Short communication

Water uptake by salts during the electrolyte processing for thermal batteries[☆]

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Abstract

Water uptake of single salts and electrolytes were measured in industrial conditions (dry-room). The water uptake rate ϑ ($g\,h^{-1}\,cm^{-2}$) was expressed with respect to the apparent area of contact of the salt with atmosphere of the dry room. The water uptake by potassium-based salts was very low. LiF and LiCl salts were found to behave similarly. For LiBr- and LiI-based salts and mixtures, we pointed out a linear relationship between the water uptake and the elapsed time. Water uptake by magnesium oxide reached a limit after 200 h.

This work provides a set of data concerning the rate of water uptake by single salts, salt mixtures and magnesia used in thermal battery electrolytes.

1. Introduction

Thermally activated batteries (thermal batteries) are electrical generators. They are mainly dedicated to military applications, due to their high reliability. They can be stored over 20 years without maintenance. Usually, the electrolyte is made of alkali halides mixtures. The electrolyte is solid and non conducting at room temperature. At temperatures higher than its melting point, it becomes an ionic conducting liquid.

Alkali halides, especially lithium halides, are known to be very hygroscopic. At high temperature, water can react with the molten salt, with hydrolysis leading to oxide and hydroxide ions formation. The presence of oxide or hydroxide ions leads to thermal battery dysfunctionning (electrolyte leakage, phase precipitation, . . .).

From a thermodynamic point of view, lithium halides salts are able to form stable hydrates $LiX \cdot nH_2O$ with X = Cl [1], Br [2], I [3,4]. Their decomposition temperatures range between 150 and 190 °C.

But only a few data, concerning the kinetic of water uptake by the salt powders, are available. Redey and Guidotti [5] estimated that the water uptake rate by LiF–LiBr–KBr was eight times higher than that by LiCl–KCl. Moreover, they found that the kinetic constant was multiplied by a factor of 10 when the water partial pressure was multiplied by 3.

Despite the careful attention paid during salts handling (thermal batteries are manufactured in dry rooms), the water uptake kinetics of new electrolytes need to be measured in industrial conditions to check the process. The aim of this work is to measure water uptake by single salts and electrolyte powders in industrial conditions and produce relevant and new data for use in process design.

2. Experimental

2.1. Materials

LiF, LiCl, LiBr, KCl, KBr, and KI were supplied from Sigma-Aldrich (+99.99% purity). 99.9% purity

Table 1
Melting points and compositions of the salts used in this study

Electrolyte	Composition (wt.%)	Composition (mol%)	References
LiF–LiCl–LiBr	9.6–22–68.4	22–31–47	[6]
LiF–LiCl–LiI	3.2–13–83.8	11.7–29.1–59.2	[7]
LiCl–KCl	44.8–55.2	58.8–41.2	[8]
LiBr–KBr	34.6–65.4	60–40	[8]
LiI–KI	58.2–41.8	63.3–36.7	[9,10]

(−200 mesh) lithium iodide was purchased from Cerac. Compositions of salt mixtures were taken from the literature. Table 1 summarizes the eutectic compositions of the mixtures used in this study.

Salts were usually dried individually under argon atmosphere in a silica crucible during 15 h. Fluoride-containing salts were fused in a special inert crucible to prevent partial silica dissolution. Salts mixtures were fused during 15 h. After recrystallisation, they were grinded and stored in glove boxes under inert atmosphere. Impurity concentrations (mainly oxides and hydroxides) were determined to be less than 10^{-4} molar fraction. In the case of LiI, a molar fraction of 5×10^{-2} was measured.

MgO powder, used as electrolyte binder (EB) in the separator, was provided by Aerospatiale batteries (ASB). It was dried by heating at 850 °C for 15 h to prevent hydration and carbonates formation. Then, it was stored under high purity argon atmosphere.

2.2. Apparatus

All the experiments were driven in an industrial dry-room of Aerospatiale batteries, where commercial thermal batteries are manufactured. The dew point was always maintained between −55 and −50 °C, whatever the season and the events. The water uptake by the salt powders was evaluated using the following home-made procedure: fixed volumes of powders were disposed in an aluminum can of 50 mm diameter and 10 mm height, and weighted twice a day during a period of 25 days, except during week-ends.

