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Study of Emulsions in Molten Salts. III. The Concentration, Stability and Particle-Size Distribution of Dispersed Lithium in Molten Lithium Chloride1)

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The concentration, stability and particle-size distribution of lithium dispersed in molten lithium chloride were investigated. The maximum content of dispersed lithium obtained by spontaneous emulsification was 4.8×10^{-3} mol/g at 678 °C. The concentration of dispersed lithium somewhat increased with the amounts of lithium oxide and nitride added to the molten salt by the mechanical agitation of the lithium-lithium chloride solution. The concentration was about 1.7 times that obtained by spontaneous emulsification except when a large amount of lithium nitride was added. Dispersed lithium in lithium chloride was shown to be fairly stable in the liquid state, as well as against the solidification of molten lithium chloride. The particle-size distribution of dispersed lithium was obtained by means of a scanning electron microscope. The sizes of the lithium particles dispersed in lithium chloride were shown to be mostly between 0.3 and 0.9 μ.

In previous papers,1,2) the authors have reported that, in addition to the true (physical) dissolution, metallic lithium was found to disperse into molten lithium chloride as colloidal particles, when a certain amount of lithium oxide was added to the molten salt or a small amount of oxygen or nitrogen was present in an argon atmosphere. The total concentration of lithium found in the solution thus obtained was considerably larger than the value for physical solubility. These facts may be ascribed to the emulsifying action of lithium oxide (or nitride) which is either simply added to the molten salt or formed by the reaction of lithium with oxygen (or nitrogen) in the atmosphere.2) Such metallic lithium–molten salt emulsions have been observed not only in molten lithium chloride but also in LiF–KF and NaCl–$CaCl_2$ systems. Larger amounts of lithium were found to disperse in LiCl and LiCl–KCl eutectic mixture where the solubilities of lithium oxide (or nitride) were almost equal to those in liquid lithium. On the other hand, the amounts of dispersed lithium were smaller in LiF–KF, LiF–LiCl and NaCl–$CaCl_2$ systems where the solubilities of oxide (or nitride) were quite different from those in lithium.1) It is interesting to further investigate the various factors governing the concentration and stability of lithium emulsions. In this paper, the concentration, stability and particle-size distribution of dispersed lithium in molten lithium chloride are reported.

Experimental

The concentration of lithium (dispersed as colloidal particles and dissolved to atomic dimensions) in molten lithium chloride was determined in the following manner. Three different instruments were designed and used. A highly-concentrated lithium solution was prepared with the apparatus in Fig. 1 (a), the stability of dispersed lithium was investigated in a stainless steel container (b), and the effect of mechanical agitation on the dispersion of lithium was studied with apparatus (c). For the measurements with (a) and (b), the amount of lithium added was sufficient to completely cover the surface of the molten salt. In the case of apparatus (c), about 1.5 mol (10 g) of lithium was added into 1.5 mol (64 g) of lithium chloride. The rate of agitation of the stirrer was 300 to 1300 rpm.

The methods of chemical analysis of lithium, lithium oxide and nitride, and of the purification of argon which was used as the atmospheric gas were the same as those described previously.1,2)

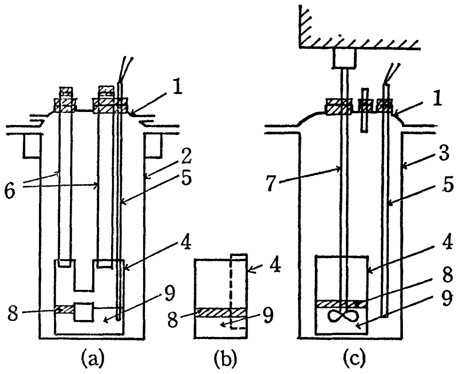

Fig. 1. Apparatus.
1: Pyrex cap, 2: stainless steel container, 3: silica container, 4: stainless steel container, 5: thermocouple, 6: stainless steel pipe, 7: stirrer, 8: molte lithium, 9: molten lithium chloride.

Furthermore, direct observations of liquid and solid samples were attempted by means of a binocular stereomicroscope and a scanning electron microscope.

Results and Discussion

Concentration of Dispersed Lithium in Emulsion. The amounts of lithium dispersed in molten lithium chloride considerably increased with time using a U-type container (a) with a by-pass in a dried argon atmosphere, as shown in Fig. 2.

