, 1.5, 2 and 2.5 g, respectively.

3. Results and discussion

3.1. Electrical conductivity of REF_3-LiF molten salts

In the present study, one of the specific purposes was determining the electrical conductivity of REF_3-LiF (RE = La and Nd) molten salts by repeated experiment. Then the composition and temperature dependences of electrical conductivity were systematically investigated based on a large number of experiment data. The testing conditions, parameters and results according to the designed experiment in advance are shown in Tables 2 and 3. Because the liquidus temperatures of REF_3-LiF molten salts with some compositions ($x$$LaF_3$ = 30 mol%–40 mol%, $x$$NdF_3$ = 40 mol%) are higher than the designed test temperature, the corresponding electrical conductivity data are not shown in Tables 2 and 3

Analysis of our results listed in Tables 2 and 3 reveals several aspects: electrical conductivity values of LaF_3-LiF and NdF_3-LiF molten salts ($x$$REF_3$ = 5 mol%–40 mol%, T = 1223–1423 K) are 4.11–9.39 and 3.62–9.51 S/cm, respectively, which is a widely available range of selection of reasonable electrolyte. Differences between the measured electrical conductivity values of LaF_3-LiF and NdF_3-LiF under the same ratio of REF_3 and temperature are quite small, an average of 0.12 S/cm. The previous research has reported electrical conductivity values of CeF_3-LiF, SmF_3-LiF and YF_3-LiF molten salts.[14] Electrical conductivity values of CeF_3-LiF ($x$$CeF_3$ = 12 mol%–30 mol%, T = 1270–1340 K), SmF_3-LiF ($x$$SmF_3$ = 10 mol%–50 mol%, T = 1270–1340 K) and YF_3-LiF ($x$$YF_3$ = 19 mol%–60 mol%, T = 1260–1340 K) molten salts are 5.69–8.13, 3.87–8.18 and 2.92–6.75 S/cm, respectively. Comparing the measured values in the present paper with these values of similar molten salts, one can easily find similar changing rule of rare earth fluoride electrolyte, and small differences of electrical conductivity between each other. The parallel physiochemical properties and similar molten ion-cluster structure may contribute

Table 1
Experimental reagents.[a]

Reagents	Purity/wt%	Manufacturer
LaF_3	>99%	Grirem Advanced Materials Co.,Ltd
NdF_3	>99%	Grirem Advanced Materials Co.,Ltd
La_2O_3	>99%	Grirem Advanced Materials Co.,Ltd
Nd_2O_3	>99%	Grirem Advanced Materials Co.,Ltd
LiF	>99%	Sinopharm Chemical Reagent Co.,Ltd
Na_3AlF_6	>99%	Sinopharm Chemical Reagent Co.,Ltd

[a] All chemicals are standard reagents and with purity stated by manufacturers.

Table 2
Electrical conductivity of LaF_3-LiF molten salts, S/cm (p = 100 kPa).[a]

T (K)	$x$$LaF_3$ (mol%)							
	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
1223.0	8.40	7.24	5.95	4.82	4.35	/	/	/
1248.0	8.51	7.38	6.08	4.97	4.46	/	/	/
1273.0	8.63	7.50	6.17	5.10	4.60	4.16	/	/
1298.0	8.76	7.58	6.32	5.27	4.74	4.31	/	/
1323.0	8.88	7.71	6.43	5.37	4.87	4.43	4.11	/
1348.0	8.98	7.85	6.56	5.48	5.02	4.59	4.25	/
1373.0	9.11	7.96	6.72	5.67	5.15	4.71	4.37	4.15
1398.0	9.25	8.13	6.83	5.76	5.31	4.85	4.50	4.32
1423.0	9.39	8.27	6.94	5.96	5.45	4.98	4.64	4.45

[a] Standard uncertainties u are $u(T) = 0.2$ K, $u(p) = 0.7$ kPa, u ($x$$LaF_3$) = 0.1% and the combined expanded uncertainty $U_c(\kappa) = 0.05$ S/cm (0.95 level of confidence).

