

EFFECT OF ELECTROLYTE ON THE PERFORMANCE IN ELECTROCHEMICAL REPAIRING TECHNIQUE FOR THE CONCRETE AFFECTED BY ASR

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Abstract

This research is to study the effect of anolyte on the performance in repairing the concrete damaged by ASR using Accelerated Lithium Migration Technique (ALMT). The cylindrical concrete specimens were designed according to ASTM C1293, made by ASR reactive aggregate with 1.25 % $\text{Na}_2\text{O}_{\text{eq}}$. ALMT tests were performed using 1N $\text{LiOH} \cdot \text{H}_2\text{O}$, 1N LiNO_3 , saturated Li_2CO_3 and saturated $\text{Li}_2\text{B}_4\text{O}_7$ as anolytes, and $\text{Ca}(\text{OH})_2$ as catholyte. 9 A/m^2 constant current density was used up to 30 days. The concentrations of Na^+ and Li^+ in catholyte were also measured during the test, and the distribution of ions in the specimens, the expansive behavior of the specimens also measured after ALMT test. The results show that using 1N $\text{LiOH} \cdot \text{H}_2\text{O}$ as anolyte was the most effective in driving alkali ion out and driving lithium ion into the concrete, and showing the better effect against expansive ASR.

Keywords: ASR, electrochemical technique, repair, lithium

1 INTRODUCTION

According to practical investigation and literatures, there are many concrete structures affected by alkali-silica reaction (ASR) mostly centering in northeast and east of Taiwan [1-2]. The research on ASR verification method was predominant in the early 1990s. The research on adding admixtures to prevent fresh concrete from ASR began in the mid 1990s [3].

In 1998, Lee conceived of removing sodium and potassium ions from the concrete based on the characteristics of anions moving toward the anode and cations moving toward the cathode, meanwhile conveying lithium ions which can inhibit ASR into the concrete. A $5.5 \times 2.5 \times 28.5$ cm cement mortar specimen was made based on this conception for fundamental research. The 4 N lithium hydroxide and lithium nitrate solutions were filled in the anode tank, the saturated $\text{Ca}(\text{OH})_2$, 4 N sodium hydroxide and sodium nitrite solutions were filled in the cathode tank. Electrified at current density of 1, 3, 6 A/m^2 for 7 weeks, it was found that the combination of 4N LiOH and saturated $\text{Ca}(\text{OH})_2$ could inhibit the swelling behavior of the specimen effectively. The quantitative analysis of ion content in catholyte and specimen proved that the alkali ions could actually be removed from the specimen through the electrochemical treatment, so that the alkali ion concentration in the specimen was reduced, and the lithium ion concentration was increased [4]. Therefore, the studies of electrochemistry repairing ASR structures were initiated.

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In 2000, The Accelerated Lithium Migration Technique (ALMT) was developed referring to the ASTM C1202 method (RCPT). ALMT uses electrochemistry to inhibit ASR, on the one hand, "accelerate removing free Na^+ (K^+) from concrete specimen" to eliminate the key factor in ASR; on the other hand, "drive Li^+ into the specimen to change the concrete properties", so as to inhibit ASR [5].

The lithium compound was usually used as the admixture to inhibit ASR in early stages, proper application of lithium compound can inhibit the expansion caused by ASR effectively. The surface charge of Li^+ is stronger than that of Na^+ and K^+ , therefore, Na^+ and K^+ in alkali-silica colloid will be substituted by Li^+ , so as to form indissoluble lithium-silica colloid with strong bonding force, so that the swelling capacity can be inhibited [3]. There are many studies of using lithium salt as the admixture to protect fresh concrete, however, there has been no study of the influence of using different lithium salt water solutions as electrolyte on electrochemical treatment effect.

This study used ASR reactive aggregate to produce a concrete cylinder specimen, the ALMT test was carried out after 28 days curing. The anolyte was changed during test, 1N lithium hydroxide monohydrate, 1N lithium nitrate, saturated lithium carbonate and saturated di-lithium tetraborate were used respectively, the voltage and the ion concentration change in the electrolyzer were measured during electrochemical treatment. The ion content in the specimen was analyzed after electrochemical treatment. And the treated specimen was put in 38°C 100 % R.H. environment for one year to measure the swelling capacity change to evaluate the effect of inhibiting ASR. We hope the results can be used as reference for selecting electrolyte type in practical application of ALMT.