Since the true solubility of lithium is about 0.7 mol% at the experimental temperature, it is obvious from the figure that a large amount of lithium was dispersed in lithium chloride. For lithium concentrations higher than 12 mol%, the sampling with a thin silica pipe was difficult owing to the considerable decrease in the surface tension of the lithium–lithium chloride solution. The maximum concentration of dispersed lithium was 17.0 mol% at 678 °C. This value is equal to 4.8×10^{-3} mol/g which is the largest in lithium–lithium chloride emulsions.

Effect of Mechanical Agitation on the Concentration of Dispersed Lithium. The effects of the agitation time, agitation speed and concentration of lithium

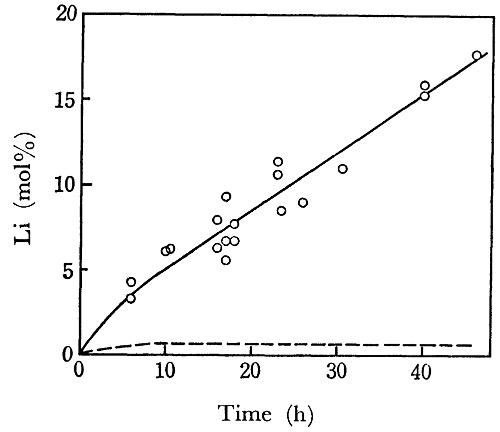

Fig. 2. Concentration of lithium in molten lithium chloride in argon atmosphere *vs.* time plot.
Temp: 678±3 °C, ----: true solubility of lithium in molten lithium chloride.

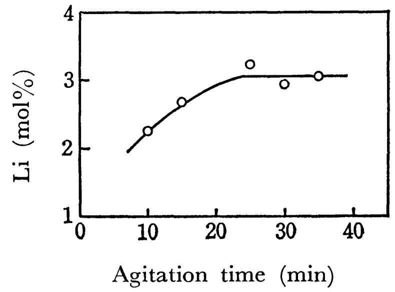

Fig. 3. Effect of agitation time on the lithium concentration.
Temp: 650 °C, agitation: 1000 rpm, added Li$_2$O: 1.14 mol%.

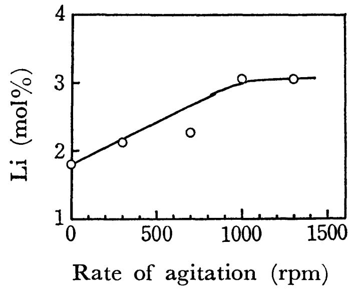

Fig. 4. Effect of rate of agitation on the lithium concentration.
Temp: 650 °C, agitation: 30 min, added Li$_2$O: 1.14 mol%.

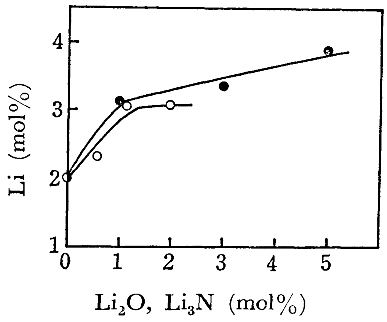

Fig. 5. Effects of lithium oxide and nitride on the lithium concentration.
○: Li$_2$O, ●: Li$_3$N.
Temp: 650 °C, agitation: 1000 rpm, 30 min.

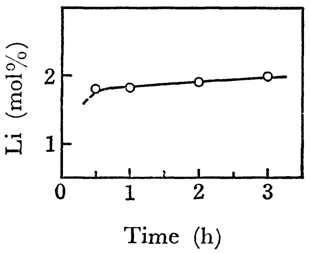

Fig. 6. Concentration of lithium *vs.* time plot in the absence of mechanical agitation.
Temp: 650 °C.

