Enhanced Electrochemical Stability of Molten Li Salt Hydrate Electrolytes by the Addition of Divalent Cations

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Supporting Information

ABSTRACT: Water can be an attractive solvent for Li-ion battery electrolytes owing to numerous advantages such as high polarity, nonflammability, environmental benignity, and abundance, provided that its narrow electrochemical potential window can be enhanced to a similar level to that of typical nonaqueous electrolytes. In recent years, significant improvements in the electrochemical stability of aqueous electrolytes have been achieved with molten salt hydrate electrolytes containing extremely high concentrations of Li salt. In this study, we investigated the effect of divalent salt additives (magnesium and calcium bis(trifluoromethanesulfonyl)amides) in a molten salt hydrate electrolyte (21 mol kg⁻¹ lithium bis(trifluoromethanesulfonyl)amide) on the electrochemical stability and aqueous lithium secondary battery performance. We found that the electrochemical stability was further enhanced by the addition of the divalent salt. In particular, the reductive stability was increased by more than 1 V on the Al electrode in the presence of either of the divalent cations. Surface characterization with X-ray photoelectron spectroscopy suggests that a passivation layer formed on the Al electrode consists of inorganic salts (most notably fluorides) of the divalent cations and the less-soluble solid electrolyte interphase mitigated the reductive decomposition of water effectively. The enhanced electrochemical stability in the presence of the divalent salts resulted in a more-stable charge-discharge cycling of LiCoO₂ and Li₄Ti₅O₁₂ electrodes.

INTRODUCTION

Aqueous rechargeable lithium batteries (ARLBs) have attracted much attention as greener, safer, and cost-efficient energy-storage technologies since being reported for the first time in 1994,¹ owing to environmental benignity, nonflammability, and low cost of aqueous electrolytes.²⁻⁵ Another appealing aspect of ARLBs is that there is no need for rigorous environments such as extremely low moisture conditions during the battery manufacturing process, unlike that of nonaqueous Li-ion batteries. However, inherently poor electrochemical stability of aqueous electrolytes hampers the use of conventional electrode materials established in nonaqueous Li-ion batteries. The cell voltage of ARLBs is inevitably limited to be less than the potential difference between the oxygen and hydrogen evolution reactions in the aqueous electrolytes (thermodynamically, 1.23 V for pure water).¹² Therefore, ARLBs with low cell voltage suffer from inferior energy density (<100 Wh kg⁻¹),¹³ which is less than half that of the nonaqueous counterparts. In particular, poor stability at the negative electrode is one of the most serious issues that should be addressed to increase the cell voltage of ARLBs: there is an enormous difference (i.e., gap) between the redox potential of commonly used negative electrodes (e.g., 1.55 V for Li₂Ti₅O₁₂, and 0.01 V for graphite vs Li/Li⁺) and the hydrogen evolution reactions (2.65 V vs Li/Li⁺ for pure water at pH = 7). In previous works, the cell voltage was increased to ~4 V by introducing lithium-conducting protective (electronically insulating) layers such as an inorganic solid electrolyte,¹⁴ a water-immiscible gel electrolyte,¹⁵ and a hydrophobic ionic liquid (IL) electrolyte¹⁶ into the interphase to separate the low-potential negative electrode and the aqueous electrolyte. However, the complicated biphasic systems may not be beneficial for ARLBs in terms of cost and fabrication process. In a recent work by Suo et al., this greatest barrier to widespread application (i.e., the insufficient reductive limit of aqueous electrolytes) was substantially improved by simply...
increasing the Li salt concentration to form a molten salt hydrate electrolyte, that is, water-in-salt electrolyte (21 mol kg\(^{-1}\) lithium bis(trifluoromethanesulfonyl)amide (LiTFSA), molar ratio \([\text{H}_2\text{O}] / [\text{LiTFSA}] = 2.6\).\(^{17}\) The potential window for the water-in-salt electrolyte expanded to 3.0 V, and successful charge—discharge of 2.3 V ARLBs was demonstrated. Yushin et al. also reported stable charge—discharge cycling of LiFePO\(_4\) electrodes by increasing Li salt molarity in aqueous electrolytes.\(^{18}\) Despite the facile approach, there is a complex rational mechanism behind the successful demonstration of moderately high voltage ARLBs with molten salt hydrate electrolytes. A high concentration of Li\(^+\) ions significantly reduces the activity of uncoordinated water, leading to the enhanced oxidative stability of the electrolyte. High lithium concentration (high Li\(^+\) activity) also causes a thermodynamic positive shift of the redox potential of the anode and cathode on the basis of the Nernst equation, and that contributes to a decrease in the difference between the negative electrode potential and the reductive decomposition potential of water since the potential of water reduction is less influenced by the lithium salt concentration.\(^{19}\) More importantly, the reductive stability was kinetically enhanced by an anion-derived passivation layer that is formed by preferential decomposition of TFSA anions at the negative electrode interface. LiF was found to be a major component of the aqueous solid electrolyte interphase (SEI) that aids in alleviating the hydrogen evolution reaction at the negative electrode.