Table 3
Electrical conductivity of NdF_3-LiF molten salts, S/cm (p = 100 kPa).[a]

T (K)	$xNdF_3$ (mol%)							
	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
1223.0	8.53	7.41	6.17	5.11	4.43	4.01	3.62	/
1248.0	8.65	7.54	6.29	5.24	4.59	4.13	3.76	/
1273.0	8.77	7.65	6.39	5.39	4.72	4.25	3.91	3.65
1298.0	8.90	7.76	6.52	5.53	4.86	4.37	4.05	3.80
1323.0	9.01	7.88	6.61	5.64	5.01	4.50	4.17	3.94
1348.0	9.14	7.97	6.73	5.75	5.12	4.63	4.31	4.08
1373.0	9.27	8.12	6.84	5.88	5.24	4.78	4.45	4.21
1398.0	9.38	8.24	6.98	6.02	5.33	4.92	4.58	4.37
1423.0	9.51	8.37	7.11	6.13	5.48	5.03	4.72	4.52

[a] Standard uncertainties u are $u(T) = 0.2$ K, $u(p) = 0.7$ kPa, u ($xNdF_3$) = 0.1% and the combined expanded uncertainty $U_c(\kappa) = 0.05$ S/cm (0.95 level of confidence).

to the above comparison which will be discussed in the following sections. The measured values reported in this paper supplemented the experimental data on electrical conductivity of rare earth fluoride electrolytes.

3.2. Composition dependence of electrical conductivity

Electrical conductivity as one significant physiochemical property that varies with the composition of the molten system. Consequently, electrical conductivity isotherms of LaF_3-LiF and NdF_3-LiF molten salts for 1223, 1273, 1323, 1373 and 1423 K are presented in Figs. 2 and 3, respectively. Curves in the figures show the composition dependence of electrical conductivity. At a certain temperature, the electrical conductivity of REF_3-LiF (RE = La and Nd) molten salts decreased with the increasing content of REF_3 which were the same results as the previous studies,[15–18,27] but it was also different from the previous viewpoint that the changing tendency did not follow the simple linear rule. The nonlinear curves drawn in the figures give an accent that there are different areas of conductivity dependence on composition. The slopes of the curves with higher values before mole percent of REF_3 reached 20 mol%, and then grew smaller with increasing mole percent of REF_3. The changing ion-cluster structure with increasing content of REF_3 in the system might be the primary cause for above change.

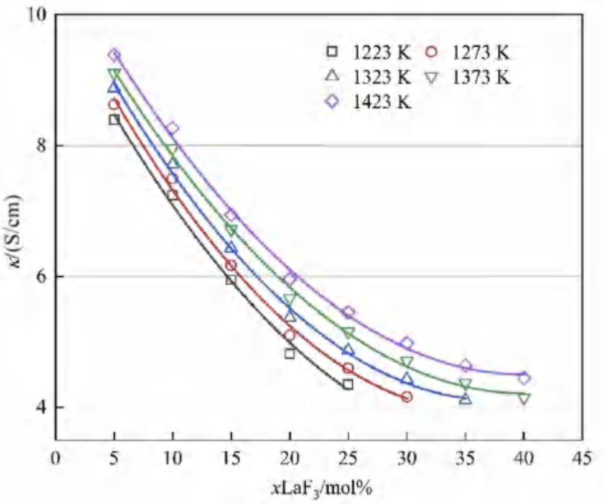

Fig. 2. Isotherms of specific conductivity vs. mole percent of LaF_3 melts from the LaF_3-LiF system at different temperatures.

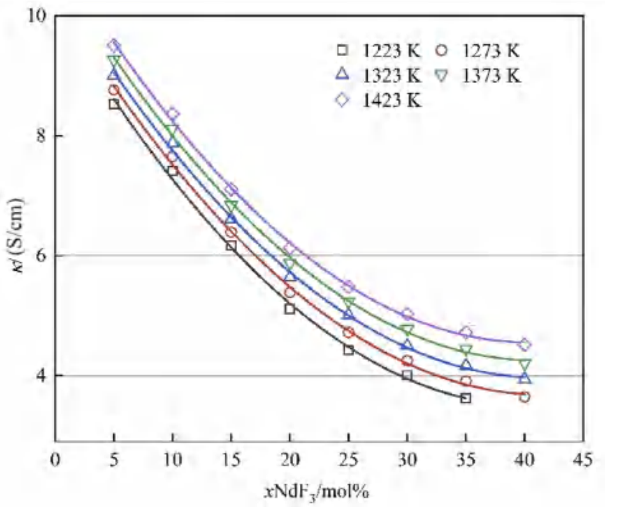

Fig. 3. Isotherms of specific conductivity vs. mole percent of NdF_3 melts from the NdF_3-LiF system at different temperatures.

