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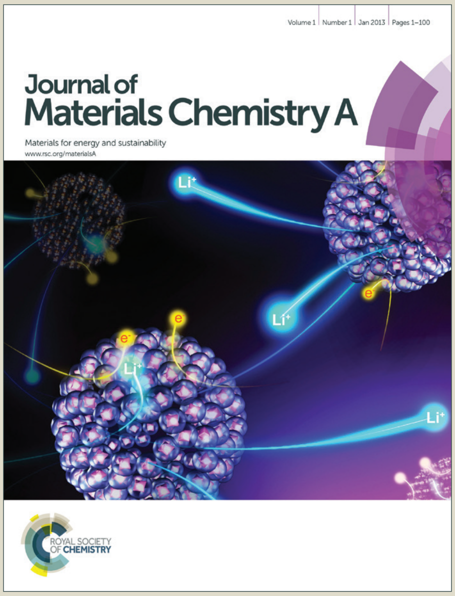

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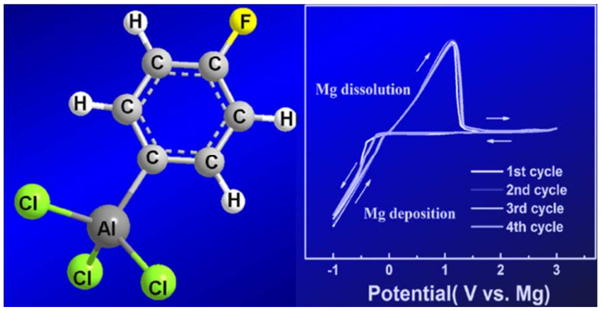

A stable 3V Mg battery electrolyte with high efficiency for Mg deposition/dissolution was prepared based on reaction between fluorine substituted complex 4-F-PhMgBr and $AlCl_3$ in THF solvent.

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Study of Fluorine Substituted Phenyl Based Complex as 3V-electrolyte for Mg Batteries

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An electrolyte with a wide electrochemically-stable window and high efficiency for reversible Mg deposition/dissolution is a key component of Mg battery systems. In the present study, functional-group-substituted phenyl-based Mg electrolytes have been prepared by direct reactions between the Lewis acid $AlCl_3$ and various fluorine substituted Lewis bases. The substitution effects of these functional groups on the anodic stability of the electrolyte and the efficiency for Mg deposition/dissolution have been studied by electrochemical analysis and DFT calculations. This study indicates that the para-substituted fluorine complex $(4\text{-F-PhMgBr})_2AlCl_3$/THF is an excellent 3 V electrolyte for Mg batteries with respect to electrochemical stability and efficiency of reversible Mg deposition/dissolution. Both the experimental results and theoretical calculations are consistent and indicate that electron-withdrawing groups with small steric effects on phenyl rings improve electrolyte stability and reversibility by decreasing the HOMO and increasing the LUMO energy levels of the complex component, while electron-donating groups have profound detrimental influences. This investigation provides further understanding of the electrolyte chemistry of Mg batteries and advances the design and optimization of new electrolytes.

Introduction

High-performance, low-cost rechargeable batteries are critical for meeting the increasing global demands for energy storage, especially for applications in stationary energy storage systems.[1, 2] Currently, Li-ion batteries are widely used in portable electronic devices and electric vehicles, but despite extensive development, they are still unable to meet the requirements of large scale energy storage (e. g. stationary energy storage systems integrated into the electrical grids) because of their resource scarcity, safety issues, and cost barriers.[1] Recently, magnesium batteries have attracted great research interest due to their potentially high volumetric energy density and environmentally friendly components, coupled with magnesium's low cost (~$2700/ton for Mg compared to $64,000/ton for Li) and high abundance (~13.9% Mg compared to ~0.0007% of Li), indicating potential cheap but better-performing batteries for large-scale applications.[2-6] Despite these attractive attributes of Mg batteries, there are still challenges pertaining to cathodes, electrolytes, anodes, and current collectors.[2, 7-11] In particular, electrolyte development is a crucial step in the research of magnesium battery systems since the electrolyte bridges positive and negative electrodes, supports charge transfer in the circuit, and consequently needs to be compatible with both the cathode and anode materials for Mg batteries.[2]