To further improve the electrochemical stability of the molten salt hydrate electrolytes, binary Li salt hydrate eutectic electrolytes have recently been proposed. Suo et al. further decreased the \([\text{H}_2\text{O}] / [\text{Li}^+]\) molar ratio to \(\sim 2\) (c.f. the aforementioned single salt electrolyte, \([\text{H}_2\text{O}] / [\text{Li}^+] = 2.6\)) by combining LiTFSA with lithium trifluoromethanesulfonate (LiTFO) for preparing the molten salt hydrate electrolyte and succeeded in applying this electrolyte with a carbon-coated TiO\(_2\) negative electrode (1.9 V vs Li/Li\(^+\)).\(^{20}\) Yamada et al. reported further improvement of the reductive stability by employing a molten salt hydrate eutectic, Li-(TFSA)\(_0.7\)BETI\(_0.3\)H\(_2\)O (BETI: bis-(pentafluoroethanesulfonyl)amide).\(^{21}\) Again, with an anion-derived passivation layer combined with the low electrocatalytic activity of the employed Al current collector for the hydrogen evolution reaction, the Li\(_4\)Ti\(_5\)O\(_12\) negative electrode was successfully applied to ARLBs. Thus, in ARLBs with molten salt hydrate electrolytes, the aqueous SEI plays a crucial role in inhibiting the hydrogen evolution reaction, and thereby, the reductive stability predominantly relies on the durability of the passivation layer during charge—discharge cycling. However, in this regard, aqueous electrolytes forming an SEI still have some room for improvement because the hydrogen evolution was not completely eliminated even in these molten salt hydrate electrolytes.\(^{22}\)

The recognition of molten salt hydrates as a specific class of electrolytes was first made during study of divalent salts, such as Mg(NO\(_3\))\(_2\),\(^{23}\) and Ca(NO\(_3\))\(_2\),\(^{24}\) wherein the divalent cations have larger hydration number (3—4, 6, and 6—8 for Li\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\), respectively) and more strongly interact with water.\(^{25—27}\) Furthermore, it was reported that the addition of divalent salts to nonaqueous Li salt electrolytes exerts a positive impact on charge—discharge performance of a LiNi\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)O\(_2\) cathode\(^{28}\) and a graphite anode.\(^{29}\) In this work, we revisit effects of divalent salts in the molten salt hydrate electrolytes for ARLBs. Magnesium bis(trifluoromethanesulfonyl)amide (Mg[TFSA])\(_2\) or calcium bis(trifluoromethanesulfonyl)amide (Ca[TFSA])\(_2\) was added to the Li-based water-in-salt electrolyte (\([\text{H}_2\text{O}] / [\text{LiTFSA}] = 2.6\)) to prepare novel binary salt hydrate electrolytes, and their electrochemical stability was investigated. In addition, the composition of a passivation layer formed in the presence of the divalent salts was characterized by X-ray photoelectron spectroscopy (XPS). Compatibility of LiCoO\(_2\) and Li\(_4\)Ti\(_5\)O\(_12\) electrodes with the binary salt hydrate electrolytes containing the divalent cations was also studied using a three-electrode electrochemical cell.