3. Results and discussion

During the 25 days of each experiment, we observed significant differences according to the nature of the salts. The results are presented separately for single salts then for mixtures. A synthesis is given for the whole results. In the fourth section, results obtained with MgO (used as electrolyte binder) are detailed.

3.1. Single salts

First of all, we give an overview of the results of water up-take by single salts. For the LiX (X = F, Cl, Br, I) and KX (X = Cl, Br, I) salts, we noticed two types of behavior with respect to:

 (i) the nature of the anion,
(ii) the nature of the cation (lithium or potassium).

First, the water uptake by potassium based single salts could be determined as very low (Fig. 1). It was found to be three decades lower than for lithium-based salts (Fig. 2). We observed no evident relation between the water uptake rates and time.

But in the cases LiBr and LiI, water uptake rates were found to be linear with time. We noticed some weight variations (periodic oscillations) around a mean straight line. These variations were attributed to the presence or absence of people inside the dry room during the industrial manufacturing.

Considering the electrolyte processing dedicated to thermal batteries, we concluded that only the LiBr and LiI salts were really sensitive to water contained in the atmosphere of the dry room. These salts do require special attention during their handling.

3.2. Mixtures

Concerning the binary and ternary mixtures studied, we observed the same trends (Fig. 3). For the LiCl–KCl eutectic, the water uptake was found to be negligible (three decades
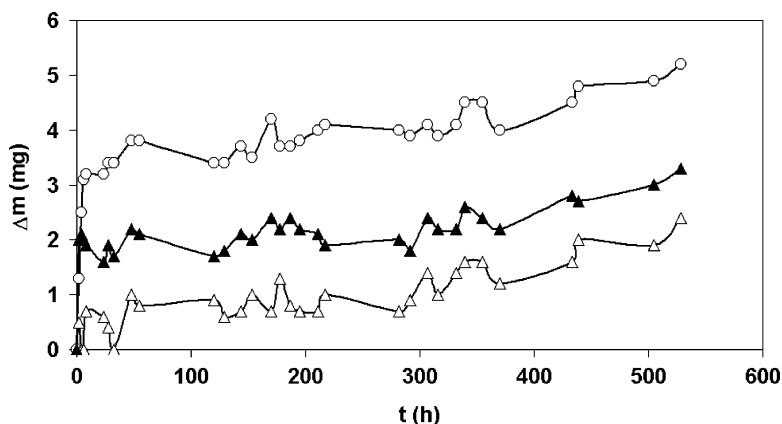

Fig. 1. Weight variations vs. time for different KX (X = Cl, Br, I) single salts, (○) KCl, (△) KBr, (▲) KI.
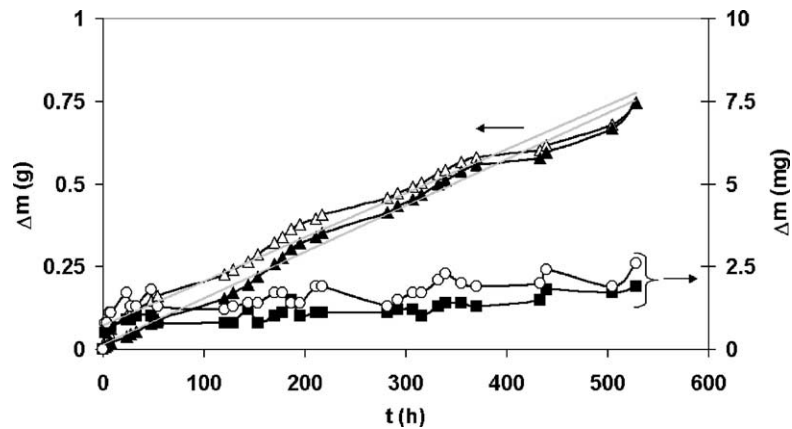
Fig. 2. Weight variations vs. time for different LiX (X = F, Cl, Br, I) single salts, (■) LiF, (○) LiCl, (△) LiBr, (▲) LiI.
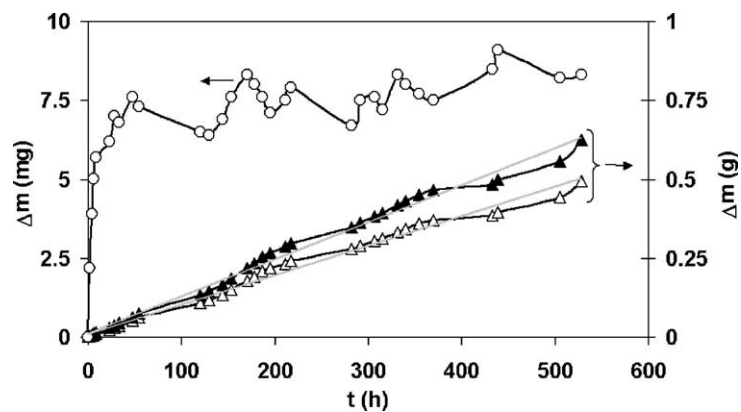