oxide or nitride on the concentration of dispersed lithium were investigated and the results are shown in Figs. 3, 4 and 5, respectively. Figure 6 shows the lithium concentration *vs.* time obtained without mechanical agitation. In this condition, the lithium concentration amounted to about 1.8 to 2 mol% by spontaneous emulsification and true dissolution. As shown in Fig. 5, mechanical agitation did not cause the dispersion of lithium when no lithium oxide or nitride was added to lithium chloride. The addition of oxide and nitride to the molten salt, however, brought about an increase in the concentration of dispersed lithium. The increase in lithium concentration may, therefore, be attributed to the emulsifying action of lithium oxide or nitride. Furthermore, lithium oxide added in excess of its solubility[3] in lithium chloride had little effect on the concentration of dispersed lithium. This result is consistent with that obtained in the absence of mechanical agitation as described in a previous paper.[2] If solid films of lithium oxide are formed on lithium particles, the activity of oxide ions in the molten salt will decrease to some extent. Under the present conditions, the dissolution of lithium oxide to make up for the decrease in the activity of oxide ions should be accelerated by mechanical agitation. Therefore, if the decrease in the activity of oxide ions is not very small, the concentration of dispersed lithium is expected to increase by mechanical agitation in concentrations of lithium oxide higher than about 1 mol%. But this expectation is not supported by the experimental results. This means that lithium oxide acts as the emulsifying agent in an ionized state. On the other hand, the concentration of dispersed lithium increased monotonically with the addition of lithium nitride because its solubility in lithium chloride was 14.6 mol%[1] at 650 °C.

Stability of Lithium–Lithium Chloride Emulsion. The apparatus was sealed when the lithium concentration reached a certain value in a dried, deoxidized argon atmosphere and the change of lithium concentration was monitored. The results are shown in Fig. 7. Since the true solubility of lithium in molten lithium chloride is about 0.6 mol% at the experimental temperature, the amounts of lithium over the solubility

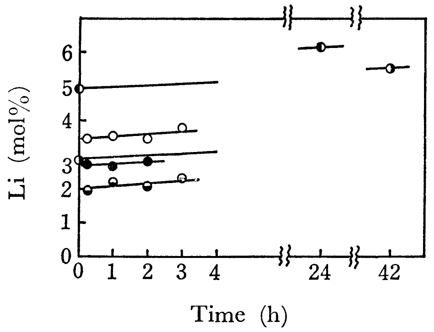

Fig. 7. Stability of dispersed lithium.
Temp: 647±2 °C.
◐: First run, ○: second run, ◑: third run, ●: fourth run, ◒: fifth run.

are those of lithium dispersed by spontaneous emulsification. The concentrations of dispersed lithium and lithium compounds[4] were both slightly larger than those obtained at the time when the apparatus was sealed. Somewhat larger increases in the concentrations were, therefore, observed in systems standing for a long time. This is probably because lithium oxide or nitride on the surface of liquid lithium was dissolved or dispersed in the molten salt, or a small amount of air entered into the apparatus. The concentration of lithium in the molten salt depends on the dispersion of lithium due to the emulsifying action of lithium oxide or nitride and the oxidation or nitridation of dispersed lithium on the surface of the molten salt. Figure 7 shows that dispersed lithium may be stable in the molten salt if it is not too oxidized or nitridized with air.

When the emulsion is solidified, it seems possible that dispersed lithium particles in the system are distorted and coalesce with each other, that is, the lithium–lithium chloride emulsion is broken. It is said that the stability of dispersed particles against the solidification of the solvent is a measure of the capability of an emulsifying agent. As shown in Table 1, the lithium concentrations after remelting of the solid samples were slightly lower than those obtained before solidification, but the differences between them are smaller than the true solubility of lithium at the experimental temperature.[5] The emulsion appears to be fairly stable upon solidification. The small decrease in the lithium concentration may be due to the phase separation of lithium physically dissolved to atomic dimensions in the molten salt.

Particle-Size Distribution of Dispersed Lithium. Direct observations of lithium particles in a molten lithium chloride–potassium chloride eutectic mixture at a certain partial pressure of nitrogen were attempted using a binocular stereomicroscope with a long focal distance (maximum magnification : 160 times), because an ordinary optical microscope was difficult to use at the high temperatures of 400 to 650 °C. If the diameter of a lithium particle was larger than 3 μ, the lithium particles could be expected to be observed, but none were found.

Table 1. Stability of dispersed lithium against the solidification of molten lithium chloride

Concentration of lithium before solidification of lithium chloride (mol%)	Concentration of lithium after remelting of lithium chloride (mol%)
2.03	1.59
6.15	5.84

Then, a cross section of a cylindrical solid sample, which was obtained by direct sampling from a salt-rich phase with a thin silica pipe, was observed by means of a scanning electron microscope. Four kinds of samples were prepared at 650 °C:

(a) Lithium chloride containing 5 mol% lithium nitride.