According to the previous literatures on the ionic structure of molten salts,[15,33–36] four different dissolution models of NdF_3 in LiF molten salt were as follows:

$$\text{Model I}\quad NdF_3+3F^- = NdF_6^{3-} \tag{2}$$

$$\text{Model II}\quad NdF_3+2F^- = NdF_5^{2-} \tag{3}$$

$$\text{Model III}\quad NdF_3+F^- = NdF_4^- \tag{4}$$

$$\text{Model IV}\quad NdF_3+1/2F^- = 1/2Nd_2F_7^- \tag{5}$$

Eqs. (2)–(5) show that the REF_3-LiF molten salts have complicated ion-cluster structure and perhaps consist of multiple RE-F ion-clusters. The lasted study on Raman spectroscopy of NdF_3-LiF-Nd_2O_3 molten salts[15,33] showed that ions of NdF_6^{3-} and $NdF_4{}^-$ coexisted in the NdF_3-LiF molten system. The ratio of $NdF_6^{3-}/NdF_4{}^-$ decreased with increasing NdF_3 according to the quantitative analysis by calculation from the determined values of density. Take the case of 1006 °C, the ratio of $NdF_6^{3-}/NdF_4{}^-$ decreased from 0.78 to 0.30 with increasing NdF_3 from 30 mol% to 40 mol%. Ion NdF_6^{3-} has a bigger volume than $NdF_4{}^-$ at a certain temperature, which causes NdF_6^{3-} to have weaker ionic motion than $NdF_4{}^-$. It can be simply assumed that the molten system was composed of Li^+, F^-, NdF_6^{3-} and $NdF_4{}^-$ and the lower ratio of $NdF_6^{3-}/NdF_4{}^-$ contributed to a relatively higher conductivity for a certain content of NdF_3. So, the conductivity decreased with increasing NdF_3, and the rate gradually decreased with decreasing ratio of $NdF_6^{3-}/NdF_4{}^-$. Considering the similarity of lanthanum and neodymium studied in this work, we hold the opinion that electromobility difference between REF_6^{3-} and $REF_4{}^-$, and the changing ratio of $REF_6^{3-}/REF_4{}^-$ from lower to higher concentration of REF_3 led to the complicated conductivity dependence on composition.

Electrical conductivities of LaF_3-LiF and NdF_3-LiF molten salts should be compared with conductivities of molten salts from other REF_3-LiF systems (RE-lanthanide). We found in the literature[14] the following ones: Ce, Sm and Y. A comparison is presented in Fig. 4 for temperature of 1340 K. Presented in Fig. 4 curves seem rather similar changing tendency that electrical conductivity gradually and nonlinearly decreased with increasing mole percent of REF_3. But it may be also noticed that with the

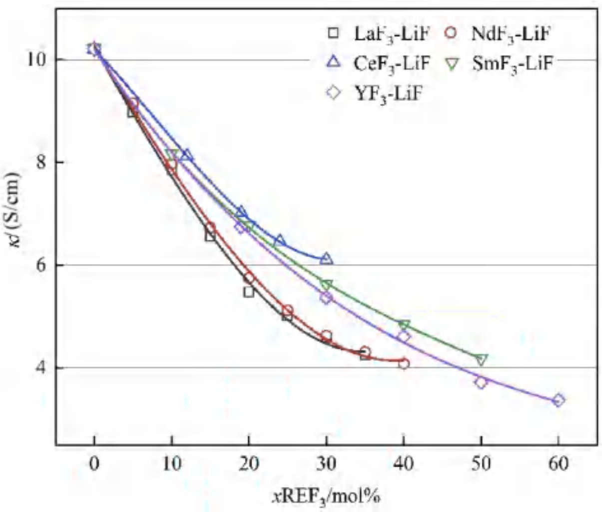

Fig. 4. Specific conductivity vs. REF_3 mole percent of melts from the REF_3-LiF system at 1340 K, according to: Ce, Sm, Y.[14] Data for LaF_3-LiF and NdF_3-LiF systems are from this work.

