ENHANCED ELECTRICAL CONDUCTIVITY BY MODIFYING LiCl-KCl MOLE FRACTION AT HIGH TEMPERATURE

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Abstract— Thermal batteries use molten salt mixture as electrolyte. The molten salt system lithium chloride-potassium chloride (LiCl-KCl) was chosen for initial investigation. They are preferred because of their compatibility with the electrode and their high conductivity. The electrical conductivity is a key factor for achieving high performance in thermal batteries. A main requirement for molten salt electrolyte, besides high conductivity, is operating temperature. One of the primary factors behind thermal battery active life is molten salt and binder composition properties that are determined simultaneously. Consequently, three factors were investigated to find high electrical conductivity of electrolytes; molten salt composition, temperature range, and binder composition by using equations and data from reliable literature. In this paper, a new composition of LiCl-KCl electrolyte and its optimum temperature were proposed to achieve higher electrical conductivity for LiCl-KCl composition design at high temperature. The electrical conductivity of the new LiCl composition was 44.37 % higher than the electrical conductivity of general LiCl compositions.

Index Terms— Composition, Electrical Conductivity, Electrolyte, Mole fraction, LiCl·KCl molten salt.

I. INTRODUCTION

The military identified the need for a high power density battery with a very long shelf life (up to 25 years) for use in equipment such as guided missiles. Thermal batteries are specially designed according to the requirements for such guidance applications. Thermal batteries contain a molten salt electrolyte that is non-conducting when solid at ambient temperatures, but which becomes an excellent ionic conductor when molten. The principle of operation is producing chemical reactions at the electrodes and molten salt electrolyte of materials to generate electricity energy. It depends on electrical conductivity that is a key factor for achieving high performance of molten salts electrolytes, which plays a key role in thermal batteries.

A. Electrolyte

The electrolyte of thermal battery is a salt mixture which is solid at room temperature and melts once the battery is thermally activated by pyrotechnics. The salt mixture produces an electrically conducting molten salt when it is melted. The electrolyte is a part of the thermal battery as shown in fig.1. The electrolyte separates into cations and anions, which disperse uniformly through molten salt.

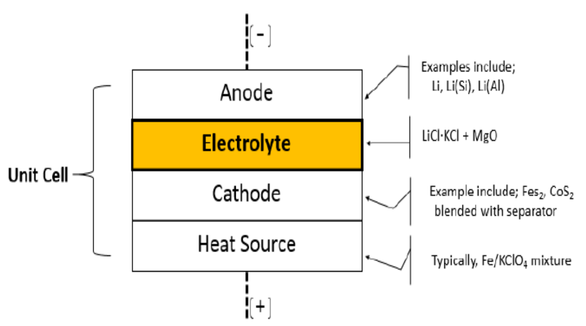


Fig.1. Schematic Representation of a Typical Thermal Battery

An electrolyte consists of a molten salt and binder as follows;

1. Molten Salt

The advantages of molten salts as battery electrolytes have high conductivity so high currents. This work chose lithium chloride-potassium chloride (LiCl-KCl) molten eutectic mixture as the electrolyte for investigation. The factor which determines strength of these salt crystal is called lattice energy or heat energy for ionization. The pure salt of LiCl-KCl mixture salt radius of ions influenced energy for ionization. A LiCl-KCl molten salt is composed of two charged ions: cations (Li^+, $K^{+)}$ and anions (Cl^-). The Li^+ ions, which are smaller than K^+ ions that may be considered a better glue for holding together the Cl^- anions. The effect of those factors is: as the size of the ions decreases, the lattice energy increases. However, lattice energy of LiCl and KCl which are quite different due to its constituent element. The lattice energy of two LiCl and KCl pure salt is compared in Fig.2.