2 MATERIALS AND METHODS

2.1 Materials and specimen

The low-alkali cement of 0.51% $\text{Na}_2\text{O}_{\text{eq}}$ was used. The reactive aggregate was metasandstone obtained from eastern Taiwan, ASTM C289, C1260 and C1293 tests shows that the aggregate has high ASR reactivity.

The mixture preparation of concrete was carried out according to ASTM C1293. But the alkali of cement was adjusted to 1.25 % $\text{Na}_2\text{O}_{\text{eq}}$ by adding NaOH. The aggregate gradation conformed to ASTM C1293. The water cement ratio was 0.58. The slump was 15 cm. A $\phi 10 \text{ cm} \times 20 \text{ cm}$ concrete cylinder specimen was made, and then cured in 23°C 100 % R.H. environment. After 28 days curing, the concrete cylinder was cut to 5cm high specimens at the middle part for ALMT test.

2.2 ALMT

The experimental design referred to RCPT (ASTM C1202), The ALMT test configuration is shown in Figure 1. The electrolyzer capacity was increased to 1 liter in the test module, and the wall thickness was reduced to accelerate heat elimination, and constant current density of 9 A/m² was applied. This study used 1N $\text{LiOH} \cdot \text{H}_2\text{O}$, 1N LiNO_3 , oversaturated LiCO_3 and oversaturated $\text{Li}_2\text{B}_4\text{O}_7$ as the anolyte respectively, and used saturated $\text{Ca}(\text{OH})_2$ as the catholyte. The electrode was #_20 304 stainless steel net. The pre-treatment of specimen was according to ASTM C1202 procedure. The voltage and cation concentration in catholyte were measured periodically, and the free cation distribution in the treated specimen was analyzed referring to AASHTO T260 method. The one-dimensional ALMT can be used in practical structure with smaller thickness, so in the two sides of structure can setup auxiliary electrode to process electrochemical treatment.

3 RESULTS

3.1 Effect of anolyte type on required voltage for maintaining constant current density

Figure 2 shows the voltage applied for maintaining the constant current density under ALMT. It shows 1N $\text{LiOH} \cdot \text{H}_2\text{O}$ has the minimum initial voltage of 8.6 V. The applied voltage reaches 93.1 V after 30

days electrochemical treatment. There is white crystal on the surface of the downstream side (see Figure 3-(a)) which is CaCO_3 as tested by XRD. It may be because there is high alkali ions concentration in the pore solution inside the specimen before ALMT test which inhibits the dissolution of free Ca^{2+} , however, the Na^+ (K^+) migrates to the cathode and the concentration decreases under the effect of electric field, the Ca^{2+} is dissolved out gradually so that the Ca^{2+} concentration in the pore solution increases. Ca^{2+} in pore solution is transmitted toward the catholyte as driven by the electric field, meanwhile the CO_3^{2-} formed from CO_2 dissolving in catholyte is transmitted toward the anode. Therefore, the CaCO_3 precipitate is formed and blocks the pore channel gradually, so the specimen impedance is increased.

The test with 1 N LiNO_3 as anolyte has the maximum initial voltage of 11.1 V. After 30 days electrochemical treatment, the increase of applied voltage is the second highest one, which is 92.2 V. It may be because there is sticky reddish brown precipitate on the surface of the downstream specimen (see Figure 3-(b)).

The increase in the voltage of oversaturated LiCO_3 and $\text{Li}_2\text{B}_4\text{O}_7$ is small, and there is no sediment on the surface of the specimen at the cathodic side after ALMT treatment.