increase of mole percent of REF_3 conductivity distinctly slows down in decreasing (after 20 mol%–30 mol% of REF_3) which is similar changing with KCl-$RECl_3$ system.[37] Finally, conductivities of LaF_3-LiF and NdF_3-LiF molten salts measured in present study seem slightly less than values of similar systems from previous literature. For instance, when the mole percent of REF_3 was 10%, the conductivities of CeF_3-LiF, SmF_3-LiF and YF_3-LiF systems were higher than the LaF_3-LiF system by 0.87, 0.63 and 0.66 S/cm, and higher than the NdF_3-LiF system by 0.57, 0.33 and 0.36 S/cm, respectively. When the mole percent of REF_3 was 30%, the differences reached a maximum which were 1.52, 1.04 and 0.78 S/cm for LaF_3-LiF system and 1.48, 1 and 0.74 S/cm for NdF_3-LiF system. These differences may be ascribed to differences of physicochemical properties among systems and technical differences of test methods.

3.3. Temperature dependence and activation energy of electrical conductivity

Temperature is usually one of the most critical factors on physiochemical properties of molten salts. The conductivity of the molten salt is mainly determined by ion movement, and the temperature is one of the most important factors on the ion movement. That is to say, we take into account general, ionic mobility in the molten system with a certain composition usually determined by temperature. So, the temperature dependence of the electrical conductivity of molten salts of predominant ionic characteristic is given in the form of a classical Arrhenius equation[15,37,38]:

$$\kappa = A\exp(-\frac{E}{RT}) \tag{6}$$

where κ is the specific conductivity, A the coefficient related to chemical composition of 161 molten salt, E the activation energy of conductance, T the temperature of the molten salt and R the universal gas constant in 8.314 J/(mol·K).

In Eq. (6), A and E are temperature-independent parameters which can be treated as a constant for a certain molten system. So, Eq. (6) can be written in the logarithm form as follows:

$$\ln\kappa = \ln A - \frac{E}{RT} \tag{7}$$

Eq. (7) can also be simplified as the following equation:

$$\ln\kappa = a \times \frac{1}{T} + b \tag{8}$$

According to Eq. (8), one can distinctly find a linear relation between $\ln\kappa$ and T^{-1}. By using the measured values of electrical conductivity in this work, dependence of conductivity of LaF_3-LiF and NdF_3-LiF molten salts on temperature is presented in Figs. 5 and 6, respectively.

A good linear relationship (more than half plots with an $R^2 \geq 0.99$) can be obviously found between $\ln\kappa$ and T^{-1} of the given compositions of the two systems from Figs. 5 and 6, and the electrical conductivity of molten salts increases with increasing temperature. When the temperature increases by 1 K, the electrical conductivity increases average by 0.005 S/cm. The higher the corresponding temperature, the more strengthened ion motion, the stronger kinetic energy, the lower dissociation energy, the longer distance and the weaker attractive force between cations and anions. This means that directional movement of ion is easier at higher temperature. What is more, the number of free ions increases because of decomposition of more ion complexes with increasing temperature. Decomposition of the ion complexes increases the ion mobility and thereby increases the electrical conductivity.

According to Eqs. (7) and (8), the linear fitting parameters of curves presented in Figs. 5 and 6 can be used to calculate the activation energy of conductance E (E is the product of absolute value of the slope a and constant R). The results of LaF_3-LiF and NdF_3-LiF systems are shown in Tables 4 and 5, respectively. Then the electrical conductivity of molten salts for different compositions and temperature can be obtained by using Eq. (7) with minimized experimental efforts and difficult experiment conditions.