### EXPERIMENTAL SECTION

**Materials.** Lithium bis(trifluoromethanesulfonyl)amide (LiTFSA) was kindly supplied by Solvay Japan. Calcium bis(trifluoromethanesulfonyl)amide (Ca[TFSA])\(_2\) was purchased from Kishida Chemical Co. (Japan). Water content of the salts was less than 50 ppm. Bis(trifluoromethanesulfonyl)amide (HTFSA) was purchased from Kanto Chemical Co. (Japan). Magnesium was purchased from Wako Pure Chemical Industries (Japan). Magnesium bis(trifluoromethanesulfonyl)amide (Mg[TFSA])\(_2\) was prepared by neutralization of HTFSA with Mg metal according to the procedure reported in the literature.\(^{30}\) The Li salt molten hydrate (abbreviated as LH) was prepared by mixing LiTFSA with ultrapure water (Milli-Q Integral 3) at a molar ratio of LiTFSA/H\(_2\)O = 1/2.6, corresponding to a molality of 21 mol kg\(^{-1}\). The divalent salts were further added to LH at a molar ratio of LiTFSA/Mg[TFSA]\(_2\)/H\(_2\)O = 1/0.03/2.6 for the Li—Mg binary salt hydrate electrolyte (LHM) and at a molar ratio of LiTFSA/Ca[TFSA]\(_2\)/H\(_2\)O = 1/0.05/2.6 for the Li—Ca binary salt hydrate electrolyte (LCH).

For the preparation of the LiCoO\(_2\) electrode, LiCoO\(_2\) powder (Nippon Chemical Industrial Co., Japan), acetylene black (AB, Denki Kagaku Kogyo, Japan), and poly(vinylidene fluoride) (PVDF, Kishida Chemical Co., Japan) were used as the active material, a conduction supporting agent, and the binder, respectively. The mass ratio of LiCoO\(_2\)/AB/PVDF was 85/9/6. A slurry of the above materials with N-methylpyrroliodine (NMP, Kanto Chemical Co., Japan) was spread on a Ti foil current collector and dried at 80 °C. For the preparation of the Li\(_4\)Ti\(_5\)O\(_12\) electrode, Li\(_4\)Ti\(_5\)O\(_12\) powder (Ishihara Sangyo Kaisha, Japan), AB, and PVDF were mixed at the mass ratio of Li\(_4\)Ti\(_5\)O\(_12\)/AB/PVDF = 85/10/6. A slurry with NMP was spread on an Al foil current collector and dried at 80 °C. The AB electrode was prepared on an Al foil at a mass ratio of AB/PVDF = 4/1 in a manner similar to that of the above electrodes.

**Measurements.** The ionic conductivity (\(\sigma\)) was determined by the complex impedance method using an electrochemical measurement system (VMP3, Bio-Logic Science Instruments) in the frequency range of 500 kHz to 1 Hz with an alternating voltage amplitude of 10 mV at 30 °C. A two-platinized platinum electrode cell (CG-511B, TOA Electronics) was used, and the cell constant was determined using 0.01 M KCl aqueous solution at 25 °C prior to the measurements. The density and viscosity were measured using a viscometer (SVM 3000, Anton Paar), and lithium salt concentration (\(c_{\text{Li}}\)) was determined from the density value at 30 °C.

The melting point (\(T_m\)) was determined using a differential scanning calorimeter (DSC7020, Hitachi High-Tech Science
Corporation). The molten salt hydrates were hermetically sealed in aluminum pans. The samples were first heated to 60 °C, followed by cooling to −150 °C, and then reheated from −150 to 60 °C at a scan rate of 1 °C min⁻¹ under a nitrogen atmosphere.

Water activity \( (a_w) \) in the molten salt electrolytes was determined by vapor pressure measurements. The vapor pressures were measured in the temperature range from 45 to 80 °C and were simply analyzed on the basis of the Clausius–Clapeyron equation. The log \( p \) versus \( 1/T \) plots fall on a straight line, suggesting that the vaporization enthalpy should be practically constant in the temperature range. Consequently, the vapor pressure was extrapolated to the value at 25 °C to evaluate the water activity \( a_w \) of the molten salt hydrates, which was defined as the ratio of the vapor pressure of the molten salt hydrates \( p \) to that of pure water \( p_0 \) at the same temperature; \( a_w = p/p_0 \).