3.2 Effect of anolyte type on ion migration

Figure 4-(a) shows that the Na^+ moves out of the specimen in the similar mode. There are high concentrations of Na^+ in the specimen at the beginning of process, and they are in front of the cation migration path, so that the flux of Na^+ in catholyte is large. When the amount of Na^+ in the specimen decreases, then the flux also decreases. The average Na^+ flux of the first nine days during ALMT is shown in Table 1, the magnitude of flux in sequence is oversaturated $\text{LiCO}_3 >$ oversaturated $\text{Li}_2\text{B}_4\text{O}_7 >$ 1N $\text{LiNO}_3 >$ 1N $\text{LiOH}\cdot\text{H}_2\text{O}$. The value of average Na^+ flux during 10~30 days is oversaturated $\text{Li}_2\text{B}_4\text{O}_7 >$ 1N $\text{LiOH}\cdot\text{H}_2\text{O} >$ 1N $\text{LiNO}_3 >$ oversaturated LiCO_3 . The above trend meets the result of total amount of Na^+ removed from specimen in Table 2: 1N $\text{LiOH}\cdot\text{H}_2\text{O} >$ oversaturated $\text{Li}_2\text{B}_4\text{O}_7 >$ oversaturated $\text{LiCO}_3 >$ 1N LiNO_3 .

Figure 4-(b) shows after the Li^+ pass through the specimen, and then moves in catholyte also in the same mode. Li^+ is adding in anolyte at the beginning of test, so it needs some time to pass through the specimen, and the time depends on the anolyte: oversaturated $\text{Li}_2\text{B}_4\text{O}_7$ (12 days) $>$ oversaturated LiCO_3 (9~12 days) $>$ 1N LiNO_3 (9 days) $>$ 1N $\text{LiOH}\cdot\text{H}_2\text{O}$ (6 days).

The flux of Li^+ after moving out of the specimen is shown in Table 1, according to different anolytes: 1N $\text{LiOH}\cdot\text{H}_2\text{O} >$ 1N $\text{LiNO}_3 >$ oversaturated $\text{Li}_2\text{B}_4\text{O}_7 >$ oversaturated LiCO_3 .

Since Na^+ is in front of migration sequence of Li^+ in ALMT test module, intuitively, if the Na^+ is transmitted fast (oversaturated $\text{LiCO}_3 >$ oversaturated $\text{Li}_2\text{B}_4\text{O}_7 >$ 1N $\text{LiNO}_3 >$ 1N $\text{LiOH}\cdot\text{H}_2\text{O}$), the following Li^+ shall pass through the specimen faster, but the fact is not so according to the results (oversaturated $\text{Li}_2\text{B}_4\text{O}_7$ (12 days) $>$ oversaturated LiCO_3 (9~12 days) $>$ 1N LiNO_3 (9 days) $>$ 1N $\text{LiOH}\cdot\text{H}_2\text{O}$ (6 days)).

There may be two reasons: (1) it is related to the pore structure change during the ALMT experiment, the sediment on the surface of treated specimen in Figure 3 shows that the partial pore near catholyte was blocked.; (2) it is related to electric quantity ratio carried by ions, the electric quantity ratio is proportional to the transference number of ions, the potential effect is described below:

Since the test module adopts 9 A/m² constant current density, the migration of ions in the solution maintains the channel. Andrade [6] indicates that for a system under the effect of pure electric field, if different ion concentrations in the electrified system can be measured, the transference number (expresses as symbol t_i) and the current density (expressed as symbol i) applied in the electrochemical treatment process can be substituted in Eq. (1) to figure out the theoretical value of each flux (expressed as symbol J_i):

$$J_j = \frac{it_j}{nF} \quad (1)$$

which, J_j is one-dimensional flux of ions (mole/cm²/s)

i is current density (A/cm²).

n is ion electrovalence number.

F is Faraday constant (96500 C/mole).

t_j is transference number of j ion.

In Eq. (1), the transference number t_j means the percentage of the current carried by j ion to total current in an electrified system is related to ionic mobility, and proportional to the concentration and relative rate of ions. The transference number t_j can be obtained from Eq. (2).

$$t_j = \frac{I_j}{I} = \frac{Z_j C_j u_j}{\sum Z C u} \quad (2)$$

which, I_j is the magnitude of current carried by j ion (A).

I is total magnitude of current of the electrified system (A).

Z_j is electrovalence number of j ion.

C_j is total concentration of j ion (mole/cm³).

u_j is the velocity of j ion in unit electric field (cm/s/(Volts/cm) i.e. cm²/Volt-s), called ionic mobility.