3.4. Electrical conductivity factor of RE_2O_3

In the practical production, RE_2O_3 needs to be continuously added in the fluoride electrolyte for supplementing the consumption. So, we became interested in studying influence of RE_2O_3 (RE = La and Nd) on electrical conductivity of electrolyte system. But the knowledge of dissolution of RE_2O_3 in the molten salt is important for a good understanding of its influence on conductance. According to the previous studies on REF_3-LiF-RE_2O_3 molten

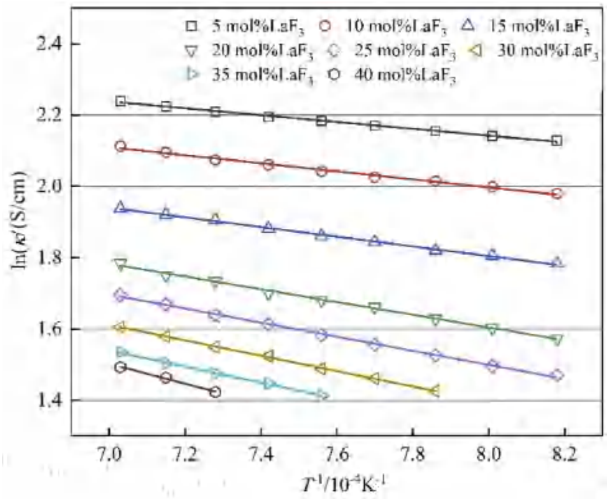

Fig. 5. Temperature dependence of specific conductivity (κ) of LaF_3-LiF melts (mole percent of LaF_3 are given in the figure) fitted with Arrhenius equation (Eq. (6)).

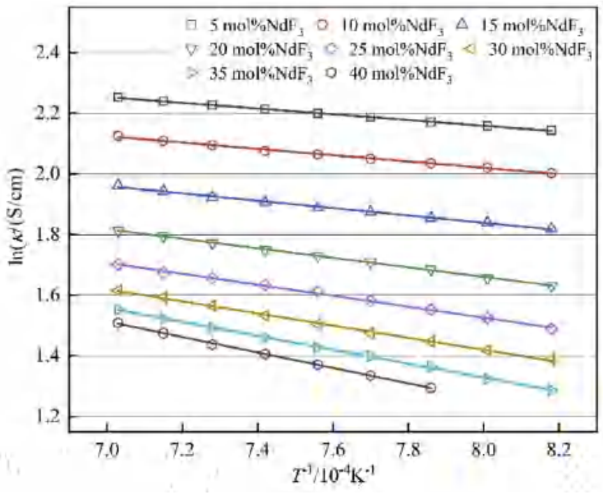

Fig. 6. Temperature dependence of specific conductivity (κ) of NdF_3-LiF melts (mole percent of NdF_3 are given in the figure) fitted with Arrhenius equation (Eq. (6)).

Table 4
Parameters of Eq. (7)-temperature dependence of conductivity of melts from LaF_3-LiF system.

$xLaF_3$ (mol%)	T (K)	ln(A/(S/cm))	E(kJ·mol)
5	1223–1423	2.91 ± 0.02	7.97 ± 0.19
10	1223–1423	2.90 ± 0.03	9.38 ± 0.32
15	1223–1423	2.89 ± 0.02	11.29 ± 0.22
20	1223–1423	3.03 ± 0.03	14.86 ± 0.35
25	1223–1423	3.08 ± 0.03	16.45 ± 0.28
30	1273–1423	3.13 ± 0.02	17.98 ± 0.21
35	1323–1423	3.12 ± 0.04	18.72 ± 0.42
40	1373–1423	3.46 ± 0.13	23.25 ± 1.48

Table 5
Parameters of Eq. (7)-temperature dependence of conductivity of melts from NdF_3-LiF system.

$xNdF_3$ (mol%)	T (K)	ln(A/(S/cm))	E(kJ·mol)
5	1223–1423	2.91 ± 0.01	7.86 ± 0.10
10	1223–1423	2.85 ± 0.02	8.66 ± 0.19
15	1223–1423	2.81 ± 0.02	10.08 ± 0.23
20	1223–1423	2.92 ± 0.01	13.09 ± 0.15
25	1223–1423	2.98 ± 0.03	15.07 ± 0.29
30	1223–1423	3.02 ± 0.02	16.60 ± 0.27
35	1223–1423	3.16 ± 0.01	19.04 ± 0.13
40	1273–1423	3.30 ± 0.02	21.19 ± 0.27

salt,[15,33,39–41] the dissolution of RE_2O_3 is a complex process, and especially its solubility is very limited. Using the data of solubility, a reasonable range of addition amount of RE_2O_3 and composition was chosen for study. On this basis, different mass of RE_2O_3 was added in REF_3-LiF system with different compositions at fixed temperature 1323 K to investigate the influence of RE_2O_3 on conductance. The results are shown in Figs. 7 and 8.