The divalent salts, Mg[TfSA]₂ and Ca[TfSA]₂, were poorly soluble in LH unlike that of the reported binary systems of Li salt hydrates such as LiTfSA/LiTfO₂/H₂O and LiTfSA/LiBETI/H₂O, where the additional Li salt can dissolve in the parent molten hydrate up to 30 mol % with respect to LiTfSA.20,21 The addition of just several mole percent of the divalent salts, such as Mg²⁺ and Ca²⁺, to the LiTfSA reached the saturation limit. Therefore, the binary salt hydrate mixture was prepared at nearly saturated conditions; 3 mol % became slightly higher than 25 °C. For cyclic voltammetry (CV) and charge–discharge tests of the LiCoO₂ electrode, LiCoO₂ (2.5 mg cm⁻², 10 mm in diameter), Li₁₋ₓCoOₓ (\( x < 0.5 \)) (4.5 mg cm⁻², 17 mm in diameter), and Ag/AgCl were used as working, counter, and reference electrodes, respectively. Li₁₋ₓCoOₓ counter electrode was prepared by preliminarily charging the LiCoO₂ electrode in 1 M LiClO₄/propanediol carbonate at 0.2 C, followed by washing with DME and drying for 1 day at 80 °C. For cyclic voltammetry (CV) and charge–discharge measurements of the LiTf₂O₁₂, Li₄Tf₃O₁₂ (2.2 mg cm⁻², 10 mm in diameter), LiCoO₂ (4.5 mg cm⁻², 17 mm in diameter), and Ag/AgCl were used as working, counter, and reference electrodes, respectively. A glass filter paper (GA-SS, Advantec) as a separator was placed between the working and counter electrodes, and the electrodes and the separator were further sandwiched between two glass substrates. This setup was soaked in the electrolyte along with the Ag/AgCl reference electrode for the electrochemical measurements. CV was performed on each electrode at 30 °C at a scan rate of 1 mV s⁻¹. Galvanostatic charge–discharge measurements were performed at 30 °C. The specific capacity of the cell was calculated on the basis of the active material loading of the working electrode. The gravimetric current densities for charge–discharge were 137 and 175 mAh g⁻¹ (1 C rate) for the LiCoO₂ and Li₄Tf₃O₁₂ electrodes, respectively.

### RESULTS AND DISCUSSION

#### Bulk Electrolyte Properties.

The saldant values, Mg[TfSA]₂ and Ca[TfSA]₂, were poorly soluble in LH unlike that of the reported binary systems of Li salt hydrates such as LiTfSA/LiTfO₂/H₂O and LiTfSA/LiBETI/H₂O, where the additional Li salt can dissolve in the parent molten hydrate up to 30 mol % with respect to LiTfSA.20,21 The addition of just several mole percent of the divalent salts with respect to LiTfSA reached the saturation limit. Therefore, the binary salt hydrate mixture was prepared at nearly saturated conditions; 3 and 5 mol % of the divalent salts were added for LMH and LCH, respectively. Table 1 summarizes electrolyte properties.

| Electrolyte | Li⁺ (mol dm⁻³) | LiClO₄ (mol dm⁻³) | η (mPa s) | σ (mS cm⁻¹) |
|-------------|---------------|------------------|----------|--------------|
| LMH         | 28.2          | 4.95             | 0.149    | 82.1         | 8.8         |
| LCH         | 27.7          | 4.80             | 0.240    | 89.5         | 6.2         |

The results showed that the viscosity and conductivity values of the molten salt hydrates, including melting point \( (T_m) \), lithium salt concentration \( (c_{Li}) \), viscosity \( (η) \), and conductivity \( (σ) \) at 30 °C in the presence or absence of the divalent salts, although \( T_m \) became slightly higher than 25 °C by the addition of the divalent salts, the molten salt hydrates remained a supercooled liquid at room temperature. Furthermore, all of the electrochemical measurements were performed in the...
molten state at 30 °C, \( c_{Li} \) remained very high for both LMH and LCH (approximately 5 mol dm\(^{-3}\)) because only a small amount of the divalent salt was added. The presence of the divalent cations significantly increased the viscosity of the molten salt hydrates, and the enhanced viscosity is responsible for the lower ionic conductivity, especially for LCH. However, the \( \sigma \)-values of LMH and LCH were higher than that of \((\text{Li(TFSI)}_{0.7} \cdot \text{(BETI)}_{0.3} \cdot 2\text{H}_{2}\text{O})\)^{37} and of a comparable level to that of organic electrolytes,\(^{38}\) and therefore sufficient for use in ARLBs.