(b) A sample prepared by dissolving lithium physically in lithium chloride with a sealed-type cell.[2]

(c) A sample prepared by dispersing lithium in lithium chloride at a partial pressure of nitrogen of 0.02 atm.

(d) A sample prepared by dispersing lithium in lithium chloride containing 5 mol% lithium nitride by means of mechanical agitation (1000 rpm, 25 min).

No small particles were found in samples (a) and (b). In sample (b), small particles which may have been formed by phase separation of lithium dissolved to atomic dimensions could possibly be observed in solid lithium chloride, but were probably not found because they were too small to be recognized or were covered with solid lithium chloride.

In almost all cases with samples (c) and (d), the recognition of small particles was considerably difficult because granular substances on the cross section were not clearly exposed and were covered with solid salt.

Figures 8, 9 and 10 were obtained with sample (d). A large number of small particles are observed in the figures. It appears that the surface in the figures where many particles exist is not a newly prepared cross section obtained by breaking a solid sample, but is instead a cave hidden inside cylindrical sample. Perhaps for this reason, small particles are clearly observed at the places not thickly covered with solid

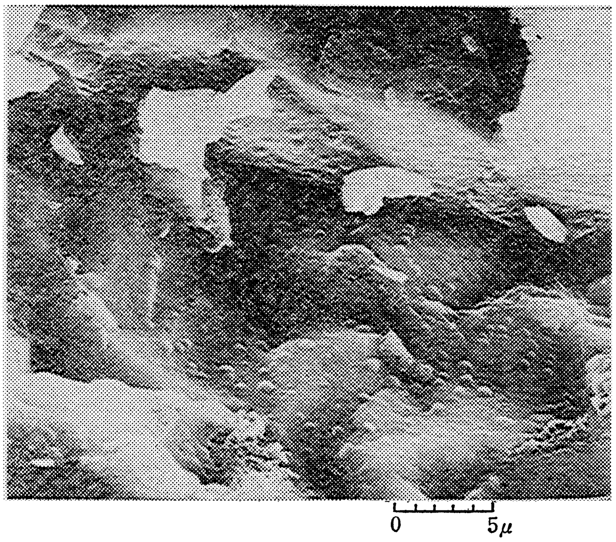

Fig. 8. Scanning electron micrograph of metallic lithium particles in lithium chloride.

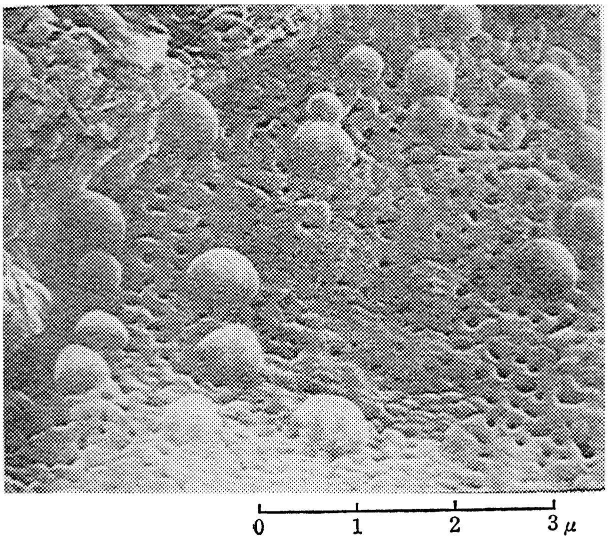

Fig. 9. Scanning electron micrograph of metallic lithium particles in lithium chloride.