Fig. 3. Weight variations vs. time for different LiX–KX (X = Cl, Br, I) eutectic mixtures, (○) LiCl–KCl, (△) LiBr–KBr, (▲) LiI–KI.

lower than that of other binary mixtures). This point agrees with the previous determinations made with the LiCl and KCl single salts.

Now considering the iodide and bromide-based mixtures, we obtained a linear relationship between weight variations and time (Fig. 4). The behaviors of the binary and ternary mixtures were found similar to these of the single compounds. A deeper analysis of the relation between water up-take rates and electrolyte compositions is provided in the next section.

3.3. Synthesis

The water uptake rates for the salts and the electrolytes considered in this study are summarized in Table 2. The rate values were expressed with respect to the area of the
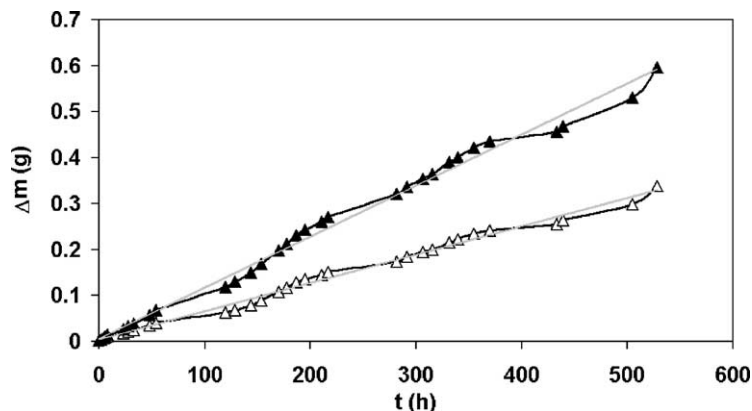

Fig. 4. Weight variations vs. time for lithium ternary electrolyte, (▲) LiF–LiCl–LiI, (△) LiF–LiCl–LiBr.

Table 2
Summary of the water uptake speeds

Salts	ϑ ($\times 10^4$) (g h^{-1} cm^{-2})
LiF	0.0002
LiCl	0.0002
LiBr	0.662
LiI	0.713
KCl	0.003
KBr	0.003
KI	0.003
LiCl–KCl	0.008
LiBr–KBr	0.458
LiI–KI	0.611
LiF–LiCl–LiBr	0.305
LiF–LiCl–LiI	0.56

salts surface in contact with the dry-room atmosphere. The water uptake speed ϑ is therefore expressed in g h^{-1} cm^{-2}. The halide molar fraction (Fig. 5) was calculated by adding the molar fractions of the components having a significant effect on hydration. In other words, it means that we took in consideration only the LiBr and LiI salts molar fractions. For bromide and iodide-based electrolytes, the water uptake rates increase with the halide amount contained in the salts. For both families of electrolytes, the water uptake rate increase follows a power law. Finally, using these master curves, we are able to estimate the water uptake of other new alkali halide-based electrolytes.

3.4. Magnesia

Magnesia is commonly used as electrolyte binder in the separator. The MgO weight fraction added in the separator depends on the electrolyte nature [11]. The magnesia water uptake was also taken in consideration in this study.

First of all, the weight variations of the MgO samples were found very different from the salt and mixture ones (Fig. 6). After 200 h of experiment, we did not observe any significant weight variation. This could be explained by the fact that a sufficient hydrated surface layer on magnesia could act as a barrier against the water molecules contained in the atmosphere.