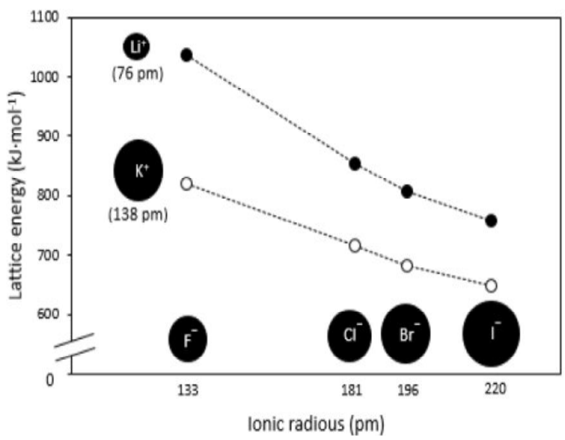


Fig.2. the Influence of LiCl and KCl Pure Salt Ions Radius on the Lattice Energy

LiCl and KCl pure salt composition of LiCl-KCl molten salt used temperature (K) to ionized of LiCl-KCl molten salt is shown the liquids lines in fig.3 that were constructed by averaging equations according to equation 1.1 and 1.2.

$$T_{mp.}(LiCl) = 607.2 - 3.4198x - 0.063255x^2$$

$$T_{mp.}(KCl) = 773.97 - 3.4562(100-x) - 0.023368(100-x)^2 - 0.00071877(100-x)^3$$

Where x is the KCl content in molar percent and temperature is expressed in degree Celsius. [1]

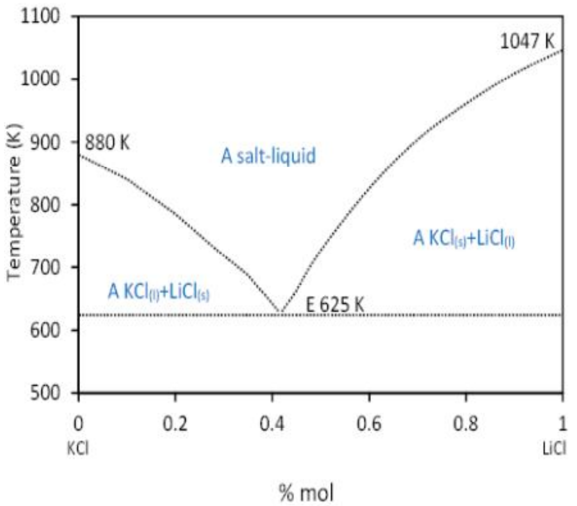


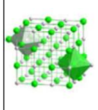
Fig.3. LiCl-KCl phase diagram

Most thermal battery designs use 58.8 %mol LiCl and 41.2 %mol KCl. The LiCl-KCl molten salt mixtures or eutectic containing are preferred because of their high conductivities and general overall compatibility with the electrode. The general melting points of lithium chloride and potassium chloride are 880 K and 1047 K respectively. The LiCl-KCl eutectic melts at 625 K that contains 58.2 %mol LiCl and 41.8 %mol KCl composition.

2. Binder

Binder is necessary to immobilize the electrolyte when it is molten. The most effective binders must provide good electrolyte immobilization in most applications under more severe conditions (e.g., high shock and vibration). Thermal batteries normally use Magnesium oxide (MgO) or magnesia as binder. The MgO suitable for use in electrolyte require certain properties and are selected that are higher melting point than LiCl-KCl molten salt to stable of pellet electrolyte and good thermal conductivity to storage heat energy. The physical property of MgO shown in Table I. MgO powders were evaluated for their suitability to act as a binder in the electrolyte [2].

Table l: Physical property of MgO binder

	Chemical formula	Density ($g \cdot cm^{-3}$)	Melting point (°C/K)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
	MgO	3.58	2,852 / 3,125	45–60

Moreover, MgO affects the system resistivity. Its resistivity rises with temperature up to about 623 K and then falls as a temperature rises further to 1,273 K. In the cooling stage, the resistivity rises continuously and it always higher than at its corresponding temperature in the heating stage. This is illustrated in Fig.4 [3] which shows resistivity measurements on a fused magnesia powder. This amount of electrolyte-binder mixed with LiCl-KCl composition is necessary to allow good interfacial contact with the electrode pellets.

