Determination of Liquidus Temperature of Aluminium Electrolysis Electrolyte by Conductivity Method

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Abstract

This paper introduces a method to determine the liquidus temperature based on electrical conductivity variation curves, designed to overcome the challenges in measuring the liquidus temperature of low-temperature aluminium electrolysis electrolyte in the NaF-KF-AlF_3 system. The conductivity of molten electrolyte is measured at multiple temperature points within a defined range both above and below the presumed liquidus temperature using the Continuous Variation of Cell Constant method (CVCC). The liquidus temperature is then identified from the "inflection point" on the conductivity-temperature variation curve. This method was applied to industrial electrolytes, and the results were compared with those obtained via the stepwise cooling curve method, showing a deviation less than 0.17 %, thus validating the method accuracy. Additionally, this method was used to determine the liquidus temperature of the NaF-KF-AlF_3 system at various molecular ratios, revealing clear and consistent patterns. This method is applicable to various electrolyte systems and has the advantage of measuring both liquidus temperature and electrical conductivity.

Keywords: Low-temperature aluminium electrolysis electrolyte, Liquidus temperature, Bath Conductivity, CVCC method, NaF-KF-AlF_3 system.

1. Introduction

The liquidus temperature of aluminium electrolysis electrolyte is a critical parameter in aluminium electrolysis production [1, 2], as it governs the temperature control during the electrolysis process. Common experimental approaches for determining this temperature include visual observation [3, 4], stepwise cooling curve method [5–7], and differential thermal analysis [8, 9]. The visual observation method incurs substantial errors due to factors such as electrolyte volatilization and subjective interpretation by the experimenter. Therefore, the stepwise cooling curve method or differential thermal analysis is commonly used to measure the liquidus temperature of electrolytes. The principles of the stepwise cooling curve method and differential thermal analysis are basically the same; that is, the electrolyte is first melted in a high-temperature-resistant crucible, and then a temperature sensor immersed in the molten electrolyte tracks the temperature changes of the electrolyte. Due to heat release during the phase change solidification process of the electrolyte, an inflection point appears on the cooling curve of the electrolyte, which helps determine the liquidus temperature of the electrolyte.

Traditional industrial electrolytes are mainly composed of sodium cryolite, excess AlF_3, CaF_2 and alumina, with relatively straightforward electrolyte compositions. The inflection point on the cooling curve during their cooling process is more distinct and clearer, allowing the stepwise cooling curve method or differential thermal analysis to accurately measure the liquidus temperature of these electrolytes. However, for electrolytes in the NaF-KF- AlF_3 system, especially at low molecular ratios, there is no distinct inflection point on the cooling curve, or the inflection point is not at the liquidus temperature. The presumed reason is that during the cooling and solidification process of molten electrolyte in the NaF-KF- AlF_3 system, multiple phases such as $KAlF_4$, K_2NaAlF_6, $K_2NaAl_3F_{12}$, $Na_5Al_3F_{14}$, and Na_3AlF_6 exist, each with different solidification and phase transition heat release temperatures. The NaF-KF- AlF_3 electrolyte system is a commonly used low-temperature electrolyte system in the research of inert anode aluminium electrolysis technology [10–12], and accurate measurement of the liquidus temperature of low-temperature electrolytes is becoming increasingly important.

In this study, a novel method based on electrical conductivity variation curves is proposed to determine the liquidus temperature, addressing the limitations of conventional approaches for low-temperature electrolyte in the NaF-KF-AlF_3 system. This method exploits the fact that the molten electrolyte remains clear above the liquidus temperature and becomes turbid below it, combined with the characteristic changes in conductivity with temperature between these two states, to accurately identify the liquidus temperature. This method successfully validated its accuracy in measuring the liquidus temperature of industrial electrolytes and was used to measure the liquidus temperature of the NaF-KF-AlF_3 system at different molecular ratios.

