Non Nucleophilic Mg Electrolytes: Recent Advances

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Abstract

The development of rechargeable Magnesium (Mg) batteries is currently hampered by the lack of a high-performance electrolyte. In the early stages of rechargeable Mg battery development, Grignard-type electrolytes were the sole option. Grignard-type electrolytes, on the other hand, have intrinsic safety difficulties and limited oxidation stability due to their nucleophilic nature and strong reactivity, which limit the development of rechargeable Mg batteries in terms of practical use. Emerging innovative Mg battery systems, such as Mg-S and Mg-O$_2$/air batteries, have recently required non nucleophilic electrolytes with good oxidation stability. This brief overview covers recent achievements in non nucleophilic Mg electrolytes, with the goal of providing insights into their electrochemical characteristics and active Mg ion structure.

Keywords: Rechargeable Mg battery; Non-nucleophilic; Coordination Mg complex; Energy storage

Introduction

Rechargeable Lithium-Ion Batteries (LIBs) have emerged as the main secondary energy storage solution after years of intense study and innovation. However, due to limited lithium supplies, meeting the rising demand for portable devices and electric cars remains a significant concern. Because of numerous significant benefits, rechargeable Magnesium (Mg) batteries have been recognized as a possible contender for revolutionary LIBs technology. The theoretical volumetric capacity of a magnesium anode is 3,833 mAh cm^{-2}, which is five times that of graphite anode–based LIB. Mg is substantially more numerous than Li, ranking eighth among the top 40 most prevalent elements in the Earth's crust. Mg's non dendritic nature makes Mg metal batteries easier to manufacture than Li-based battery systems. Other obvious advantages over Li-ion batteries include decreased cost and improved safety. However, due to a number of intrinsic issues, the advantage of rechargeable Mg batteries has not been thoroughly shown. The actual energy density is still significantly lower than planned due to low discharge voltage and capacity; also, the battery's cycle performance is exceedingly poor. The passivation effect on the Mg anode in electrolytes is a significant contributor to the unsatisfactory operating voltage and low cyclability of Mg-based batteries. Even in non-aqueous electrolytes, a surface passivation coating composed of

ionic Mg compounds is generated during stripping/plating. Unlike in Li or Na batteries, such passivation coating prevents Mg^{2+} migration, resulting in significant over potential and irreversible stripping/plating.

Grignard reagents and their analogues were the only electrolytes that allowed high efficiency stripping/plating in the early stages of rechargeable Mg battery development. The first Mg electrolyte with reversible deposition capabilities was produced by the researcher, which is based on a Grignard reagent activated by $AlCl_3$. Many studies have now concentrated on Mg organo halo aluminate salts produced by the complexation of Grignard reagents RMgX with $AlCl_3$ in ether solutions. The creation of a new rechargeable Mg-S, Mg-O_2/air battery system increases the need for non nucleophilic Mg electrolytes. Because sulphur and oxygen are easily attacked by nucleophiles, standard nucleophilic electrolytes are incompatible with Mg-S, Mg-O_2/air batteries. Even in Mg-ion batteries based on intercalation chemistry, nucleophilic electrolytes have limitations. Most nucleophilic Mg electrolytes have low oxidative stability due to the usage of organomagnesium precursors, limiting the use of high-voltage cathode materials. The very sensitive and caustic nature of Grignard-based electrolytes makes production problematic.

The creation of a Grignard reagent free, non nucleophilic Mg electrolyte not only meets the criteria of rechargeable Mg-S and Mg-O_2/air batteries, but also meets the requirements of practical rechargeable Mg ion battery production step by step. We covered the evolution and recent achievements in non nucleophilic electrolytes in this mini review. Their electrochemical performance and ionic coordination structure were addressed in order to give fresh insights for future Mg-based electrolyte development.