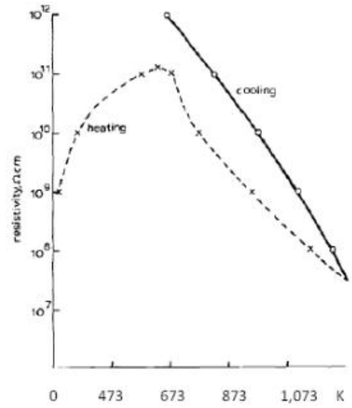


Fig.4. Resistivity measurements on a fused MgO powder

B. Electrical Conductivity

Electrical conductivity is the reciprocal of electrical resistivity and measures a molten salt's ability to conduct an electric current. Electrical conductivity is the sum of electronic conductivity and ionic conductivity. It is commonly represented as κ. Its SI unit is Siemens per meter ($S \cdot m^{-1}$).

Electrical conductivity (κ)= (Electronic+ionic) conductivity This work assumed electrical conductivity equal ionic conductivity because of electronic conductivity in molten salt is very low. Electrical conductivity is a key factor for performance of molten salt in batteries which involves electrons and ions transportation. High electrical conductivity is essential for high performance batteries. Conductivity is a measure of matter's ability to accommodate the transport of an electric charge that observed in fig.5. This paper, the electrical conductivity was determined as a function of temperature range and composition for LiCl-KCl molten salt electrolyte.

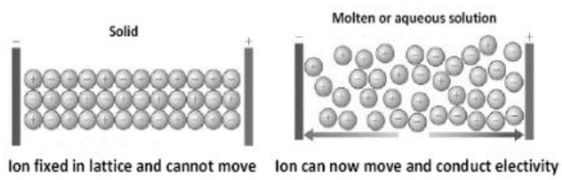


Fig.5. Charges motion in molten salt

The following fig.6 [4] gives the electrical conductivity of LiCl and KCl pure salt as function of concentration refer to 293 K that show less than 20 $mS \cdot cm^{-1}$ electrical conductivity of pure salt. The mixture of LiCl and KCl, called molten salt, has interesting features in that it becomes molten at high temperatures with increased electrical conductivity. Adjustment of the ratio of LiCl-KCl should be the way to increased electrical conductivity.

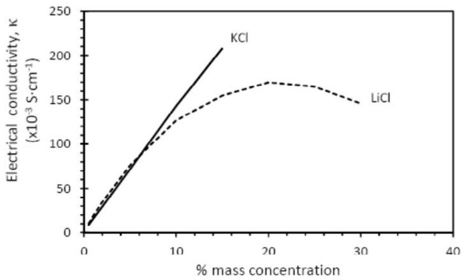


Fig.6. Electrical conductivity, κ (S·cm^{-1}) for the indicated concentration in % mass

This paper determined the factors which influence electrical conductivity in order to design compositions of molten salt electrolyte for pre-experimental research.

II. METHODOLOGY

This section describes the algorithm to analyze electrical conductivity occurring inside a LiCl-KCl molten salt electrolyte. Investigation was divided into 3 parts;

A. Determination of Molten Salt Composition and Operating Temperature

The electrical conductivity was determined as a function of temperature that was calculated from equation 2.1 [4] of the form:

$$\kappa = \kappa^0 \exp\left(\frac{E_a}{RT}\right) \qquad (2.1)$$

Where κ is electrical conductivity, κ^0 is the pre-exponential factor, E_a represents the activation energy, R the gas constant (R = 8.3145 J·mol^{-1} K^{-1}) and T is the absolute temperature.

Table ll: Electrical conductance data of LiCl·KCl molten salt

mol %	Constance Equation (S·cm^{-1}) (R=8.31441 J·K^{-1}mol^{-1})	T range (K)
100-0	Κ = 13.662exp(-6433.84444/RT)	910-1050
81.77-18.23	Κ = 13.886exp(-9982.35421/RT)	810-890
70.36-29.64	Κ = 19.585exp(-13822.91206/RT)	730-870
58.8-41.20	Κ = 23.021exp(-16204.90311/RT)	670-850
40.45-59.55	Κ = 13.21exp(-13995.71415/RT)	870-1010
9.96-80.04	Κ = 8.595exp(-11537.15462/RT)	990-1110
0-100	Κ = 7.884exp(-18178.91548/RT)	1070-1191

For LiCl-KCl mol fraction system (0-100 %mol), LiCl-KCl molten salt is found in an equation system format in data Table ll [7] that was used to determine electrical conductivity for possible use in applications requiring operating temperatures and high electrical conductivity.