2. Experimental Method

2.1 Determination of Temperature Range

Before the experiment, the electrolyte to be tested was crushed and mixed evenly, then dried at a constant temperature of 200 °C for more than 48 hours in a vacuum drying oven and stored in a desiccator for later use.

The electrolyte was placed in a lidded corundum crucible, heated and held in a well-type furnace until completely melted. Then the crucible lid was opened, and a thermocouple was inserted into the molten electrolyte to measure its temperature in real time. After turning off the furnace and allowing it to cool naturally, the transition process of the molten electrolyte from a clear to a turbid state was observed visually. The temperature at the inflection point, at which the liquid changed from clear to significantly turbid was recorded (rough value, assumed liquidus temperature), and the temperature range for measurement was determined based on the temperatures of the molten aluminium electrolyte in its clear and turbid states respectively.

2.2 Conductivity Measurement

The Continuous Variation of Cell Constant method (CVCC) is a commonly used technique for measuring the conductivity of molten electrolytes. Its principle is as follows: in a fixed molten salt circuit, an alternating current signal of constant frequency is applied, and the total resistance of the circuit has a linear relationship with the cell constant. The linear coefficient is a constant related to the molten salt conductivity, and the change in cell constant is caused by the change of the conductivity cell, namely (Equation (1)):

$$\kappa = {}^{1}\Big/_{A(\frac{dR}{dL})_{average}} \tag{1}$$

where:

κ Conductivity, S/cm

A Electrode area of the conductivity cell, cm^2

$(\frac{dR}{dL})_{average}$ Average slope of molten salt resistance relative to the change in electrode spacing, Ω/cm.

To ensure measurement accuracy, the parameter A in Equation (1) must first be calibrated using a standard potassium chloride solution of known concentration to determine the electrode area of the conductivity cell.

Figure 1 shows the schematic diagram of the conductivity measurement device. During the experiment, the electrolyte is heated by controlling the well-type furnace with a temperature control device. After the electrolyte is completely melted and stabilized at the target temperature, the working electrode is lifted from the bottom of the crucible using the lifting device to change the length of the conductivity cell. The resistance of the molten salt electrolyte at that temperature is measured using AC impedance spectroscopy. Then, experimental data at multiple temperature points within the previously defined temperature range are measured sequentially. The conductivity of the molten salt electrolyte is calculated using Equation (1). The resulting conductivity data are then segmented and curve-fitted based on the distinct trends in how conductivity changes with temperature across different states. The liquidus temperature of the electrolyte is determined from the intersection point of the two fitted curves.

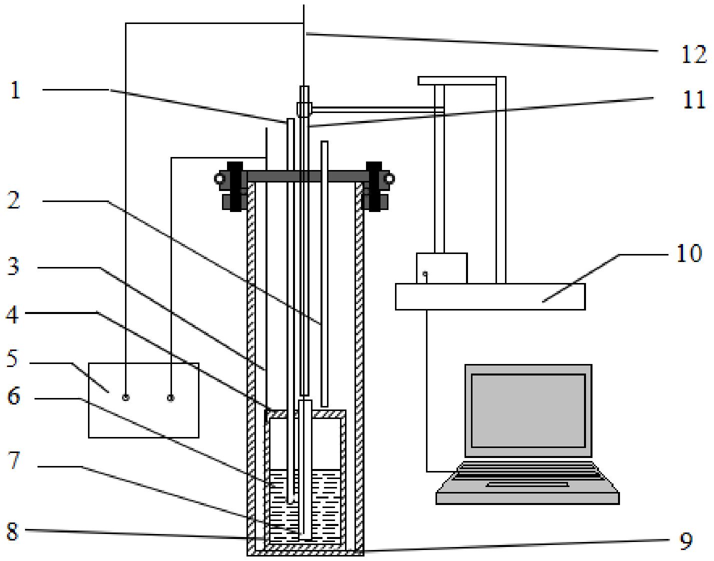


Figure 1. Schematic diagram of the conductivity measurement device with CVCC method. 1 - Thermocouple; 2 - Vent pipe; 3 - Counter electrode; 4 - Crucible lid; 5 - Digital bridge; 6 - Electrolyte; 7 - Pyrolytic boron nitride tube; 8 - Crucible; 9 - Furnace body; 10 - Lifting device; 11 - Insulating sleeve; 12 - Working electrode (tungsten wire).