In this study, only the type of anolyte is changed, according to Eq. (1), the Na⁺ and Li⁺ flux values are proportional to transference number t_j . According to Eq. (2), t_j will be influenced by Li⁺ concentration. The Li⁺ concentration in this study is LiOH.H₂O (1 N) = LiNO₃ (1 N) > oversaturated LiCO₃ (0.38 N) > oversaturated Li₂B₄O₇ (0.11 N). As the former two have the same concentration much higher than the latter two, the Na⁺ transference number of the latter two is larger than that of the former two, and the initial flux of Na⁺ moving out of specimen of the latter two is greater than that of the former two. On the contrary, the transference number of Li⁺ of the former two is larger than that of the latter two, and the flux of Li⁺ in catholyte of the former two is larger than that of the latter two. However, the correct sequence is still influenced by other ion concentrations in the electrified system and the specimen pore channel structure change during the electrochemical treatment.

3.3 Effect of anolyte type on removing Na⁺ from specimen

Table 2 shows that the amount of removed Na⁺ from different anolyte specimens after 30 days electrochemical treatment accounts for about 76.6~87.5 % of total content in specimens. The consolidated form of residual quantity accounts for 6.4~12.3 % of designed content, compared with the unelectrified control group that the consolidated Na⁺ accounts for 37 % of designed content, it is obvious that in the ALMT test process, although the anolytes used are different, they dissolve the consolidated Na⁺ from hydration products.

As shown in Table 2, the percentage of total residual Na⁺, free and consolidated proportions of residual Na⁺ in treated specimen according to the anolytes is: 1N LiOH.H₂O < oversaturated Li₂B₄O₇ < oversaturated LiCO₃ < 1N LiNO₃, matching Figure 4-(a) Na⁺ flux trend.

3.4 Effect of anolyte type on inhibiting ASR

The aim of ALMT treatment is to reduce alkali inside the specimen and drive Li⁺ into the specimen for inhibiting ASR expansion. For new structures, in order to prevent ASR expansion, the reactive aggregates shall be avoided, and the alkali content shall be limited, including alkali content in cement to 0.6 % Na₂O_{eq}, or total content of Na₂O_{eq} in concrete < 3 kg/m³ according to Canada specifications. If the alkali content

exceeds the standard, Li salt can be added in as the inhibitor. General studies have found that Li/Na molar ratio > 0.74 can inhibit ASR effectively.

Next we will review whether ALMT treatment has attained the expected goal, as shown in Table 3, although the used anolytes are different. After 30 days electrochemical treatment, the total content of $\text{Na}_2\text{O}_{\text{eq}}$ inside specimen is decreased from the design value 4.96 kg/m^3 to total content of average free $\text{Na}_2\text{O}_{\text{eq}}$ $0.38 \sim 0.53 \text{ kg/m}^3$. And the infed Li^+ makes the average free Li/Na molar ratio to be $6.67 \sim 10.16$, so the ALMT treatment goal has been attained.

The ALMT treated specimen was put in 38°C 100 % R.H. environment for 1 year accelerated curing, and the expansion was measured, as shown in Figure 5. The change in the expansion in the radius direction of top and bottom sides of the cylinder specimen is not obvious. It is mainly because this measured area is a round plane, the tensile stress of the specimen dilation in the diameter direction is restricted by the round shape. A good swelling resistance is generated. Therefore, it can be observed that the plane is unlikely to have cracks.

The expansion in the height direction of cylinder specimen is related to the average $\text{Na}_2\text{O}_{\text{eq}}$ content in specimen and Li/Na molar ratio. As shown in Figure 5, the expansion of untreated control group is 0.289 %, whereas the expansion of the specimens using 1N $\text{LiOH} \cdot \text{H}_2\text{O}$, 1 N LiNO_3 , oversaturated LiCO_3 and oversaturated $\text{Li}_2\text{B}_4\text{O}_7$ as the anolyte is -0.252 %, -0.084 %, -0.034 % and -0.026 % respectively, the effect of inhibiting ASR is proved. In addition, Table 3 shows that the average free Li/Na molar ratio in the specimen using 1N $\text{LiOH} \cdot \text{H}_2\text{O}$ solution as the anolyte is highest, and the residual average free $\text{Na}_2\text{O}_{\text{eq}}$ content is lowest and thus best at inhibiting ASR.

