

Short communication

Predictions of the optimum ternary alkali-carbonate electrolyte composition for MCFC by computational calculation

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Abstract

Various kinds of phase diagrams for Li–Na–K ternary carbonate systems were plotted and the vapor pressures of chemical species such as alkali cations and oxygen molecule at various compositions and various temperatures were calculated by computational manipulation of thermodynamic databases. The liquidus temperature of $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ – $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$, $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$ – $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$, and $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$ – $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ binary systems decrease with the increase of Li_2CO_3 content without any ternary intermediate compound. Total vapor pressure of alkali metal species governed by the summation of the vapor pressure of free Na and K and the vapor pressure of alkali metal species starts to decrease abruptly when the content of $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ is over 70 mol% in $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ – $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$ system while over 50 mol% in $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$ – $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ system. On the contrary, the equilibrium vapor pressure of oxygen molecule abruptly increases at the same composition range.

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1. Introduction

An MCFC stack must be kept up its performance up to 5 years to be competitive in the commercial electric power market. Among the several lifetime determining factors of MCFC stack, electrolyte depletion, separator corrosion, and poisoning of internal reforming catalysts are strongly related with the vapor pressure of electrolytes [1]. The vapor of cations such as K or Na corrodes separator parts even where the electrolyte is not directly contacted with, and deteriorates the internal reforming catalysts by destroying active sites. The loss of electrolyte caused by the continuous evaporation of cations after the long-term operation over 2 years, moreover, caused not only the change of electrolyte composition but also the depletion of electrolyte resulting in degradation of stack performance due to the breakdown of triple phase boundary where reaction gases meets the electrolytes and electrodes and the electrochemical reactions of the fuel cells take place. Therefore, the management of electrolyte is one of the most important key technologies for the commercialization of MCFC.

The state-of-the-art MCFC stacks use binary Li–K or Li–Na carbonate mixtures as an electrolyte. While high vapor pressure of cations and NiO solubility are considered as the crucial problems of Li–K electrolyte, high reactivity with stainless steel and low chemical oxygen solubility are the drawbacks of Li–Na electrolyte. To resolve the problems of those binary electrolytes, recently, several research groups started to study about the ternary Li–Na–K carbonate system [2–5]. The aims of those researches are to find out the optimum composition of the ternary Li–Na–K carbonate electrolyte with low NiO solubility, low vapor pressure and low reactivity with stainless steel as well as high chemical oxygen solubility. However, only a few researches studied about the ternary Li–Na–K carbonate system have been reported yet. In this study, “FactSage” computer program was used to calculate the liquidus temperatures and vapor pressures of chemical species such as alkali cations and oxygen molecule of ternary Li–Na–K carbonate mixture with various compositions at various temperatures to predict the optimum compositions of electrolyte for MCFC.

2. Calculations

FactSage is an integrated thermodynamic databank system that provides the tools for thermodynamic calculations includ-

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ing the determination of equilibrium thermodynamic properties and construction of equilibrium phase diagrams based on the Gibb's free energy minimization method [6]. In this study, at first, three each binary composition-temperature phase diagrams for Li–K, Li–Na, and K–Na carbonate systems were plotted using FactSage to check the integrity of computer program and its thermodynamic databases, and the results are given in Fig. 1. The results shown in Fig. 1 confirmed that all three simulated phase diagrams are identical to those experimentally obtained in literatures [7]. The generally used electrolytes for MCFC are $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$, A in Fig. 1(a), and $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$, B in Fig. 1(c), of which melting points are 486 and 500 °C, respectively. As you can see in Fig. 1(a), the composition of Li–K carbonate electrolyte is corresponded to the binary eutectic composition of KLiCO_3 and Li_2CO_3 , not that of K_2CO_3 and Li_2CO_3 .