In a previous report on LH, a molecular dynamics (MD) simulation showed that the Li\(^+\) ion was coordinated by approximately two oxygen atoms from water and two oxygen atoms from TFSI in the first solvation sheath and 15% of water molecules remained uncoordinated as “free” water in LH on bulk on average.\(^{37}\) In the later MD simulation and neutron scattering experiments, the liquid structure of LH was found to be nanosegregated into water-rich and TFSI-rich domains.\(^{34}\) In the present study, water activity \( a_w \) was also determined from the vapor pressure of the molten salt hydrates (Figure 1).

\[ a_w = 0.18 \text{ for LH} \]

This value corroborates the previous estimation by MD simulation. The amount of free water was further reduced by coordination with the additional divalent cations. Although the change in \( a_w \) was not significant upon the addition of Ca[TFSI]\(_2\), the addition of Mg[TFSI]\(_2\) reduced \( a_w \) to 0.12 because of the smaller ionic radius of Mg\(^{2+}\) than that of Ca\(^{2+}\). Namely, the smaller \( a_w \)-value for LMH is attributed to the stronger interaction of Mg\(^{2+}\) with water. The nonzero \( a_w \)-values suggest that a small amount of free water was still present in both LMH and LCH. These \( a_w \)-values are slightly higher than that of saturated LiCl solution\(^{39}\) but comparable to that of \((\text{Li(TFSI)}_{0.7} \cdot \text{(BETI)}_{0.3} \cdot 2\text{H}_{2}\text{O})\).\(^{21}\) These values are much lower than the reported \( a_w \)-values of saturated aqueous solutions of other inorganic salts (e.g., 0.780 for NaCl, 0.453 for K\(_2\)CO\(_3\), and 0.333 for MgCl\(_2\)).\(^{35,36}\)

To gain insight into the hydration structure, ATR-IR spectra were recorded for LH, LMH, and LCH. Figure 2 shows ATR-IR spectra corresponding to the OH stretching vibrations. These spectra are represented on the basis of the apparent molar IR absorption coefficient for each molten salt hydrate. It is well known that the OH vibration band has a peak at 3450 cm\(^{-1}\) with a shoulder at 3225 cm\(^{-1}\) for pure water and the absorption in the frequency range of 3225–3450 cm\(^{-1}\) decreases when a Li salt is added.\(^{37–40}\) There were three discernible peaks at 3250, 3530, and 3620 cm\(^{-1}\) for LH, in which the absorption in the lower-frequency region for pure water obviously reduced. A similar decrease in the peak intensity in the lower-frequency region has also been reported in the Raman spectra of \((\text{Li(TFSI)}_{0.7} \cdot \text{(BETI)}_{0.3} \cdot 2\text{H}_{2}\text{O})\).\(^{21}\)

Small but significant changes in IR absorption can be seen in the presence of the divalent salts for LMH and LCH. The variation is more visible in the difference spectra shown in the inset of Figure 2. The IR absorption was intensified at around 3250 and 3480 cm\(^{-1}\) but was lowered at about 3630 cm\(^{-1}\) in LMH. On the other hand, LCH shows a decrease in the IR absorption at 3250 cm\(^{-1}\) whereas the IR absorption increases around 3500 cm\(^{-1}\). Although the spectral change depends on the type of the metal ion species, the observed variation in the OH stretching bands evidently reveals that the small amount of divalent metal ions can affect the hydration structure in both LMH and LCH.

**Electrochemical Oxidative and Reductive Stability.** It was previously reported that the oxygen evolution potential in LH remarkably shifts to a more-positive potential from the thermodynamic value for pure water at pH = 7 (1.02 V vs Ag/AgCl).\(^{17}\) This can be interpreted as being a result of the lowered highest occupied molecular orbital (HOMO) energy level of water upon coordination with metal cations in a similar manner as for highly concentrated organic electrolytes.\(^{41}\) The depletion of free water in proximity to the positively charged electrode also accounts for the enhanced oxidative stability in the molten salt hydrates.\(^{42}\) Furthermore, the electrode materials affected the oxidation potential of LH: The Pt electrode showed a higher electrocatalytic activity than that of Au and glassy carbon electrodes.\(^{43}\) To study the effect of the divalent cations on the electrochemical oxidative stability of the molten hydrate electrolyte, LSV was performed on the Pt electrode. In Figure 3a, the onset of significant oxidation current associated with the oxygen evolution reaction was observed at around 1.6 V (vs Ag/AgCl) and the positive shift of this potential was less-pronounced even by the addition of the divalent cations, suggesting a similar HOMO energy level for LH, LMH, and LCH. Since the difference in \( a_w \) was not significant, or very small, in the molten salt hydrates studied here, it is reasonable that their oxidative stabilities were comparable from a thermodynamic point of view. At 1.2 V, a small oxidation current was detected in LH, while the oxidation current was marginal in LMH and LCH. This small current is probably attributed to the oxidative decomposition of free water at the electrode interface. The total concentration of water was lower and that of TFSA was higher in LMH and LCH. Therefore, the more-pronounced accumulation of TFSA anion at the positively charged electrode interface may contribute to the improved stability.
at 1.2 V for LMH and LCH. As a result, the addition of the divalent salts did not significantly expand the oxidation limit, but it mitigated a minor oxidative reaction at 1.2 V.