3. Accuracy Validation

To validate the accuracy of this method, three representative types of electrolytes were selected from the current aluminium smelters: a high-lithium electrolyte (LiF = 5.2 %), a high-potassium electrolyte (KF = 5.8 %), and a purified electrolyte (LiF and KF contents both less than 1.5 %). The liquidus temperature of each sample was measured using both the stepwise cooling curve method and the proposed conductivity method.

Figure 2 shows the liquidus temperature and corresponding curve of the high-lithium electrolyte measured by the stepwise cooling curve method, and Figure 3 shows the conductivity variation curve of the high-lithium electrolyte measured by the conductivity method.

As shown in Figure 2, the liquidus temperature of the high-lithium electrolyte measured by the stepwise cooling curve method is 929.1 °C.

When measuring the liquidus temperature of the high-lithium electrolyte using the conductivity method, the transition from clear to turbid molten electrolyte was first observed visually at approximately 928 °C (assumed crystallization temperature), and the temperature range was identified as 916–950 °C. Within this range, the conductivity of the high-lithium electrolyte was recorded. As shown in Figure 3, within the range of 916–950 °C, as the temperature increases, the conductivity gradually increases from 2.18 to 2.45 S/cm. It also indicates that the conductivity-temperature trend at the first five temperature points is significantly different from that at the subsequent seven temperature points. The conductivity values were fitted in segments, and the inflection point of the fitted lines is at 928 °C, and this inflection point temperature is regarded as the liquidus temperature of the high-lithium electrolyte. Notably, this result is in agreement with the value obtained using the stepwise cooling curve method. At this temperature, the conductivity was also identified as 2.22 S/cm.

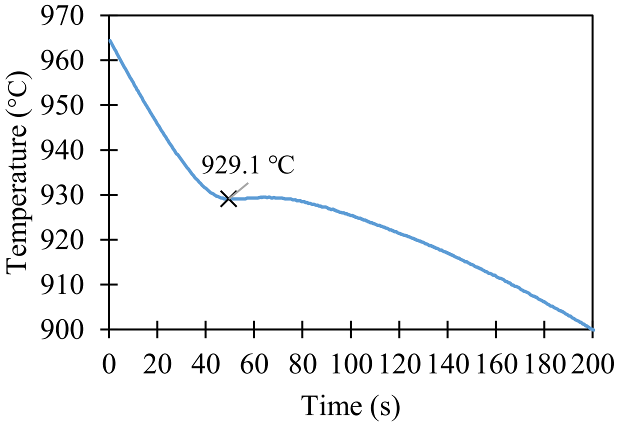


Figure 2. Liquidus temperature of high-lithium electrolyte measured by stepwise cooling curve method.

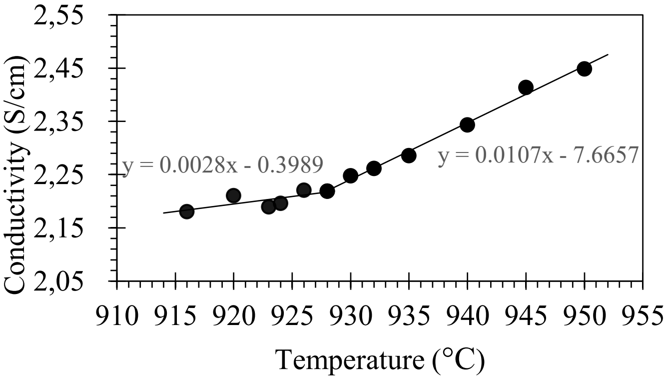


Figure 3. Relationship between conductivity and temperature of high-lithium electrolyte.