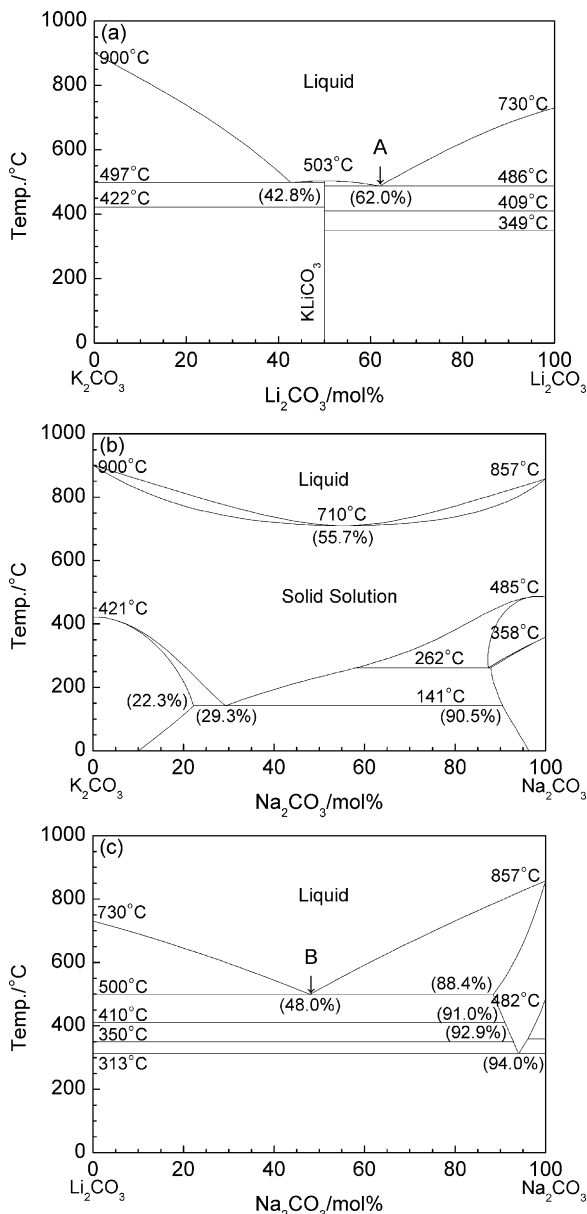


Fig. 1. Phase diagrams of (a) K_2CO_3 – Li_2CO_3 , (b) K_2CO_3 – Na_2CO_3 , and (c) Li_2CO_3 – Na_2CO_3 binary systems made using computer program.

The phase diagrams of Li_2CO_3 – K_2CO_3 – Na_2CO_3 ternary system at various temperatures and 1 atm obtained by computer simulation are illustrated in Fig. 2. The eutectic composition and its melting point of ternary mixture in Fig. 2 are 44 mol% Li_2CO_3 –30 mol% Na_2CO_3 –26 mol% K_2CO_3 , C in Fig. 2(d), and 401 °C, respectively. As shown in Fig. 2(e), about 19.75% of a whole composition range was composed of only liquid at 500 °C in the Li–K–Na carbonate ternary system. Since the melting point of generally used $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ electrolyte is 500 °C, it is supposed that all the compositions composed of only liquid at 500 °C in the Li–K–Na carbonate ternary system can be used as electrolyte materials for MCFC. Line AB in Fig. 2(e) and (f) connects the compositions of $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ and $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ while line BC and CA the composition of $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ and $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$, and $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$ and $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$, respectively. In this study, the binary phase diagrams corresponding to line AB, BC, and CA were plotted then vapor pressures of chemical species for these binary phase diagrams at various temperatures were calculated using computer program.