4 DISCUSSION

In summary, ALMT using 1N $\text{LiOH} \cdot \text{H}_2\text{O}$, 1N LiNO_3 , oversaturated LiCO_3 or oversaturated $\text{Li}_2\text{B}_4\text{O}_7$ as the anolyte, the key factor Na^+ causing ASR in concrete can be removed, and the Li^+ for inhibiting dilation can be fed in at the same time, so that can inhibit the ASR expansion when alkali ingresses concrete from outer environment in future.

Although the anolytes used are different, as the Na^+ distribute in the specimen at the beginning of electrochemical treatment, and they are in front of cation migration path, so that they will be transmitted to the catholyte earlier than Li^+ at the beginning of electrochemical treatment. The initial flux of Na^+ is large, and then the flux decreases as the Na^+ in specimen decrease. The Li^+ is behind the Na^+ in the cation migration path, so it needs some time to pass through the specimen, and then the flux increases gradually.

The test results show that the anolyte of 1N $\text{LiOH} \cdot \text{H}_2\text{O}$ electrified for 30 days has the maximum average Na^+ flux, the maximum total quantity of Na^+ removed from specimen, the minimum time of 6 days for removing Li^+ from specimen, the maximum flux of Li^+ removed from specimen, the maximum average free Li/Na molar ratio in the treated specimen, and the minimum expansion of specimen after one year accelerated curing. All the results show that using 1N $\text{LiOH} \cdot \text{H}_2\text{O}$ as the anolyte can obtain the best ASR repair effect under ALMT treatment.

However, using 1N $\text{LiOH} \cdot \text{H}_2\text{O}$ as the anolyte still has to overcome some problems, the CaCO_3 may block the pores at the end of electrochemical treatment that increases the impedance, so that the service voltage needs to be increased and the Li^+ flux decreases.

5 CONCLUSIONS

This study has obtained the following conclusions:

- (1) ALMT using lithium solutions as the anolyte can remove the Na^+ causing ASR problem and feed in the Li^+ having inhibitory effect on dilation at the same time.
- (2) The Na^+ will enter the catholyte earlier than Li^+ because it is in front of the cation migration path at the beginning of electrochemical treatment. The initial flux of Na^+ is large, and then the flux decreases gradually as the Na^+ inside specimen decrease. The Li^+ need a period of time to pass through the specimen, and then the flux increases gradually.
- (3) When 1N $\text{LiOH} \cdot \text{H}_2\text{O}$ is used as the anolyte, the total quantity of Na^+ removed from specimen is at the maximum, the time for Li^+ removing from specimen is at the minimum, the average Li/Na molar ratio in the treated specimen is at the maximum, and the expansion of specimen after one year accelerated curing is at the minimum, it shows the best ASR repair effect can be obtained.
- (4) Using 1N $\text{LiOH} \cdot \text{H}_2\text{O}$ as the anolyte still has to overcome some problems, the CaCO_3 may block the pores at the end of electrochemical treatment that increases the impedance, so that the service voltage needs to be increased and the Li^+ flux decreases.

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Analyte	Average flux $\times 10^{-10}$ (mole/cm ² /s)		
	Na ⁺		Li ⁺
	1~9 days	10~30 days	Since passing through test block ~ 30 days
1 N LiOH · H ₂ O	4.56	0.91	2.84
1 N LiNO ₃	4.68	0.73	2.31
Oversaturated Li ₂ CO ₃	5.02	0.14	1.76
Oversaturated Li ₂ B ₄ O ₇	4.83	1.18	1.83

Analyte type	Percentage of total removed quantity (g) to designed content (%)	Residual Na ⁺ in treated specimen						
		Percentage of total residual quantity (g) To designed content (%)	Free form			Consolidated form		
			Free form quantity (g)	To total residual quantity (%)	To designed quantity (%)	Consolidated form quantity (g)	To total residual quantity (%)	To designed quantity (%)
1 N LiOH · H ₂ O	0.929 (87.5)	0.133 (12.5)	0.065	48.9	6.1	0.068	51.1	6.4
1 N LiNO ₃	0.814 (76.6)	0.248 (23.4)	0.117	47.2	11.0	0.131	52.8	12.3
Oversaturated Li ₂ CO ₃	0.875 (82.4)	0.187 (17.6)	0.080	42.8	7.5	0.107	57.2	10.1
Oversaturated Li ₂ B ₄ O ₇	0.914 (86.1)	0.148 (13.9)	0.073	49.3	6.9	0.075	50.7	7.0

Note: 1. The designed content of Na⁺ in the specimen before electrochemical treatment is 1.062 g.