Figure 4 shows the liquidus temperature and corresponding curve of the high-potassium electrolyte measured by the stepwise cooling curve method, while Figure 5 presents the conductivity-temperature curve obtained by the conductivity method for the same electrolyte.

As shown in Figure 4, the liquidus temperature of the high-potassium electrolyte measured by the stepwise cooling curve method is 945.2 °C.

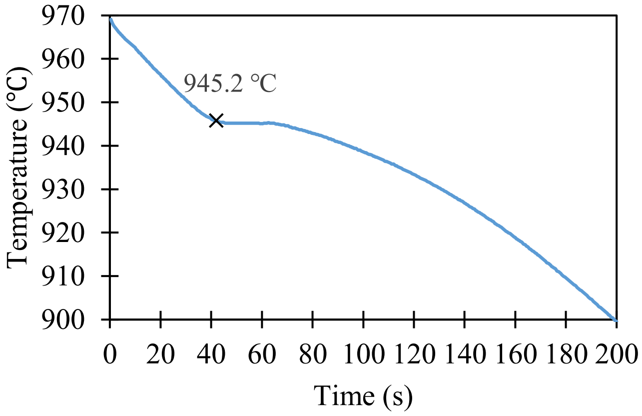


Figure 4. Liquidus temperature of high-potassium electrolyte measured by stepwise cooling curve method.

When measuring the liquidus temperature of the high-potassium electrolyte using the conductivity method, the transition from clear to turbid molten electrolyte was first observed visually at approximately 942 °C (assumed crystallization temperature), and the temperature range was identified as 930–960 °C. Within this range, the conductivity of the high-potassium electrolyte was recorded. As shown in Figure 5, within the range of 930–960 °C, as the temperature increases, the conductivity gradually increases from 1.93 to 2.30 S/cm. It also indicates that the conductivity-temperature trend at the first five temperature points is significantly different from that at the subsequent six temperature points. The conductivity values were fitted in segments, and the inflection point of the fitted lines is at 944 °C. This inflection point is regarded as the liquidus temperature of the high-potassium electrolyte. Notably, this value is consistent with the inflection point observed in the stepwise cooling curve. At this temperature, the conductivity was also identified as 2.02 S/cm.

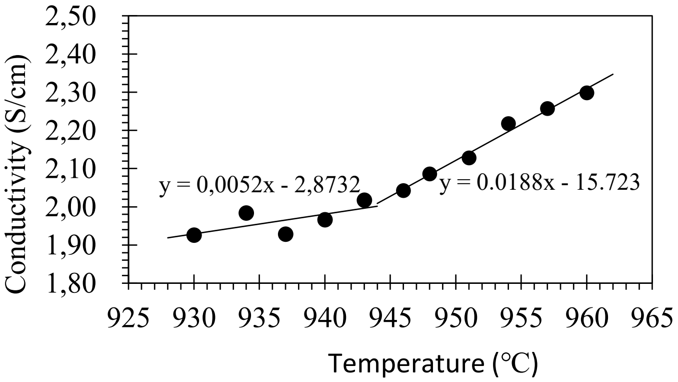


Figure 5. Relationship between conductivity and temperature of high-potassium electrolyte.

Figure 6 shows the liquidus temperature and corresponding curve of the purified electrolyte measured by the stepwise cooling curve method, while Figure 7 presents the conductivity–temperature curve obtained by the conductivity method.

As shown in Figure 6, the liquidus temperature of the purified electrolyte measured by the stepwise cooling curve method is 942.6 °C.