3. Results and discussion

3.1. Binary phase diagram

The composition-temperature binary phase diagrams for line AB, BC, and CA in Fig. 2(e) and (f) are given in Fig. 3. Although those are phase diagrams for simple binary systems, such kind of phase diagrams with mixtures such as $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$, $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$, or $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$ as an ended composition is practically impossible to find out in the literature. Since Na_2CO_3 forms solid solution with Li_2CO_3 as can be seen in Fig. 1(c), both the left-ended part of Fig. 3(a) and right-ended part of Fig. 3(c) are somewhat complicated. Fig. 3 also indicates that the liquidus temperature of Li–Na–K ternary carbonate mixtures inversely proportional to the content of Li_2CO_3 in the composition range of triangle ABC. It is considered that there is no ternary intermediate compound in this composition range because the liquidus temperatures in these phase diagrams changes monotonously. Fig. 3(b) and (c) also indicated that ternary solid solution, intermediated temperature phase of Li_2CO_3 , and binary compound of KLiCO_3 are melted congruently at ternary eutectic point. Those results confirm that all the compositions in the range of triangle ABC can be used as electrolyte materials for MCFC.

3.2. Vapor pressure of alkali metal species

The equilibrium vapor pressures of cations for various compositions of ternary carbonate mixtures at various temperatures are given Fig. 4. Since the vapor pressure of all other cation species are less than one thousandth of those, the vapor pressure of cations are determined by the summation of vapor pressure of free Na and K vapor in this study. The typical results for the calculation of the equilibrium vapor pressure of chemical species for Li–Na–K ternary carbonate mixture are given Table 1. It can be seen from Fig. 4(a) that the vapor