The most probable fitted curve was obtained with Eq. (1):
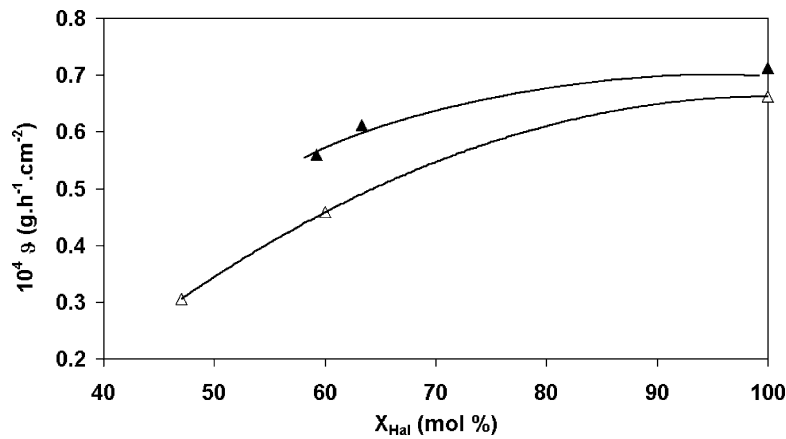
$$\Delta m(t) = A_0[1 - \exp(-kt)] \tag{1}$$

Fig. 5. Water uptake speed ϑ vs. the halide molar fraction, ($\triangle$) bromides, ($\blacktriangle$) iodides.
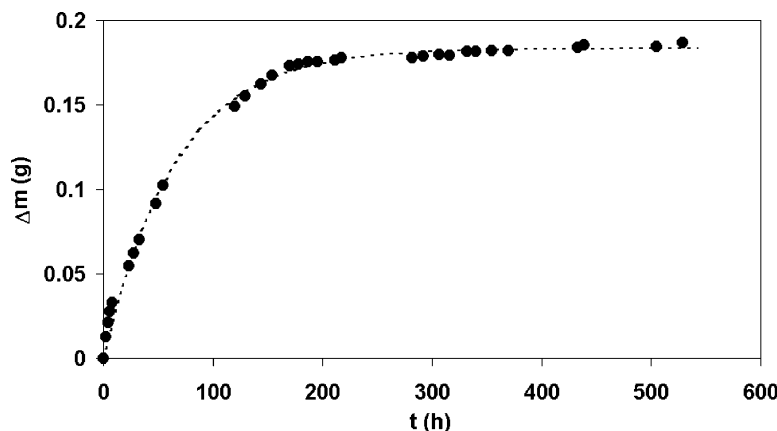

Fig. 6. Weight variations vs. time for MgO powder, ($\bullet$) experimental points, (- - -) fitted line.

The optimum values for A_0 and k, determined by a last square regression fit, were: $A_0 = 0.1834\,\text{g}$, $k = 54.84\,\text{h}^{-1}$ which yields the numerical expression expressed by Eq. (2):

$$\Delta m(t) = 0.1834[1 - \exp(-54.84t)] \tag{2}$$

But, considering the thermal battery process, it is realistic to think that the time elapsed between the drying step and the battery encapsulation under inert atmosphere does not exceed a few tens of hours. The saturation should not be reached during the electrolyte process.

4. Conclusion

Water uptake of (i) single salts LiX, KX, (ii) binary mixtures LiX–KX (X = Cl, Br, I), (iii) LiF–LiCl–LiI and LiF–LiCl–LiBr electrolytes, and (iv) MgO were experimentally measured in industrial conditions (e.g. dry-room). We found that the water uptake by potassium-based salts was very low (three decades lower than others). LiCl and LiF salts exhibited similar behaviors.

For other single salts (LiI and LiBr) and mixtures (except LiCl–KCl), we pointed out a linear relationship between the water uptake and the time elapsed. The water uptake rate increased when the lithium fraction increased. Moreover, the iodide-based salts were found more hygroscopic than bromide-based salts.

Concerning magnesia, which is used as electrolyte binder, a limiting value was reached after 200 h.

This work provides a complete set of data concerning the water uptake by single salts and electrolytes used in thermal batteries.

References

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