B. Determination of Density

Density of LiCI-KCl molten salts system is important factor to design operational and safety. The density of a LiCl-KCl molten salt can be calculated for LiCl-KCl mol fraction system (0-100 %mol) using equation (2.2).

$$\rho = a + bT \qquad (2.2)$$

Where a and b constant value of composition is shown in Table III.

Table III: Density data of LiCl-KCl molten salt

mol %	Density Equation (g·cm^{-1})	T range (K)
100-0	ρ = 1.8842-4.328×10^{-4}T	894-1054
81.77-18.23	ρ = 1.9689-4.8908×10^{-4}T	820-920
70.36-29.64	ρ = 1.9945-5.0738×10^{-4}T	740-860
58.8-41.20	ρ = 2.0285-5.2676×10^{-4}T	680-860
40.45-59.55	ρ = 2.0768-5.612×10^{-4}T	860-1000
9.96-80.04	ρ = 2.1172-5.7764×10^{-4}T	980-1120
0-100	ρ = 2.1359-5.831×10^{-4}T	1053-1212

C. Determination of Binder Composition

Magnesium oxide (MgO) or magnesia was used as a binder in electrolyte to retain the molten salt for good electrolyte immobilization when it is molten. LiCl-KCl molten salt mixes were prepared with MgO powders and pellets were characterized, to correlate key physical properties and chemical properties to select of the MgO powders used in thermal battery. However, MgO composition in the molten salts is important factor which had given effect to the electrical conductivity. Mass fraction of MgO powder was determined from literature that was expressed as equation

$$\kappa = \kappa^0 \exp\left(\frac{E_a}{RT}\right) \psi^{\alpha}\ \mathrm{MgO} \qquad (2.3)$$

Where the parameter ψ MgO represents the mass fraction of magnesia (MgO) and the parameter α depends on the nature of the electrolyte [4]. In past, literature studies ratio MgO to reduce electrolyte leakage of electrolyte pellets are shown in fig.7. [2]

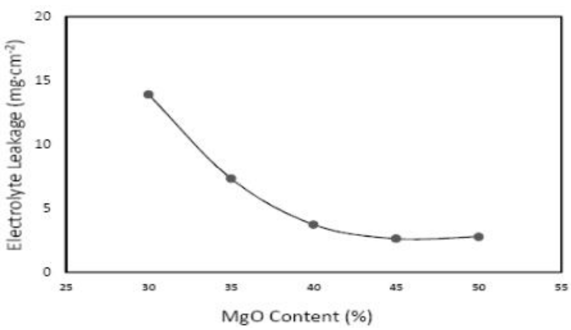


Fig.7. Relation of MgO content affect electrolyte leakage (mg·cm^{-2})

In Fig.7, electrolyte leakage of the electrolyte pellets made with the various MgO powders of content. The lectrolyte leakage dropped to a plateau near 40% MgO content.

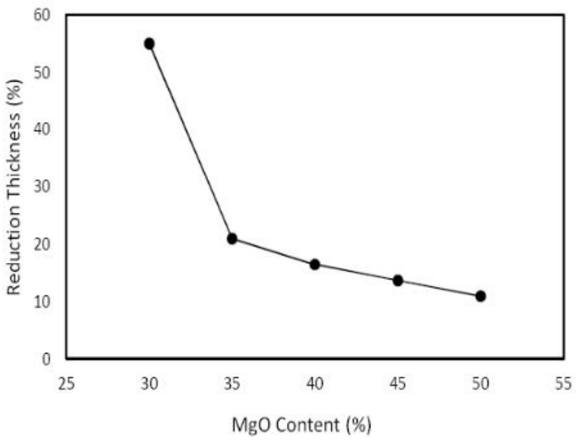


Fig.8. Relation of MgO content affect reduced thickness %

The effect of binder content upon the deformation is shown in Fig. 8. The reduction thickness sharply increased when the MgO content was reduced below 35%.