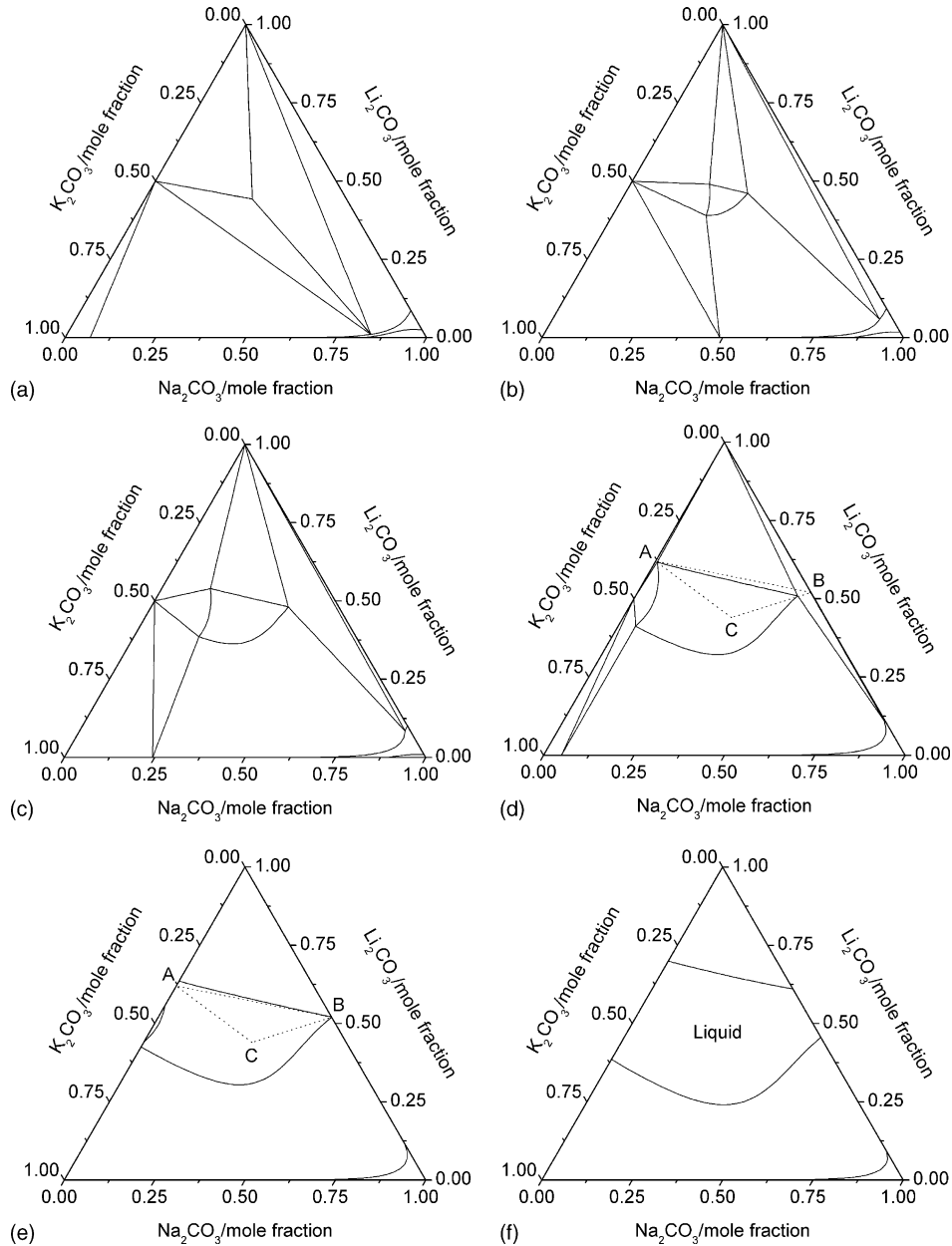


Fig. 2. Ternary phase diagrams of Li_2CO_3 – Na_2CO_3 – K_2CO_3 systems at (a) ternary eutectic temperature, (b) 425°C , (c) 450°C , (d) binary eutectic temperature of KLiCO_3 – Li_2CO_3 , (e) binary eutectic temperature of Na_2CO_3 – Li_2CO_3 , and (f) 550°C .

pressure of Li–Na electrolyte is lower than that of Li–K electrolyte although the liquidus temperature of this system given in Fig. 3(a) almost kept constant. As shown in Fig. 4, total vapor pressure of alkali metal species starts to decrease abruptly when the content of $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ is over 70 mol% in $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ – $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$ system while over 50 mol% in $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$ – $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ system. Comparing with Fig. 3, it is considered that the abrupt changes of the vapor pressures of alkali metal are related with the formation solid solution between Na_2CO_3 and Li_2CO_3 that makes the phase diagrams complicated as mentioned in the previous section.

Fig. 4(b) and (c) indicate that the vapor pressure of alkali metal species increased with the decrease of liquidus temperature. So, using ternary eutectic composition for the electrolyte of

MCFC looks no merit in vapor pressure management. In Fig. 4, however, it can be seen that the vapor pressure of alkali metal species decreased by one order when temperature decrease by 50°C . Since the liquidus temperature of ternary eutectic composition is lower than that of Li–K or Li–Na electrolyte by 150°C , reduced temperature MCFC stack using ternary eutectic composition of Li–Na–K carbonate system as an electrolyte material seems to be feasible. Moreover, reduced temperature MCFC has more benefits: lower the rate of separator corrosion, nickel dissolution, and anode creep as well as the cost down of separator manufacturing by using cheap materials. Meanwhile, degradation of stack performance due to the low ionic conductivity and low electrode activity should be resolved. Therefore, the study on the effect of electrolyte composition on separator corrosion, NiO solubility, ionic conductivity, and chemical oxygen solu-