When measuring the liquidus temperature of the purified electrolyte using the conductivity method, the transition from clear to turbid molten electrolyte was first observed visually at approximately 940 °C (assumed crystallization temperature), and the temperature range was identified as 927–961 °C, within which the conductivity of the purified electrolyte was recorded. As shown in Figure 7, within the range of 927–961 °C, as the temperature increases, the conductivity gradually increases from 1.96 to 2.40 S/cm. It also indicates that the conductivity-temperature trend at the first six temperature points is significantly different from that at the subsequent nine temperature points. The conductivity values were fitted in segments, and the inflection point of the fitted lines is at 941 °C. This inflection point temperature is regarded as the liquidus temperature of the high-lithium electrolyte. This temperature is consistent with the inflection point temperature of the step-cooling curve. At this temperature, the conductivity was identified as 2.08 S/cm.

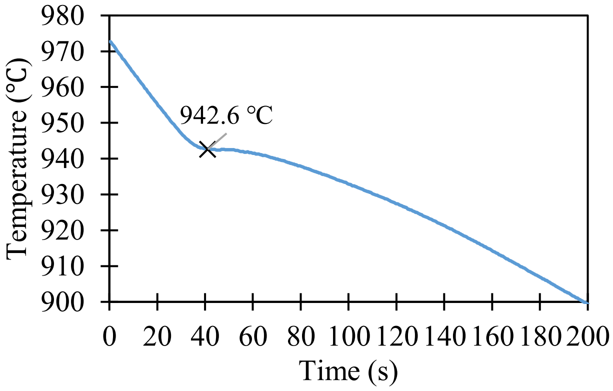


Figure 6. Liquidus temperature of purified electrolyte measured by stepwise cooling curve method.

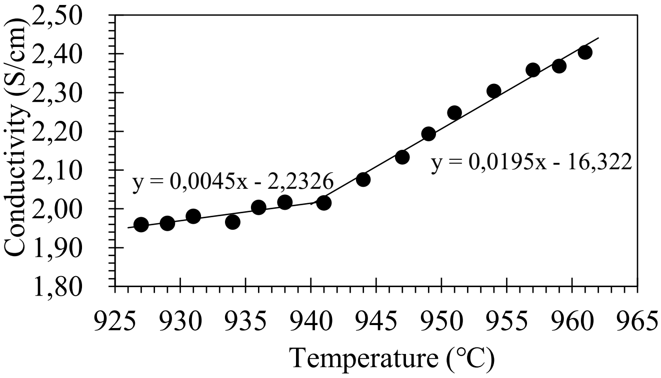


Figure 7. Relationship between conductivity and temperature of purified electrolyte.

Table 1 lists the liquidus temperature values of three representative types of industrial electrolytes measured by the stepwise cooling curve method and the conductivity method. Comparative analysis shows that the results of the two methods agree well, with an error less than 0.17 %, confirming that the conductivity method is both accurate and reliable for determining the liquidus temperature of industrial electrolytes.

Table 1. Error analysis.

Sample	Liquidus temperature (°C)		Error (%)
	Stepwise cooling curve method	Conductivity method	
High-lithium electrolyte (LiF = 5.2 %)	929.1	928	0.12
High-potassium electrolyte (KF = 5.8 %)	945.2	944	0.13
Purified electrolyte (LiF and KF both < 1.5 %)	942.6	941	0.17

4. Measurement of Liquidus Temperature of NaF-KF-AlF_3 System

To address the challenge of determining the liquidus temperature of low-temperature electrolytes in the NaF-KF-AlF_3 system, a series of studies were carried out on low-temperature electrolytes using the above conductivity measurement method. The laboratory first measured the liquidus temperature of a low-temperature electrolyte with CR = 0.82 (where CR is the molar ratio of NaF to AlF_3, containing 20 % KF). When the stepwise cooling curve method was applied, the inflection point was not clearly discernible, and the system-suggested value for the liquidus temperature was 786.3 °C, as shown in Figure 8.