The poor reduction stability of aqueous electrolytes is the key issue for aqueous Li-ion batteries because the redox potential of typical anode materials is situated in a more-negative potential range than the reduction limit of all reported aqueous electrolytes including LH and related systems, as discussed in the Introduction. Indeed, the cathodic stability on the Pt electrode was much less affected by the salt concentration.21 The catalytic activity of hydrogen evolution reactions depends on the electrode materials. The Al electrode was found to greatly suppress the hydrogen evolution with an anion-derived passivation film by a kinetic means and thus considered to be a practical choice for the negative electrode current collector of aqueous Li-ion batteries.21 We also confirmed that the reduction potential of the hydrogen evolution reaction on the Al electrode was around −1.5 V (vs Ag/AgCl) in LH (Figure 3b), which is much more negative than the theoretical value (−0.214 V for pure water at pH = 7). Noteworthy is that the reduction stability of LH was further enhanced by the addition of Mg[TfSA]2 or Ca[TfSA]2: the reduction potential shifted even further to negative potential by more than 1 V in both LMH and LCH (Figure 3b). This raises the possibility that components of the passivation layer formed in the presence of the divalent cations differ from those of the aqueous SEI in LH, and it inhibits the reductive decomposition of water more effectively. Consequently, the addition of divalent salts was found to afford an electrochemical potential window exceeding 4.0 V.

**Surface Characterization.** The components of the passivation film on the Al electrode were characterized by XPS measurement after cathodic polarization. In previous works, LiF was found as the dominant decomposition product of TFSA in LH, and the LiF-based compact layer serves as a passivation film to suppress the reductive decomposition of water.17,20−22 As shown in Figure 4a, the presence of LiF (∼56 eV)43,44 was suggested in the Li 1s spectral range (52−65 eV) in agreement with the previous works. On the contrary, for LMH and LCH, there are no peaks in the Li 1s spectra, suggesting the absence of any Li species such as LiF even after the Ar etching for 60 s. The XPS F 1s, S 2p, and C 1s spectra of all of the samples suggest that TFSA residues (identified by comparison with previously reported peak positions)45 were present at the outermost surface but were eliminated by Ar etching (Figure S1). Aluminum oxide was also detected in the O 1s (∼533 eV) and Al 2p spectra (∼76 eV)32 of LH and LMH. The absence of any analogous Al 2p peak for LCH is attributed to a relatively thicker SEI (Figure S1). The peak in the Mg 2p spectra (∼51 eV)46 can be assigned to MgF2 in LMH (Figure 4b), and the peak in the Ca 2p spectra at ∼348 eV47 indicates the formation of CaF2 in LCH (Figure 4c). We note here that we cannot exclude the possibility for the presence of a small proportion of MgCO3 or CaCO3 in these spectra (due to the similar peak position of the carbonates),48,49 which may be formed through the reduction of a minute amount of O2 and CO2 dissolved in LMH and LCH, respectively.22 Thus, the main components of the passivation...
film in the presence of a small amount of the divalent salts differ from those found in LH, and the inorganic salts originated from the divergent cations would passivate the Al electrode in LMH and LCH instead of the Li-derived decomposition products. The solubility of MgF₂, CaCO₃, and CaF₂ in water is 2 orders of magnitude lower than that of LiF (Table S1).⁵⁰ These divalent salts are more unlikely to dissolve in LMH and LCH with the reduced a_w. Therefore, the less-soluble passivation film could be stabilized in the aqueous electrolytes, whereby the reductive decomposition of water on the Al electrode was remarkably suppressed, leading to the extraordinary negative potential shift of the reduction limit (Figure 3b). Although the detailed formation mechanism needs more investigation, we speculate a possible pathway to form the different type of passivation layer in LMH and LCH. Given that the concentration of Li ions is much higher than that of the divergent cations in LMH and LCH, it is reasonable that LiF is initially formed at the electrode interface along with the reductive decomposition of TFSA, as is the case for LH.¹⁷

The slightly soluble LiF can dissociate into the ions in the electrolyte, and then Li⁺ is replaced by the divergent cations to form the fluoride salts with a lower solubility product constant in equilibrium. In the initial stage on the cathodic polarization, the hydrogen evolution reaction can also compete with the reductive decomposition of TFSA and hydroxide salts would form as the intermediates of aqueous SEI at the electrode interface. An aqueous SEI can form through the soluble intermediates, and more-soluble Ca(OH)₂ than Mg(OH)₂ may result in the formation of a thicker SEI in LCH (Table S1).