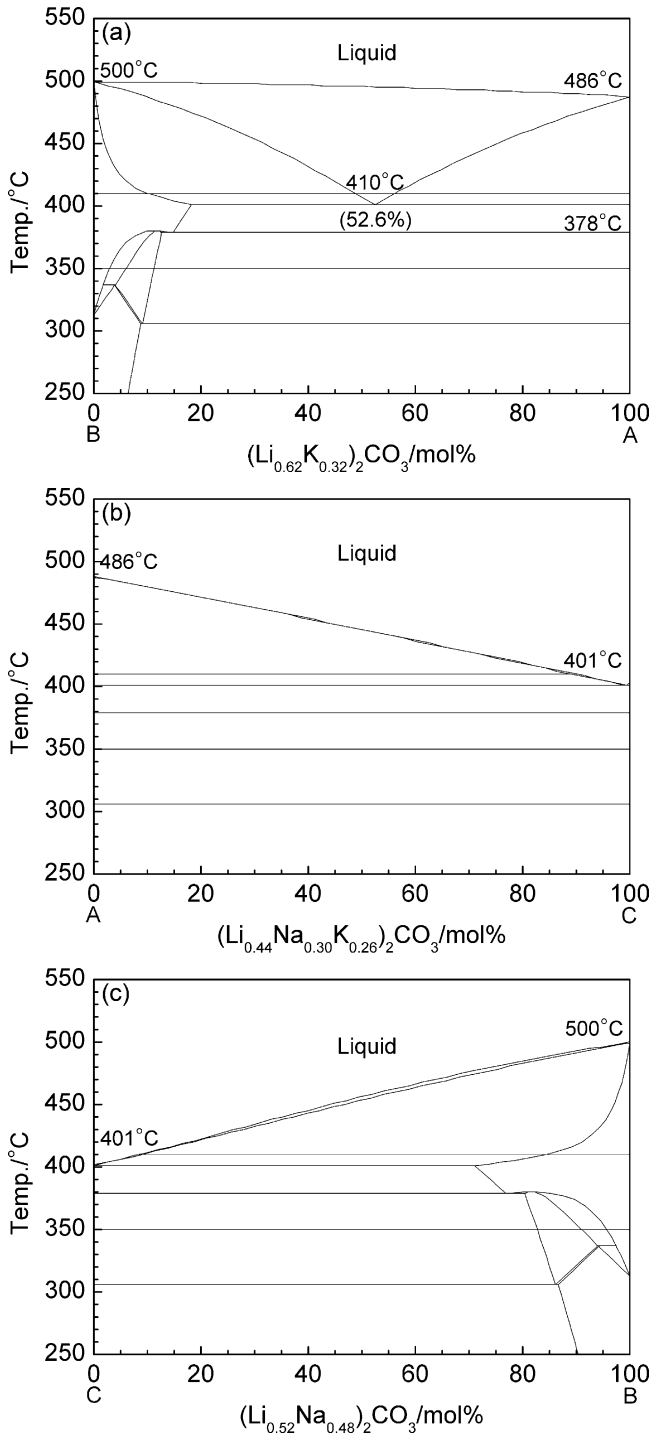


Fig. 3. Phase diagrams of (a) $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ – $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$, (b) $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$ – $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$, and (c) $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$ – $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ binary systems.

bility are now being performed to evaluate the possibility of operating a MCFC stack at reduced temperature.

3.3. Vapor pressure of oxygen molecule

The equilibrium vapor pressure of oxygen molecule, given in Fig. 5, also abruptly changed at the same composition