Figs. 7 and 8 show influence of RE_2O_3 on electrical conductivity of REF_3-LiF-RE_2O_3 molten salt with different compositions. It can be seen that electrical conductivity decreased with increasing content of RE_2O_3 and REF_3 in molten system. When the content of RE_2O_3 was fixed, the changing law of electrical conductivity with variable of REF_3 was similar to the pure REF_3-LiF system. It is different from the influence of REF_3 on conductivity with nonlinear changing, RE_2O_3 got a good linear relationship with conductivity. Although both additions of NdF_3 and RE_2O_3 can decrease concentration of F^- in system, this difference should be ascribed to the fact that the increasing REF_3 can obviously change the ratio of REF_6^{3-}/REF_4^- and the very limited addition of RE_2O_3 has a weak influence on the ratio of $RE_2OF_{10}^{6-}/REOF_5^{4-}$. Based on the assumption that the ionic structure of the two kinds REF_3-LiF-RE_2O_3 (RE = La and Nd) molten salts is similar, influence of increasing content of RE_2O_3 on REF_3-LiF-RE_2O_3 system with a certain composition can be comprehensively analyzed as follows. According to the ionic theory, RE_2O_3 is an alkaline oxide, which promoted the disbanding of the complex ions and forming the new complex anions in the REF_3-LiF molten salt system. Raman spectroscopy of the NdF_3-LiF-Nd_2O_3 molten salts[15,33] shows that ions of NdF_6^{3-} and NdF_4^- coexist in the NdF_3-LiF system, $NdOF_5^{4-}$ and $Nd_2OF_{10}^{6-}$ are most possible Nd—O—F complicated ion-cluster in NdF_3-LiF-Nd_2O_3 molten salts. On the basis, the dissolution reaction of Nd_2O_3 in NdF_3-LiF molten system has four possible reactions as follows:

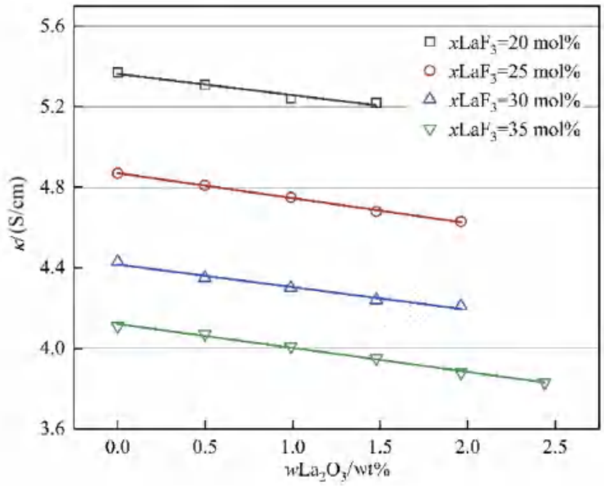

Fig. 7. Influence of La_2O_3 content on conductance of LaF_3-LiF-La_2O_3 molten salt.

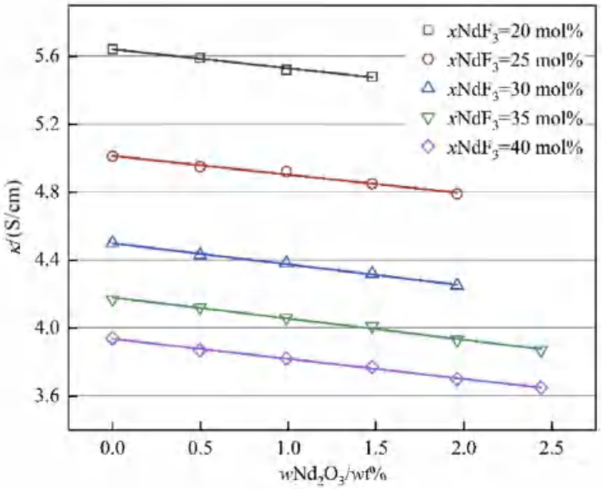

Fig. 8. Influence of Nd_2O_3 content on conductance of NdF_3-LiF-Nd_2O_3 molten salt.