However, it was observed visually that the molten electrolyte was completely clear at 780 °C and became noticeably turbid at 739 °C, as shown in Figure 9. These observations indicate that, for NaF-KF-AlF_3 systems with low CR values, the "inflection point" on the stepwise cooling curve can no longer accurately reflect the true liquidus temperature. As a result, the conductivity method was used to measure the liquidus temperature, with the temperature range set as 739–780 °C. Measurements were taken at every 3–4 °C interval to record the conductivity data. The results are presented in Figure 10.

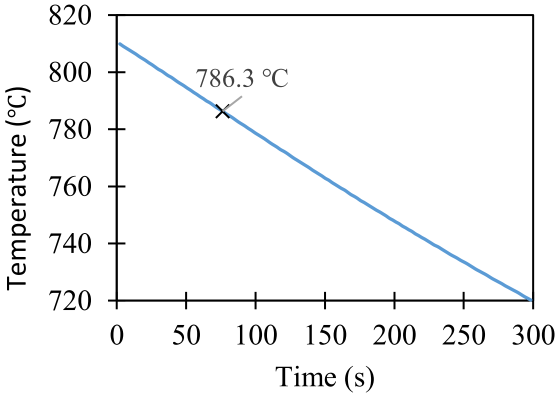
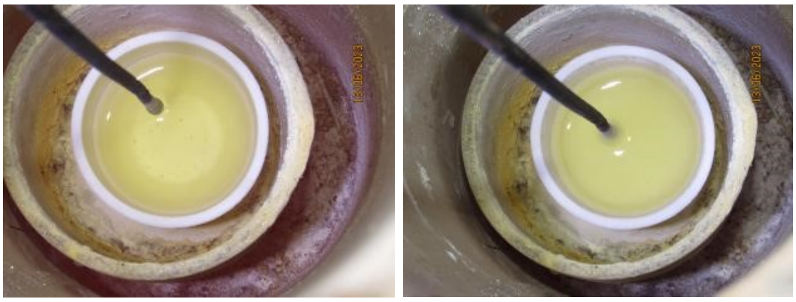


Figure 8. Liquidus temperature of low-temperature electrolyte with CR = 0.82 measured by stepwise cooling curve method.



a) at 739 °C (b) at 780 °C

Figure 9. Temperature range of CR = 0.82 low-temperature electrolyte determined by visual observation.

According to the conductivity-temperature trend, the pattern observed at the first seven temperature points differs significantly from that at the subsequent eight points. The conductivity values of the two parts were fitted in segments, and the "inflection point" of the fitted lines was 753 °C. This temperature was taken as the liquidus temperature, and the conductivity at this temperature was also identified as 1.08 S/cm.