III. RESULT AND DISCUSSION

A. Molten Salt Composition and Operating Temperature

This part A was determined to optimize LiCl-KCl molten salt mole fraction using actual operating temperature of thermal battery. From electrical conductance equations of LiCl-KCl molten salt in Table ll shown as a function of temperature range that was calculated and presented in fig.9. They can summarize trends and relationships between factors of mole fraction and different temperature range. The result shown that operating temperature increased as electrical conductivity increased. Conductivity involves migration of ions. In fact, ions have significantly higher conductivity which is attributed to the fast ions transport at high temperature of electrolyte. Moreover, mole fraction also influence the electrical conductivity shown mole fraction of LiCl increased as electrical conductivity increased. Movement of Li^+ ions greater than K^+ ions in molten salt because of Li^+ ion smaller size particles than K^+ ions as higher electrical conductivity. Fig.9. Relation of temperature (K) affect electrical conductivity ($S{\cdot}cm^{-1}$) of LiCl·KCl Fig.9 was obtained in Table lV based on actual operating temperature range of 673-773 K. This Table shown electrical conductivity of 70.36 and 58.80 %mol LiCl at 673, 729 and 773 K. In general, most thermal battery designs have used 58.8 %mol LiCl because it is eutectic to give lower melting point. However, when compared to both of mole fractions as the result of 70.36 %mol fraction of LiCl, 729 K is 2.0084 S·cm-1 that obtain better electrical conductivity performance.

Table IV: Density data of LiCl·KCl molten salt T range(K)

T range (K)	Electrical conductivity ($S{\cdot}cm^{-1}$)	
	70.36 % mol LiCl	58.8 % mol LiCl
673	-	1.2726
729	**2.0084**	1.5940
773	2.2807	1.8507

B. Density

Part B was determining density. Table lll lists equations of LiCl-KCl molten salt density as a function of temperature in the range of interest. Their values are calculated and shown in fig.10. The result shown that temperature increased as density deceased. This happens because heat is added to the molten salt resulting in greater kinetic energy of the molecules and there are also more vibrations. Together these mean that each atom in LiCl-KCl takes up more space as the temperature increases.

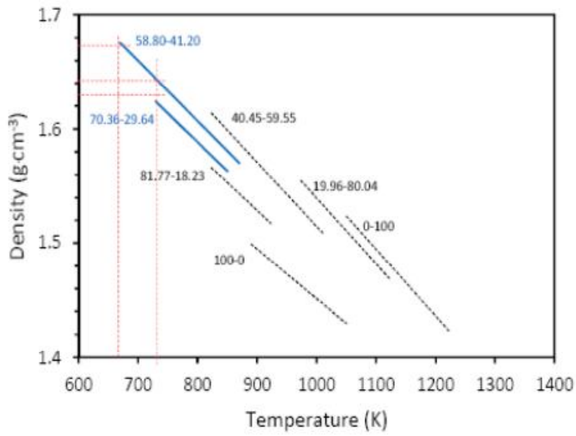


Fig.10. Relation of temperature (K) affects density ($g{\cdot}cm^{-3}$) of LiCl-KCl

Fig.10 was obtained in Table V that shows density of 70.36 and 58.80 %mol LiCl. 673-773 K operating temperature were selected for molten salt melt. From part A was determined to find the best mole fraction of LiCl-KCl molten salt in operating temperature range. The result shows 70.36 %mol LiCl that affect 2.0084 $S{\cdot}cm^{-1}$ electrical conductivity and 1.6241 g·cm-3 density at 729 K.

Table V: Density data of LiCl·KCl molten salt T range (K)

T range (K)	Density ($g{\cdot}cm^{-3}$)	
	70.36 % mol LiCl	58.8 % mol LiCl
673	-	1.6756
729	**1.6241**	1.6440
773	1.6022	1.6212

Since thermal battery are applied to military equipment that are exposed to dynamic changes such as shock, vibration, acceleration and spin. The density of molten salt is of importance during the design step because density in the liquid state is 20-25 % lower than in the solid state. It may lead to an over pressure and electrolyte leakage in the cell stack.

C. Binder Composition

The effectiveness of electrolyte immobilization was determined by measurement of electrolyte leakage when molten and the deformation of pellets resulting in reduction in thickness. MgO increased as electrolyte leakage decreased while thickness increased too. Increasing the MgO binder content of the electrolyte can assist in reducing the tendency for overheating by decreasing electrolyte leakage. Unfortunately, the higher binder content will increase the overall impedance of the battery, so some tradeoffs will be necessary. From electrolyte leakage and reduction in thickness in fig.7 and fig.8, respectively were analyzed simultaneously with MgO content and is illustrated in Fig.11. The result shows 35 % content of MgO that made reduced 7.4 mg·cm-2 electrolyte leakage and 27 % thickness. MgO content containing 35 wt% were selected for using in the electrolyte.