$$Nd_2O_3+NdF_4^-+11F^-=3NdOF_5^{4-} \tag{9}$$

$$Nd_2O_3+4NdF_4^-+14F^-=3Nd_2OF_{10}^{6-} \tag{10}$$

$$Nd_2O_3+NdF_6^{3-}+9F^- = 3NdOF_5^{4-} \tag{11}$$

$$Nd_2O_3+4NdF_6^{3-}+6F^- = 3Nd_2OF_{10}^{6-} \tag{12}$$

On the one hand, it can be seen from Eqs. (9)−(12) that no matter which reaction the dissolution process followed, the conductive carrier of F^- was decreased by forming the new ion-cluster , and the decreased concentration of F^- most probably contributed to the decreasing of electrical conductivity. On the other hand, the newly formed RE−O−F ion-cluster has a bigger volume than RE−F, which may also result in increasing directional migration resistance of another conductive carrier of Li^+. So, it is obvious that electrical conductivity decreased with increasing content of RE_2O_3. But the influence of RE_2O_3 on conductivity was relatively small for the very limited solubility of RE_2O_3 (less than 3 wt%).[41] Within the range of this work, When the content of RE_2O_3 increases by 0.5 wt%, electrical conductivity decreases by average of 0.05 S/cm. What is more, it could be found from Figs. 7 and 8 that the influence of REF_3 on conductivity with a certain content of RE_2O_3 should not be overlooked. Take the case of REF_3 content that increased from 25 mol% to 30 mol%, the conductivity of LaF_3-LiF-La_2O_3 and NdF_3-LiF-Nd_2O_3 system decreased by about 0.42 and 0.51 S/cm, respectively. This is in accordance with previous literatures that REF_3 is a significant factor on physicochemical properties of its molten salts, such as electrical conductivity, density, viscosity and surface tension.[39,42−44] Therefore, to control the addition of RE_2O_3 within its solubility and select the reasonable ratio of REF_3 is crucial for the satisfaction of requirement in electrical conductivity of electrolyte in the practical production.

4. Conclusions

The electrical conductivity of REF_3-LiF (RE = La and Nd) molten salts ($x$$REF_3$ = 5 mol%−40 mol%) was systematically measured over the temperature range from 1223 to 1423 K by using CVCC method. The composition and temperature dependences of electrical conductivity and the influence of RE_2O_3 (RE = La and Nd) on electrical conductivity are discussed. The results supplement the present electrical conductivity data of rare earth fluoride electrolyte, and the conclusions can be summarized as follows:

(1) Electrical conductivity values of LaF_3-LiF and NdF_3-LiF molten salts ($x$$REF_3$ = 5 mol%−40 mol%, T = 1223−1423 K) are 4.11−9.39 and 3.62−9.51 S/cm, respectively. At a certain temperature, the electrical conductivity nonlinearly decreases with the increasing mole percent of REF_3, which is tightly tied to the changing of ion-cluster structure in molten salts.

(2) The temperature dependence of the electrical conductivity of REF_3-LiF molten salts is well consistent with the classical Arrhenius equation that the natural logarithm of electrical conductivity ($\ln\kappa$) is plotted against the reciprocal of the absolute temperature (T^{-1}), which can be interpreted by a linear relationship. The electrical conductivity linearly increases with increasing temperature.

(3) It is an important factor of RE_2O_3 on electrical conductivity for the complex dissolution reaction that to form different RE−O−F ion-clusters. Within the range of this work, when the content of RE_2O_3 increases by 0.5 wt%, electrical conductivity decreases by average of 0.05 S/cm. But because of the very limited solubility of RE_2O_3, the influence of RE_2O_3 on conductivity is small.

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