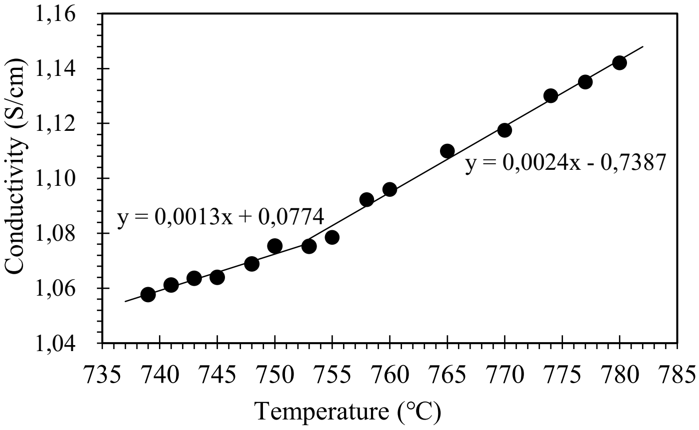


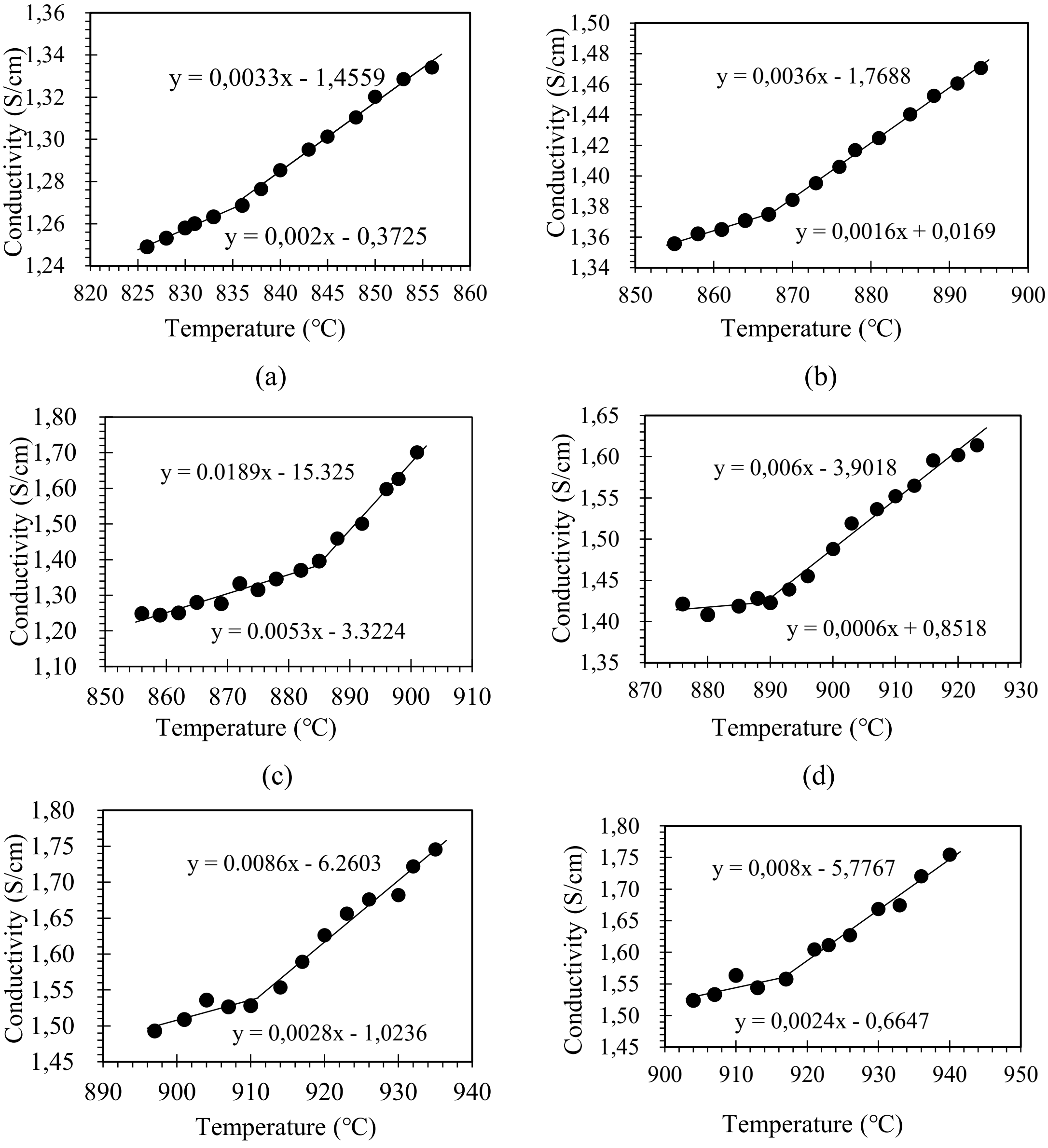
Figure 10. Relationship between conductivity and temperature of NaF-KF-AlF_3-based low-temperature electrolyte (CR = 0.82).

Based on the above measurements, we prepared low-temperature electrolytes of the NaF-KF-AlF_3 system with different molecular ratios (CR = 1.2–2.2) by adjusting the electrolyte composition and measured their liquidus temperatures with the conductivity method. The temperature ranges and measurements of the low-temperature electrolytes are shown in Table 2, and the conductivity curves are shown in Figure 11.