**Electrochemical Behavior of LiCoO₂ and Li₄Ti₅O₁₂ Electrodes.** LiCoO₂ electrodes have been well studied as positive electrodes for aqueous Li-ion batteries.⁵¹⁻⁵⁵ Recently, successful charge–discharge of a Li₄Ti₅O₁₂ electrode (as a negative electrode) was also reported with a hydrate-melt electrolyte, (Li(TFSA))ₓ(BETI)ₙ·2H₂O.²¹ Here, the electrochemical behavior of LiCoO₂ and Li₄Ti₅O₁₂ electrodes in the molten hydrate electrolytes was studied using a three-electrode cell. As seen in Figure 5a, the capacity gradually declined with charge–discharge cycling in LH and deteriorated to about half of the initial capacity in the 50th cycle. On the other hand, in LMH and LCH, the capacity degradation was much smaller and the discharge capacity remained high (e.g., 132.4 mAh g⁻¹ in LCH) even after 50 cycles (Figure 5b,c). Coulombic efficiencies in LMH and LCH were also found to be high (∼99.5%) over 50 cycles (Figure S2).

It was reported that the capacity fading of the LiCoO₂ electrode in the aqueous systems is due to the parasitic insertion of H⁺, which can be generated by the oxidative decomposition of water into LiCoO₂.⁵⁴,⁵⁵ Hence, the enhanced oxidative stability at 1.2 V for LMH and LCH, as discussed in the former section, is primarily responsible for the improved charge–discharge performance of LiCoO₂ electrodes. Yushin et al. suggest that the formation of a resistive CoO layer on the particles’ surface is another cause of the degradation of the LiCoO₂ electrode in aqueous electrolytes. At a higher concentration of lithium salt, there is less growth of the CoO layer due to a lower free water concentration.⁵⁶ Further lowering the water activity with the addition of divalent cation might be expected to have a similar effect. The effect of the divergent cations on the improved charge–discharge behavior of LiCoO₂ electrodes in LMH and LCH was further elucidated by cyclic voltammetry on each component of the composite electrode (i.e., Ti current collector and AB conductive additive). We first confirmed that no oxidation current was observed at 1.2 V, which is the cutoff potential for charging, on the Ti electrode in all of the molten salt hydrates (Figure S3). At a glance, the LiCoO₂ electrode showed similar voltammograms in the molten salt hydrates, and the Nernst shift of the LiCoO₂ redox potential was also negligible because of similar ηL values (Figure 6). However, larger oxidation current was clearly observed at 1.2 V

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**Figure 5.** Charge–discharge curves of three-electrode cells measured at 1 C (342 μA cm⁻²) using LiCoO₂ as the working electrode, Li₁₋ₓCoO₂ as the counter electrode, and Ag/AgCl as the reference electrode in (a) LH, (b) LMH, and (c) LCH.

**Figure 6.** Cyclic and linear sweep voltammograms on LiCoO₂ (broken lines) and AB (solid lines) electrodes, respectively, in LH, LMH, and LCH at a scan rate of 1 mV s⁻¹. The inset shows the enlarged view.
in LH on the AB electrode. Therefore, the addition of the divalent salts reinforced the oxidative stability on AB conductive additives, leading to the improved charge–discharge performance of the LiCoO₂ composite electrode.

Figure 7 shows charge–discharge curves of Li₄Ti₅O₁₂ electrodes in the molten salt electrolytes. In LH (Figure 7a), the discharge capacity largely exceeded the theoretical value (175 mAh g⁻¹) and the reductive decomposition of LH persisted at around −1.5 V at the sixth cycle. This indicates that the reductive decomposition of water becomes dominant over the insertion of Li⁺. In LMH (Figure 7b), the capacity gradually faded with cycling, although the reductive decomposition was mitigated in comparison with the case for LH. On the other hand, in LCH (Figure 7c), the Li₄Ti₅O₁₂ cell delivered a high initial discharge capacity of 149 mAh g⁻¹ at the 1 C rate and showed relatively stable charge–discharge cycles. Coulombic efficiencies in LMH and LCH were ∼80% and 90%, respectively, and were much greater than that in LH (Figure S4). We suggest that the better cycle performance and higher Coulombic efficiencies in LCH are probably linked to the lower solubility (or higher durability) of the Ca-salt-based passivation layer that effectively shielded the electrode surface.