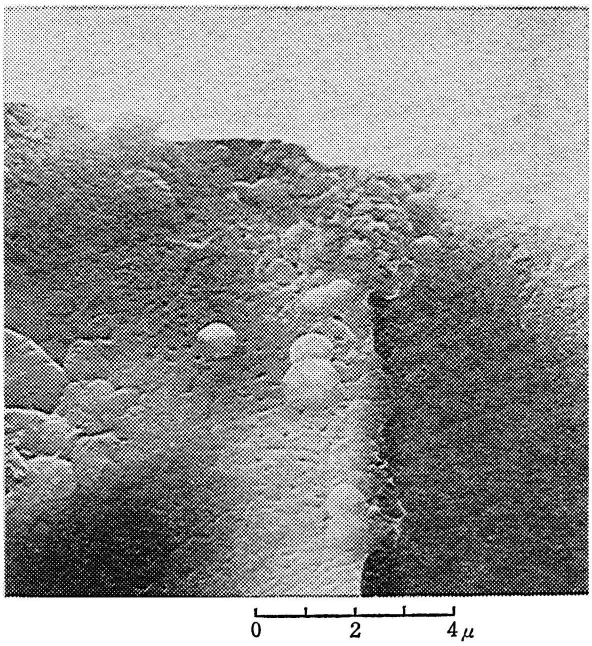

Fig. 10. Scanning electron micrograph of metallic lithium particles in lithium chloride.

salt. Elemental analysis was then carried out by means of an X-ray microanalyser in order to confirm whether these small particles were lithium metal. The distribution of lithium atoms cannot be found directly since the intensity of X-rays emitted by lithium atoms is too weak to be detected efficiently. Therefore, the X-ray intensities emitted from chlorine atoms were compared with each other by applying an electron beam to a small particle and its surroundings on as flat a surface as possible. Both the diameters of an electron beam and its transmission depth are 1 μ. Accordingly, if the diameter of a small particle is less than 1 μ or the small particle is covered with a thin film of solid salt, it is possible that chlorine atoms present around the particle or in the film of the solid salt would be detected and that the difference of both chlorine intensities would not be large. Actually the intensities for chlorine atoms obtained with small particles in the center of Fig. 10 were only slightly smaller than those obtained from their surroundings. If small particles in the figures are not lithium metal but solid salt, the chlorine intensities obtained from the projecting small particles would be considerably larger than those obtained from their surroundings because both concentrations of chlorine atoms are equal. Consequently, the small particles in the figures are regarded as lithium metal.

Now, the following situations should be taken into account when the particle sizes of dispersed lithium metal in the molten salt are evaluated from the small particles in the figures:

(1) Whether or not the coalescence of lithium particles occurred on rapid solidification of the sample.

(2) It is possible that small particles which were formed by the coalescence of lithium dissolved physically to atomic dimensions were mixed in the colloidal lithium.

(3) If lithium particles are covered with solid salt, they may be observed as particles larger than their true sizes.

(4) Since the temperature at which the sample was prepared was different from that at which a scanning electron micrograph was taken, it is necessary to correct for the contraction of the particles.

The particle-size distribution for 100 particles was obtained by taking the above problems into consideration and is given in Fig. 11. Most of the particles are distributed in the range of 0.3 to 0.9 μ and the largest particle has a diameter of 1.2 μ. The sizes of lithium particles in emulsion are then expected to be distributed in this range.

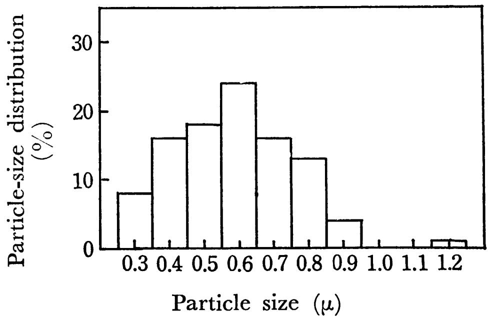

Fig. 11. Particle-size distribution of dispersed lithium in lithium chloride.

Generally, particles formed by spontaneous emulsification are smaller than those formed by mechanical agitation. In other words, it is expected that particles with larger diameters are formed by agitation, and thus the particle-size distribution also becomes slightly broader. For this reason, no lithium particles should be found by direct observation of the liquid state.

References

1) Part II of this series. T. Nakajima, K. Nakanishi, and N. Watanabe, *Nippon Kagaku Kaishi*, **1975**, 617.

2) N. Watanabe, K. Nakanishi, and T. Nakajima, *Nippon Kagaku Kaishi*, **1974**, 401.

3) 1.14 mol%. Ref. 1.

4) Lithium nitride and oxide. The amounts are not shown in Fig. 7.

5) 0.6 mol%. T. Nakajima, R. Minami, K. Nakanishi, and N. Watanabe, *Bull. Chem. Soc. Jpn.*, **47**, 2071 (1974).