It remains a challenge to achieve a practical Mg battery electrolyte with good anodic stability, ionic conductivity, Mg deposition/dissolution efficiency, and chemical stability.[8-10, 12] Aiming to address these issues, researchers have taken great efforts to develop new electrolyte systems. Reversible magnesium deposition/dissolution was first demonstrated electrochemically within Grignard reagents such as ethylmagnesium bromide and butylmagnesium chloride, but their anodic stability was usually limited below 1.5 V *vs.* Mg.[13] Gregory *et al.* discovered that the anodic stability of the Mg electrolyte could be improved by mixing Lewis base and acid couples of dibutylmagnesium and tri-n-butylborane; however, the coulombic efficiency for reversible Mg deposition and dissolution was still low within the electrolyte.[14] It was the pioneering work of Aurbach *et al*. that first shed light on the reversible deposition and dissolution of magnesium in tetrahydrofuran (THF) solution of magnesium organohalo-aluminate salt $Mg(AlCl_2EtBu)_2$/THF, with excellent coulombic efficiency and relatively wide anodic stability window (i.e., up to ~ 2.2 V *vs*. Mg).[2] Systematic studies indicated that the efficiency of Mg deposition/dissolution depends strongly on the identity of the organic alkyl ligands in the complex, while the ratio of Lewis acid/Lewis base plays a crucial role in the anodic stability of the electrolyte.[15-17] It was found that the strength of the Al-C bond, formed by transmetalation between the Lewis base and Lewis acid AlR_nX_{3-n} (R=Et, Bu or Phenyl, X=F, Cl, or Br, $0 \leq n \leq 3$), is critical to the anodic stability of the electrolyte (*i.e.* stronger bond of Al-C, corresponding to shorter bond length, leads to a wider stable electrochemical window).[15, 16] Based on that, two approaches have been successfully employed to improve the anodic stability of the electrolyte: changing to a new type of Lewis base, and tuning the electron density of the Lewis acid by utilizing different functional groups.[14] For example, after replacing the Et and Bu alkyl groups in $Mg(AlCl_2EtBu)_2$ with phenyl or hexamethyldisilazide groups, the resulting electrolytes exhibited stable electrochemical windows of above 3 V.[3, 18, 19] Comparison of electron effects of different Lewis bases on the anode stability of electrolyte indicated that fluorine substitution was effective for improving electrolyte stability.[20] Recently Guo *et al*. modified the Lewis acid side of the $(MgPhCl)_2AlCl_3$/THF electrolyte using tri(3,5-dimethylphenyl)borane (Mes_3B) instead of $AlCl_3$, and found that the stable window of the electrolyte was improved to 3.5 V.[19] This progress demonstrate crucial electron effects of Lewis base/acid on the improvement of electrolyte, which requires further study and understanding, especially the effects of substituting electron–withdrawing or –donating groups on the anodic stability of the electrolyte.

In this study, we initiate the synthesis and understanding of new electrolytes by using electron withdrawing- or donating-group-substituted phenyl magnesium compounds as Lewis bases and $AlCl_3$ as a Lewis acid. The substitution effects of these electron-withdrawing or -donating groups (such as fluorine and alkyl groups) on the anodic stability of the electrolyte and reversibility of Mg deposition/dissolution were studied. First-principles density functional theory (DFT) calculations have also been employed to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of these target complexes. The HOMO/LUMO energy analyses of the complexes illustrate the mechanism underlying the observed behaviors of electrochemical stability and reversibility of Mg deposition/dissolution.

Experimental

Synthesis of fluorine substituted electrolyte

The electrolyte $(4\text{-F-PhMgBr})_2AlCl_3$/THF (0.3 M) was synthesized by direct reaction of the Lewis base 4-F-PhMgBr with the Lewis acid $AlCl_3$ in THF solvent. To avoid moisture, the whole synthesis was carried out in an argon-filled glove box (Mbraun Inc., Germany) with controlled moisture and oxygen below 1 ppm. The starting materials are 4-F-PhMgBr (1M in THF) and $AlCl_3$ (anhydrous, 99.99%), which were purchased from Aldrich and used without further purification. The THF solvent (inhibitor-free) was pretreated by refluxing with sodium and then distilled for purification. A stoichiometric amount of anhydrous $AlCl_3$ was first slowly dissolved in THF solvent. Then a stoichiometric amount of 4-F-PhMgBr/THF solution was gradually dropped into the above $AlCl_3$/THF solution under magnetic stirring over the course of 24 h. In order to study the substitution effects on the anodic stability and Mg deposition/dissolution efficiency, electrolyte with compositions of $(3\text{-F-PhMg})_2AlCl_3$/THF, $(3,4\text{-F-F-PhMg})_2AlCl_3$/THF, $(\text{cyclohexane-PhMg})_2AlCl_3$/THF, $(3,5\text{-methyl-PhMg})_2AlCl_3$/THF, and $(3,5\text{-Bis(trifluoromethyl)PhMg})_2AlCl_3$/THF were also prepared by similar synthesis approaches. For comparison of these new electrolyte with the first and second generations of Mg electrolyte, $Mg(AlCl_2EtBu)_2$/THF and $(MgPh)_2AlCl_3$/THF were prepared according to the literature.[2, 18]