The effect of the divalent cations on the charge–discharge behavior of Li₄Ti₅O₁₂ electrodes was also investigated by cyclic voltammetry on both the AB conductive additive and the Li₄Ti₅O₁₂ composite. Figure 8 shows cyclic and linear sweep voltammograms on Li₄Ti₅O₁₂ and AB electrodes. The insertion of the divalent cations into Li₄Ti₅O₁₂ with large particle size would be negligible because of the kinetically sluggish reaction of the divalent cations. The redox potential of Li₄Ti₅O₁₂ did not change regardless of the presence/absence of the divalent cations; however, the reduction current at −1.5 V (i.e., cutoff voltage of charge–discharge tests) on the AB electrode was much lower in LMH and LCH, suggesting that the hydrogen evolution reaction was more suppressed. Previous studies reported the formation of a Li-ion-based passivation film including LiF and Li₂O on the charged Li₄Ti₅O₁₂ electrode. Likewise, the Mg- or Ca-based passivation film can be formed on the Li₄Ti₅O₁₂ composite electrode with AB conductive additive as well as Al current collector (as revealed in Figure 2b), and it contributed to the improved charge–discharge performance in LMH and LCH. The small reduction current at −1.5 V on the AB electrode also indicates that the reductive decomposition of water was not completely avoided on the Li₄Ti₅O₁₂ composite electrode even in LCH, and it would result in the Coulombic efficiency of ∼90%. As seen in Figure 8, the reductive decomposition generating OH⁻ was not completely suppressed at −1.5 V in all of the electrolytes. Therefore, the corrosion of Al current collector under basic conditions may deteriorate the electron-conduction pathway, and it would be responsible for the gradual capacity fading of the Li₄Ti₅O₁₂ electrode.

CONCLUSIONS

The binary salt hydrate electrolytes, LMH and LCH, were prepared by the addition of Mg[TFSA]₂ or Ca[TFSA]₂ to LH to reduce the amount of free water in the molten salt hydrate electrolytes. The divalent cations were hydrated with the remaining free water in LH, leading to a lower δw and an enhanced oxidative stability. Despite the relatively small amount of the additional salt, the divalent cations have a great influence on the components of the passivation layer formed by reductive decomposition of the electrolyte on the Al electrode. A more sparingly soluble SEI consisting of the inorganic fluorides and carbonate salts of the divalent cations was formed for LMH and LCH, and that was responsible for the increase in the reductive stability. As a result, the electrochemical potential window was expanded to more than 4.0 V. In the charge–discharge test of the LiCoO₂ electrode, the capacity deterioration became less-pronounced and Coulombic efficiency increased to ∼99.5% by the addition of the divalent salt. In the charge–discharge test of the Li₄Ti₅O₁₂ electrode, the addition of the divalent salt greatly suppressed the hydrogen evolution reaction, particularly for...
LCH, and it led to the more-stable charge–discharge cycling with relatively high Coulombic efficiency of ~90%. The charge–discharge performance of the Li$_{2}$Ti$_{2}$O$_{12}$ electrode in the present binary salt hydrate electrolytes with the divalent salt additives was still insufficient for a long-life practical use in ARLBs. However, this study provides an insight into future optimizations of aqueous electrolytes that are capable of forming a more-durable aqueous SEI using multivalent salt additives.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b06251.

XPS patterns (F 1s, S 2p, C 1s, O 1s, N 1s, and Al 2p) of the Al electrode; the solubility of LiF, MgCO$_{3}$, MgF$_{2}$, CaCO$_{3}$, and CaF$_{2}$ in water at 20 °C; Coulombic efficiency and discharge capacity of the LiCoO$_{2}$ electrode; linear sweep voltammetry on Ti electrode at a scan rate of 1 mV s$^{-1}$ at 30 °C; Coulombic efficiency and discharge capacity of the Li$_{2}$Ti$_{2}$O$_{12}$ electrode (PDF).

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**Notes**

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