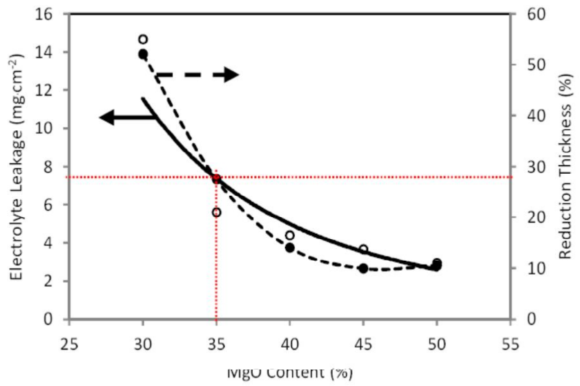


Fig.11. MgO content effects on electrolyte leakage and reduction thickness

In the previous investigation of LiCl-KCl systems, electrical conductivity was calculated and compared for four LiCl-KCl systems in fig.12. Electrical conductivity was taken from the equation (2.2). Addition of 35 %MgO content in electrolyte led to a reduction in the electrical conductivity due to increased resistance in the system. On the other hand, increasing mole fraction of LiCl provides higher electrical conductivity.

In the general system of LiCl, the electrical conductivity was 0.7647 S·cm-1 for 58.58 %mol LiCl, 35 % MgO content at 673 K In a new LiCl-KCl composition system, the electrical conductivity of 1.2111 S·cm-1 was obtained on 70.36 %mol LiCl, 35 %wt MgO at 729 K. Table Vl compares electrical conductivity for two systems. The electrical conductivity of the new LiCl composition is 44.37 % higher than the electrical conductivity of general LiCl composition.

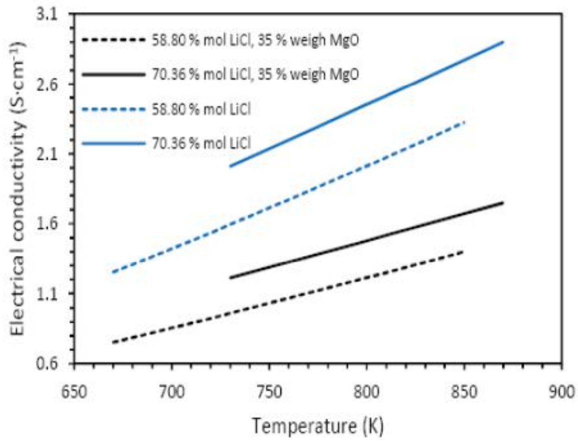


Fig.12. Relation of temperature (K) affects density (g·cm-3) of LiCl-KCl

Table VI: electrical conductivity data of LiCl·KCl molten salt

LiCl-KCl (%mol)	Operation temperature (K)	ρ ($g \cdot cm^{-3}$)	MgO (% wt)	EC ($S \cdot cm^{-1}$)
58.8 - 41.2 (general)	673	1.6756	35	0.7647
70.36 - 29.64 (new)	729	1.6241	35	1.2111

CONCLUSION

The most popular type of electrolyte is the LiCl·KCl mixture contain 58.8 %mol LiCl, 41.2 %mol KCl and 35% wt MgO, with an operating temperature of 673 K and has a calculated electrical conductivity of 0.7647 S·cm-1. Increasing mole fraction of LiCl to 70.36 %mol fraction increased electrical conductivity to 1.2111 S·cm-1 at 729 K operation temperature. The electrical conductivity of the new LiCl composition was 44.37 % higher than the electrical conductivity of general LiCl composition. New composition is proposed to enhance power density of thermal battery by increasing mole fraction of LiCl that is in an acceptable operating temperature range. Even though melting temperature increased, but this electrical conductivity provides additional power density. In future, this preexperiment data can be used to design electrolyte pellets and can be further improved to lower operating temperature.

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