Table 2. Temperature ranges and measurement data of low-temperature electrolytes with different molecular ratios.

Molecular ratio (CR)	KF (%)	Temperature range (°C)	Liquidus temperature (°C)	Conductivity (S/cm)
1.2	16.1	826–870	836	1.27
1.4	15.4	855–894	867	1.38
1.6	14.7	856–891	885	1.40
1.8	14.0	876–923	890	1.42
2.0	13.5	897–935	910	1.53
2.2	12.9	904–940	917	1.56

As seen in Figure 11, the liquidus temperatures of low-temperature electrolytes with CR = 1.2–2.2 determined by the conductivity method are 836 °C, 867 °C, 885 °C, 890 °C, 910 °C and 917 °C respectively.



(a) (b)

(c) (d)

(e) (f)

Figure 11. Relationship between conductivity and temperature of NaF-KF-AlF3-based low-temperature electrolyte.
(a) CR=1.2; (b) CR=1.4; (c) CR=1.6; (d) CR=1.8; (e) CR=2.0; (f) CR=2.2.

Figure 12 shows the liquidus temperature and conductivity variation curves of low-temperature electrolytes with different molecular ratios. As illustrated in the figure, when CR ranges from 1.2 to 2.2, each 0.1 increase in molecular ratio leads to an average increase of 8.1 °C in the liquidus temperature of the low-temperature electrolyte. This observation is consistent with existing literature regarding the effect of molecular ratio on the liquidus temperature of low-temperature electrolytes, indicating that the conductivity method is feasible for measuring the liquidus temperature of this system. Moreover, Figure 12 also demonstrates that the conductivity of the electrolyte increases with molecular ratio. Specifically, each 0.1 increase in molecular ratio leads to an average rise of 0.036 S/cm in conductivity.

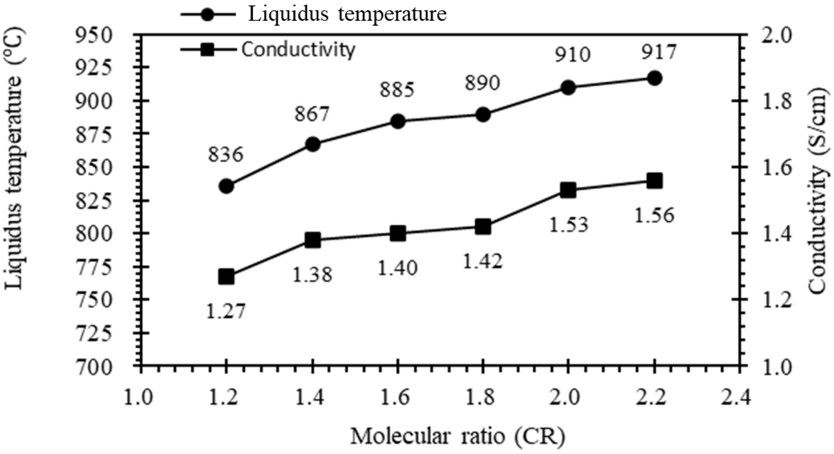


Figure 12. Liquidus temperature and conductivity variation curves of low-temperature electrolytes with different molecular ratios.

5. Conclusions

The method of determining the liquidus temperature from the electrical conductivity variation curve has an error less than 0.17 % compared to the stepwise cooling curve method, indicating its high accuracy. This method can be used not only to measure the liquidus temperature of industrial electrolytes but also for the NaF-KF-AlF3 low-temperature electrolyte system. It effectively addresses the limitations of the traditional stepwise cooling curve method, which struggles to accurately measure the liquidus temperature of low-temperature electrolytes in the NaF-KF-AlF3 system. Additionally, it provides conductivity data during the measurement of the liquidus temperature.

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