Nonnucleophilic mg electrolytes' electrochemical performance

Electrolytes based on hexamethyldisilazide

By adding Lewis acid $AlCl_3$ to hexamethyldisilazide magnesium chloride (HMDSMgCl) in THF, the first efficient non nucleophilic Mg electrolyte was prepared, demonstrating Coulombic Efficiency (CE) of > 95% with an increased Mg deposition current density by nearly a factor of seven compared to HMDSMgCl-only electrolyte. The discharge capacity of Mg-S coin cell utilising HMDSMgCl-$AlCl_3$ electrolyte was originally 1,200 mAh g^{-1}, however it reduced to 394 mAh g^{-1} in the subsequent cycle. Later, stable, commercially available $(HMDS)_2Mg$ was utilised to replace HMDSMgCl, which demonstrated extremely good oxidative stability (3.5 V vs. Mg) and reversible Mg deposition up to 40 cycles with a 150 mV over potential. $MgCl_2$ was used to convert $HMDSAlCl_2$ into active species in order to overcome the disadvantage of byproduct $HMDSAlCl_2$ generation in $(HMDS)_2$ Mg-$AlCl_3$ electrolyte. In Mg-S battery, this innovative electrolyte demonstrated a discharge potential of 1.65V, which was close to the expected thermodynamic value. Researcher refined the technique by generating [(HMDS) $MgCl_2$-Mg_2Cl_3] by reverse Schlenk equilibrium from the reaction of $(HMDS)_2$ Mg and $MgCl_2$. The replacement of $MgCl_2$ for Lewis acid $AlCl_3$ successfully prevented the usual Al deposition reported in electrolytes containing $AlCl_3$. In terms of ionic conductivity (0.5 mS cm^{-1}), oxidative stability (2.8 V vs. Mg), and Mg stripping/plating CE, it performed similarly to HMDSMgCl-$AlCl_3$ (99%).

Electrolytes from MACC

Because of their simplicity and low cost, all-inorganic $MgCl_2$-$AlCl_3$ complex (MACC) electrolytes are of special interest when using non nucleophilic and inexpensive Mg^{2+} sources of $MgCl_2$. In 2005, preliminary research on MACC electrolyte was completed; nevertheless, it demonstrated poor electrochemical characteristics with 0.9 V depositions over potential and 37% cycle efficiency. Scientist produced a series of MACC electrolytes in Dimethoxyethane (DME) with reversible Mg deposition capability by simply raising the $MgCl_2$ content some years later. One of the finest can achieve a CE of at least 99%, over potential of 200 mV, and anodic stability of up to 3.1 V over 50 cycles. The MACC complex is generated by an acid-based reaction that produces solvated $Mg_2Cl_3^+$ active cations, analogous to the transmetalation process in Grignard-type complexes. Scientists discovered that

the electrochemical conditioning process, which involves multiple CT scans or charge-discharge cycles, may reduce the over potential of MACC electrolytes. Other inorganic chlorides, such as $InCl_3$, $SnCl_2$, $SbCl_3$, and $BiCl_3$, based binary chloride complexes, with modest Mg cycling ability, were also explored. Scientist established a straightforward "mono-Cl abstraction" technique to manufacture highly active coordination cations based on a retrosynthetic investigation of the Mg^{2+}/Cl/THF coordination cation production process. A rechargeable Mg battery with a Mo_6S_8 cathode and a 0.3 M $MgCl_2$-$AlEtCl_2$ electrolyte produced a first discharge capacity of 104 mAh g^{-1} and may retain 95.1% of its initial value after 100 cycles. The electrochemical performance and water-tolerant feature of the MACC electrolyte may be greatly enhanced by adding 0.03 M magnesium bis(trifluoromethane sulfonyl) imide [$Mg(TFSI)_2$]. Even without conditioning, the CE of Mg $(TFSI)_2$-MACC electrolyte was enhanced to 97%, with Mg deposition potential of 350 mV. The electrolyte's resistance to moisture and impurities is an intriguing trait. After 100 cycles, a Mo_6S_8-Mg battery with this electrolyte may give a capacity of 92 mAh g^{-1} at 0.2°C.