2. The consolidated Na⁺ accounts for 37 % of the designed content in the untreated control group.

Analyte type	Electrified specimen												
	Water dissolution method lithium/sodium molar ratio in each segment						Free Na ₂ O _{eq} in each segment (kg/m ³)						
	Distance to positive terminal (cm)					average	Distance to positive terminal (cm)					average	
	0~1	1~2	2~3	3~4	4~5		0~1	1~2	2~3	3~4	4~5		
1 N LiOH · H ₂ O	21.58	12.04	10.12	4.63	2.40	10.16	0.42	0.45	0.37	0.41	0.42	0.41	
1 N LiNO ₃	17.31	13.31	8.33	8.98	2.23	10.03	0.40	0.39	0.49	0.41	0.97	0.53	
Oversaturated Li ₂ CO ₃	12.12	7.51	6.52	5.12	2.05	6.67	0.38	0.43	0.41	0.38	0.43	0.41	
Oversaturated Li ₂ B ₄ O ₇	19.27	12.79	7.24	6.10	1.91	9.46	0.37	0.36	0.42	0.39	0.38	0.38	

Note: the design value of total content of Na₂O_{eq} in specimen is 4.96 kg/m³.

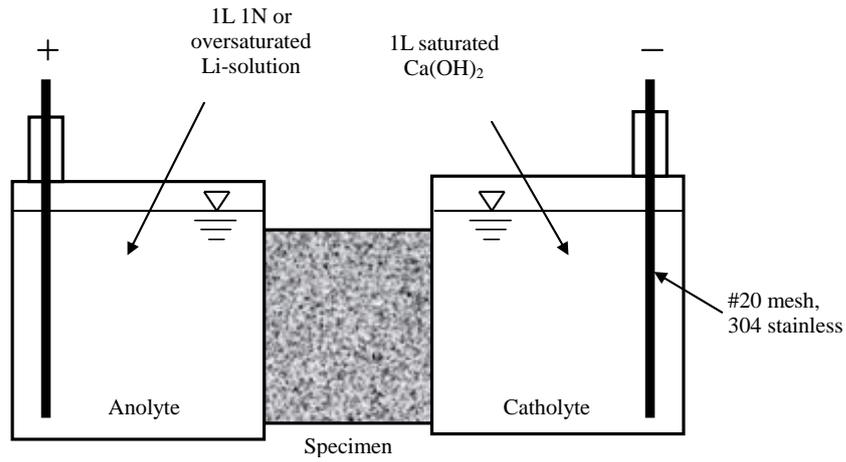


FIGURE 1: Schematic diagram of ALMT test configuration.