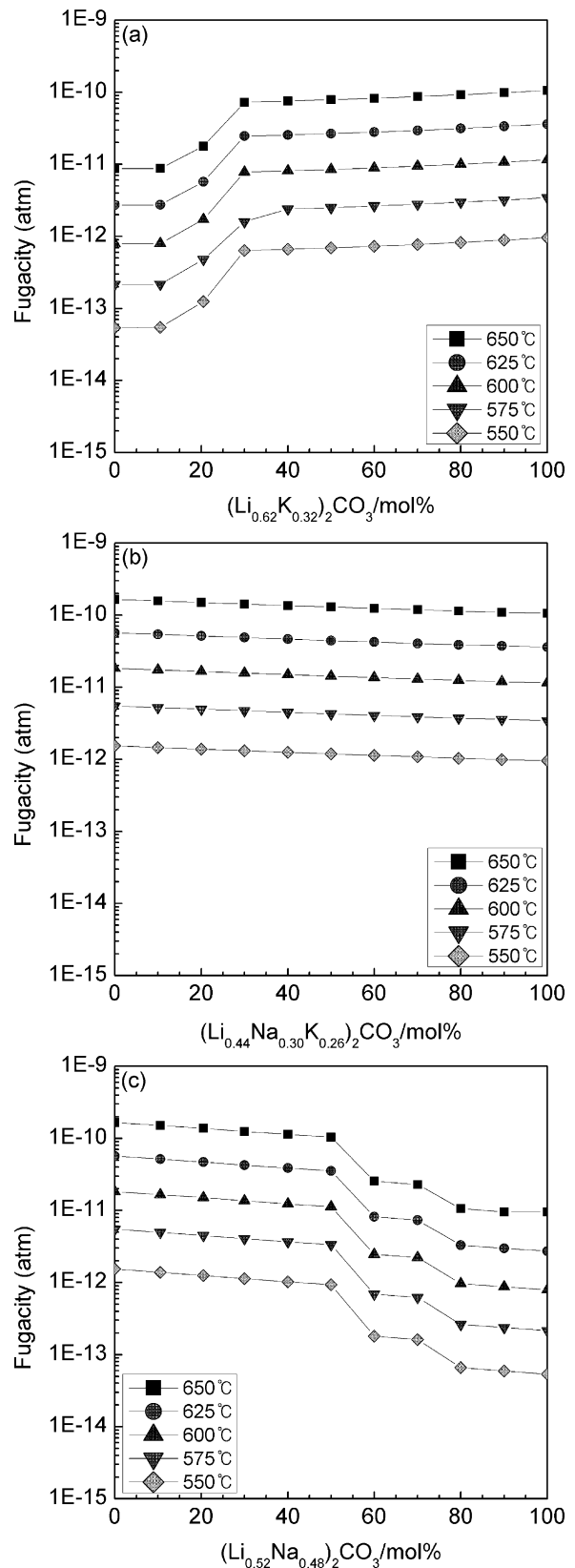


Fig. 4. Vapor pressure of alkali metal species at various temperatures in (a) $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ – $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$, (b) $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$ – $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$, and (c) $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$ – $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ binary systems.