Electrolytes based on Mg $(TFSI)_2$ and Mg $(CF_3SO_3)_2$

Mg $(TFSI)_2$ has a high solubility in diverse solvents, strong ionic conductivity, and great oxidative stability. Even at high temperatures, electrolytes containing a single Mg $(TFSI)_2$ exhibited a substantial over potential (>2.0 V) and a low CE (50%). Mg $(TFSI)_2$ electrolytes were extremely sensitive to impurity species, negatively influencing their Mg stripping/plating characteristics. Cl can protect the surface of Mg against passivation by a tiny quantity of moisture via a complicated and dynamic interaction between Cl and H_2O. As a result, incorporating $MgCl_2$ into Mg $(TFSI)_2$ electrolytes was an effective technique for achieving reversible stripping/plating and decreased over potential. According to the report, the first to disclose the $Mg(TFSI)_2$-$MgCl_2$ combination in DME, with increased performance of 80% CE, 400 mV over potential, and 3.5 V anodic stability limit. When the Cl^-/$TFSI^-$ ratio was changed from 1:5 to 1:2, CE increased from 12% to 93%, while the average capacity in a Mo_6S_8-Mg rechargeable battery increased by 15%. It should be noted that the performance of $Mg(TFSI)_2$ electrolytes is strongly reliant on the purity of the Mg salt and can be enhanced by using a scavenging reagent other than $MgCl_2$. Reversible Mg stripping/plating cycling can be achieved in a $Mg(TFSI)_2$/tetraglyme (G_4) electrolyte by adding a trace amount of $Mg(BH_4)_2$ as a moisture scavenger at onset potentials of around 0.35 V (plating) and 0 V (stripping), with CE up to 84% over the initial cycles and 75% for 500 cycles overall by adding a trace amount of $Mg(BH_4)$ Dimethylamine (DMA) was used as a co solvent to create a Cl-free, noncorrosive $Mg(TFSI)_2$ electrolyte that demonstrated promising Mg stripping/plating. It demonstrated polarisation of 210 mV over 1,500 minutes in symmetric Mg cell cycling, which was equal to the performance in APC electrolyte. The CE rose to 75% when DMA-THF-G_4 was used as a mixed solvent, compared to 38% when a $Mg(TFSI)_2$-G_4 electrolyte was used.

Although $MgCl_2$ electrolytes including $Mg(TFSI)_2$ have been widely examined and exhibited strong stripping/plating capabilities, $Mg(TFSI)_2$ for electrolyte still requires relatively high purity and low moisture content, resulting in higher cost. Low-cost trifluoromethanesulfonate [$Mg(CF_3SO_3)_2$, $Mg(OTf)_2$] is commercially accessible with high purity and ultralow moisture as a relatively "simple" Mg salt, giving an alternative to $Mg(TFSI)_2$. $Mg(OTf)_2$-$AlCl_3$-$MgCl_2$ dissolved in THF and G_4 mixed solvents with anthracene as a stabilising agent yielded a high-performance electrolyte with a low over potential of 200 mV and a CE of up to 98.5% without any conditioning step. Based on this electrolyte, the Mg-S battery demonstrated the greatest capacity of 1,193.8 mAh g^{-1} and maintained a capacity of 420 mAh g^{-1} without variation for 50 cycles. Later, by simply dissolving $Mg(OTf)_2$, $MgCl_2$, and $AlCl_3$ in DME, an improved $Mg(OTf)_2$ based electrolyte was developed. It displayed 99.1% efficiency and good anodic stability up to 3.5 V, as well as exceptional performance in Mg-S batteries, with a high capacity of 866 mAh g^{-1} at 200 mA g^{-1} and power density of 550 W kg^{-1}.

Other MgCl$_2$-containing electrolytes

High-performance Mg electrolytes may be made utilising simply MgCl$_2$ salt and a suitable sulfone as a co-solvent. The use of a MgCl$_2$-sulfone-THF electrolyte allowed for highly reversible Mg stripping/plating without the use of AlCl$_3$, Mg(TFSI)$_2$, or Mg(CF$_3$SO$_3$)$_2$. When Dipropyl Sulfone (DPSO) with a melting point of 29°C to 33°C was mixed with THF co-solvent and solute, the melting point of the resultant electrolyte was successfully decreased below 10°C. MgCl$_2$/DPSO-THF electrolyte showed usual conditioning behaviour over sequential 200 CV cycles and then improved significantly with CE value increasing from 76.2% to 92.3%. In the galvanostatic charge-discharge test, the CE value grew fast from 68.5% to > 90% in the first 150 cycles. A Mo$_6$S$_8$-Mg cell treated with the aforementioned electrolyte demonstrated outstanding cycle performance up to the 300th cycle, with a consistent specific capacity of 70 mAh g^{-1} to 75 mAh g^{-1} and a high CE value (98% to 99%).