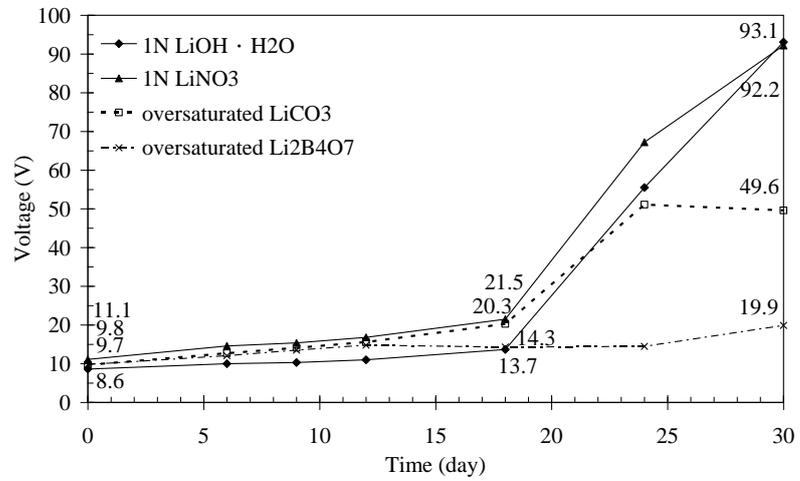


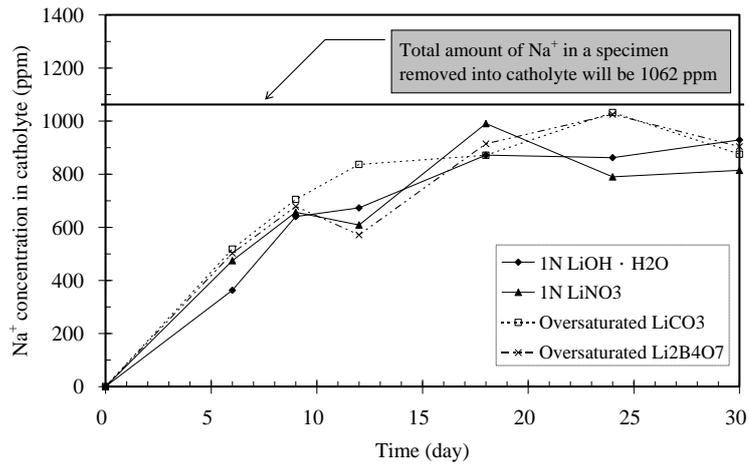
FIGURE 2: Effect of anolyte type on required voltage for maintaining constant current density.



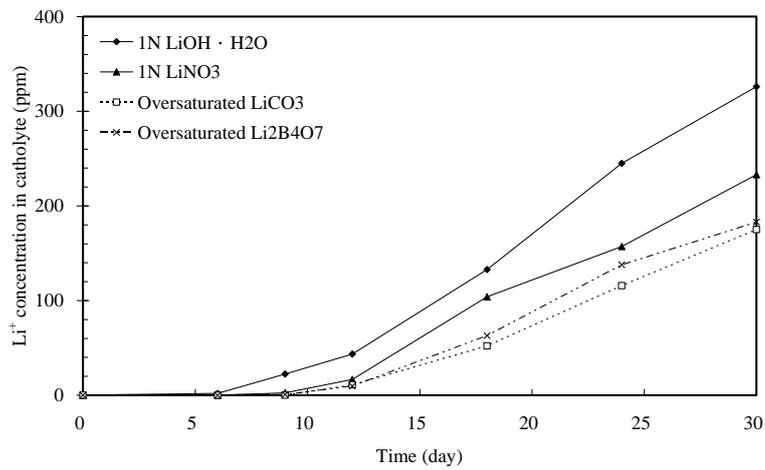
(a) Use 1N LiOH · H₂O as anolyte

(b) Use 1N LiNO₃ as anolyte

FIGURE 3: Photos on the surface of specimen at the cathodic side after ALMT treatment.



(a)



(b)

FIGURE 4: Ion concentration in catholyte during ALMT test.

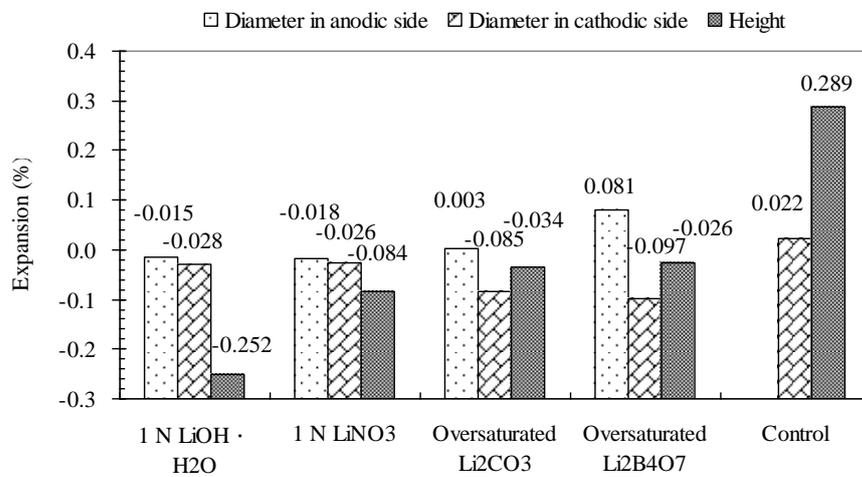


Figure 5: Expansion of specimens after 1 year storage in 38°C 100% R.H. environment.