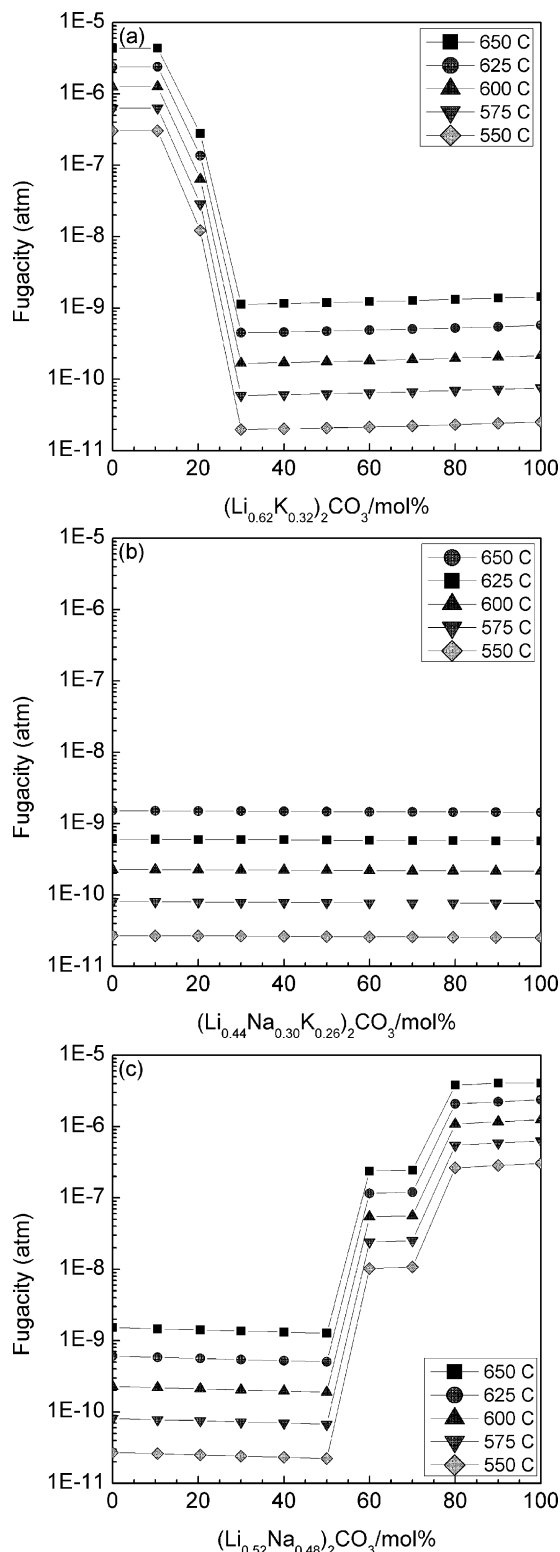


Fig. 5. Vapor pressure of oxygen molecule at various temperatures in (a) $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ – $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$, (b) $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$ – $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$, and (c) $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$ – $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ binary systems.

Table 1

Equilibrium amount of the gaseous phases of $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$ at 650 °C and 1 atm

Species	Fugacity (atm)
CO_2	2.5157×10^{-5}
O_2	2.4638×10^{-9}
K	8.5630×10^{-11}
Na	5.2376×10^{-11}
CO	1.7643×10^{-12}
KO	2.2982×10^{-15}
NaO	2.2106×10^{-15}
Li_2O	1.8141×10^{-15}
Li	1.0365×10^{-15}
O	6.1562×10^{-16}
LiONa	1.0077×10^{-16}
LiO	2.2026×10^{-17}
Li_2O_2	2.4811×10^{-18}
Na_2	2.7676×10^{-21}
K_2	1.4552×10^{-21}
O_3	2.5402×10^{-25}
Li_2	3.4472×10^{-29}
C	1.5332×10^{-51}
C_2O	1.0985×10^{-51}
C_3O_2	3.0634×10^{-56}
Total	2.5155×10^{-5}

in the case of vapor pressure of alkali metal species. Contrary to the vapor pressure of alkali metal species, however, vapor pressure of oxygen molecule starts to decrease when the content of $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ is over 70 mol% in $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ – $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$ system while over 50 mol% in $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$ – $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ system. Meanwhile, it is reported that $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ electrolyte has lower chemical oxygen solubility than $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$ electrolyte [8]. Chemical oxygen is a charged oxygen such as O_2^- , O_2^{2-} , or O^{2-} that forms carbonate ion, CO_3^{2-} , through the electrochemical reaction. Therefore, it is concluded from the results in Fig. 5 that solubility of chemical oxygen in electrolyte is governed by the electrochemical reaction took place at triple boundary, not by the dissolution of oxygen molecule in atmosphere.

4. Conclusions

By using computational calculation with thermodynamic databases, various kinds of phase diagrams with complicated systems of Li–Na–K ternary carbonate mixture were effectively obtained, and the vapor pressures of chemical species at various compositions and various temperatures were estimated. From these results, the following conclusions can be drawn:

- (1) Phase diagrams for $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ – $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$, $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$ – $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$, and $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$ – $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ binary systems indicate that the liquidus temperature of Li–Na–K ternary carbonate mixtures is inversely proportional to the content of Li_2CO_3 in this composition range. The monotonous change

of liquidus temperatures in these phase diagrams implies that there is no ternary intermediate compound in this composition range.

- (2) Total vapor pressure of alkali metal species can be expressed by the summation of the vapor pressure of free Na and K because the vapor pressures of all other alkali metal species are less than those by over three orders of magnitude. The vapor pressure of alkali metal species starts to decrease abruptly when the content of $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ is over 70 mol% in $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ – $(\text{Li}_{0.62}\text{K}_{0.32})_2\text{CO}_3$ system while over 50 mol% in $(\text{Li}_{0.44}\text{Na}_{0.30}\text{K}_{0.26})_2\text{CO}_3$ – $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ system.
- (3) The equilibrium vapor pressure of oxygen molecule also abruptly changed at the same composition in the case of vapor pressure of alkali metal species. Contrary to the solubility of chemical oxygen reported in literature, the vapor pressure of oxygen molecule increase with the increase of $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ content, implying that chemical oxygen is not a reaction product of dissolved oxygen but that of electrochemical reaction at triple boundary.

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