Mg electrolytes with boron centers

Non nucleophilic electrolytes based on chloride are nevertheless corrosive to all cell components to some extent. Boron (B-) anions are compatible with Mg anode and cell components, making them potential options for nonnucleophilic electrolytes. Scientists created the first B-based chloride-free electrolyte, Mg(BH$_4$)$_2$ in THF or DME. The Mg(BH$_4$)$_2$/DME performed better electrochemically, with a stripping/plating onset potential of 0.03 V to 0.34 V and a CE of 67%. Rechargeable Mg battery with Mg(BH$_4$)$_2$/DME and Mo$_6$S$_8$ cathode achieved 40 cycles of reversible cycling at 128 mA^{-1}. However, Mg(BH$_4$)$_2$ reductivity resulted in limited electrochemical windows (1.7 V vs. Mg). The application of weakly coordinating anions to Mg^{2+} can minimise the critical step in the Mg$^+$-mediated reductive breakdown, which is one approach for broadening the electrochemical window of Mg electrolyte. Hydroborates with weak coordination ability, such as B$_{12}$H$_{12}$$^{2-}$, were expected to have higher anodic stability of 3.2 V than BH$_4$$^{2-}$, making them appropriate for possible B-based electrolyte anion. Unfortunately, MgB$_{12}$H$_{12}$ is insoluble in low-polarity, widely used ether solvents for Mg batteries due to the weakly coordinating feature of B$_{12}$H$_{12}$$^{2-}$. A halogen-free, simple type electrolyte based on modified clusters of hydroborates CB$_{11}$H$_{12}$^{2} was developed and shown strong oxidative stability and increased solubility. CB$_{11}$H$_{12}$$^{2-}$ is more lipophilic than B$_{12}$H$_{12}$$^{2-}$ due to charge reduction, and hence more soluble in low-polarity ethers such as triglyme (G$_3$) and G$_4$. MMC salt/G$_4$ electrolytes have a high CE of more than 94.4% and anodic stability up to 3.8 V. Due to the strong electronegativity of fluorine atoms, a series of Mg salts containing weakly coordinating fluorinated alkoxyborate anions displayed good solubility in aprotic solvents. Among them, the Mg[B(hfip)$_4$]$_2$/DME electrolyte demonstrated a high CE of > 98% Mg stripping/plating for more than 100 cycles. The anodic current density reached 45 mA cm^{-2} and the oxidative voltage stability reached 4.3 V. A magnesium fluorinated pinacolatoborate (Mg-FPB) based electrolyte is noncorrosive, highly electrochemically active, and chemically stable. The electrolyte performed exceptionally well electrochemically, with CE > 95%, over potential of 197 mV, and anodic stability up to 4.0 V. A Mg|Mg-FPB|Mg symmetric cell can cycle at 0.1 mA cm^{-2} for over 500 hours while maintaining stable polarisation.

Conclusion

Non nucleophilic electrolytes have emerged as new trends in Mg electrolyte research, particularly in light of the recent fast development of Mg-S and Mg-O$_2$/air batteries. Although new non nucleophilic electrolytes have solved many of the disadvantages of classic Grignard-based electrolytes, preparing Mg electrolytes for practical application remains difficult. MACC, Mg(TFSI)$_2$-MgCl$_2$, and (HMDS)$_2$Mg-MgCl$_2$ have outstanding process ability and great performance but are nevertheless corrosive to many current collectors and cell components, especially when strong Lewis acid AlCl$_3$ is present. Mg(BH$_4$)$_2$ has low anodic stability and restricted solubility in Cl-free B-centered electrolytes. Magnesium carbaborate and alkoxyborate derived from Mg(BH$_4$)$_2$ have a broad electrochemical window, but with a difficult synthesis method. Most Mg electrolytes have several common drawbacks, such

as high raw material costs, moisture sensitivity, and long-term preconditioning behavior. Understanding the process of Mg stripping/plating, including anode-electrolyte interface chemistry, Mg coordination chemistry, and Mg cation electrochemistry, is another critical problem in Mg electrolyte research. Although plausible theories have been given with theoretical modeling and experimental data, researchers still need to investigate the chemical and electrochemical processes during reversible Mg deposition in depth.

To encourage the development of viable rechargeable Mg batteries, it is preferable to design non nucleophilic, noncorrosive, less air/moisture sensitive electrolytes with a broad electrochemical window and high Mg deposition reversibility. It is strongly advised to make Mg electrolyte from low-cost, commercially accessible ingredients using a simple process. More research is also required to better understand the ion structure of the electrolyte, the electrode-electrolyte interface, and their impact on electrochemical performance.