Characterization

Electrochemical analyses, including linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were carried out in a three-electrode cell on a CHI660D electrochemical workstation. The three-electrode cell consisted of a working electrode (Pt or carbon paper purchased from Aldrich), counter and reference electrodes (Mg purchased from Aldrich), and the synthesized Mg electrolyte. The scan rates of the electrochemical tests were set to 1 mV/s within various potential ranges. The conductivity of the electrolyte was measured using a portable conductivity meter (HI991301, HANNA).

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed using a Hitachi S-3500N operating at an accelerating voltage of 20 kV. It should be noted that the electrodes were washed with THF three times and dried in vacuum before conducting SEM and EDX analyses.

Theoretical calculation

The first principles density functional theory (DFT) calculations were performed using the Gaussian 09 software package in a tight fit configuration (Ref. [S1], Supporting Information). Similar to the approach made by Pourr *et al.*,[16] the B3LYP/6-31+G(d, p) level of computation was used for all structures to optimize structures and to obtain the energies. The solvent (THF, ε=7.58) was taken into account via the integral equation formalism polarizable continuum model (IEFPCM).[21] The anions' structures in solvent were fully optimized before we calculated the energy levels of molecular orbitals from which we obtained their energies of the HOMO and the LUMO. The energy gap was the orbital energy difference between HOMO and LUMO. The charge distribution on each atom was evaluated based on Mulliken population analysis.

Due to the complexity of species within the electrolyte solutions, it is necessary to select specific target species for the calculations. Usually anodic stability of the electrolyte solution is related to most oxidation-susceptible components in the electrolyte, which are either solvents or components of salts. As reported in the study of $(PhMgCl)_2$-$AlCl_3$/THF solution,[16] the possible equilibrium species of $[Ph_4Al]^-$, $[Ph_2AlCl]^{2-}$, $[PhAlCl_3]^-$ and $AlCl_4^-$ may exist in the solution. We herein select the species of $[X\text{-}PhAlCl_3]^-$ (X=F, CH_3 and CF_3) as the target molecule for the following reasons. Because of its negative formal charge, it has the highest tendency toward oxidation and may act as the basic unit during the formation of other components in the electrolyte. In addition, the anodic stability of the electrolyte solution is dominated by the most oxidation-susceptible component, which is suggested to be a molecule or anion containing an Al-C bond, like $[X\text{-}PhAlCl_3]^-$.

Results and discussion

We first select fluorine as an electron-withdrawing functional group and study its substitution effects on the phenyl ring by synthesizing $(4\text{-}F\text{-}PhMgBr)_2AlCl_3$/THF (0.3M) electrolyte. The ionic conductivity of the electrolytes at various concentrations was measured and is shown in Table 1.

Table 1: Ionic conductivity of $(4\text{-}F\text{-}PhMgBr)_2$-$AlCl_3$/THF electrolyte at various concentrations.

Concentration (mol/L)	0.2	0.3	0.4	>0.5
Ionic conductivity (mS/cm)	1.49	1.75	1.86	NA

It is found that the ionic conductivity is similar to the value of conventional Li-ion battery electrolyte and increases with increasing electrolyte concentration. The anodic stability of such a complex was first examined by linear sweep voltammetry (LSV) in a three-electrode cell configuration with Pt as the working electrode and Mg as the counter and reference electrodes.

From the first and second LSV scans (Figure 1a), one can find that the stable anodic window of the $(4\text{-}F\text{-}PhMgBr)_2AlCl_3$/THF is 2.8 V on a Pt electrode, and no hysteresis or side reactions were observed within the voltage window from open circuit potential (OCP) to 2.8 V. It is better than the anodic stability of F-PhMgBr in THF solution without $AlCl_3$ species (2.4 V).[20] For comparison, we also synthesized the typical $Mg(AlCl_2EtBu)_2$/THF and $(PhMgCl)_2AlCl_3$/THF electrolyte and did LSV analyses at the same scan speed. As shown in Figure 1b, $Mg(AlCl_2EtBu)_2$/THF shows a stable

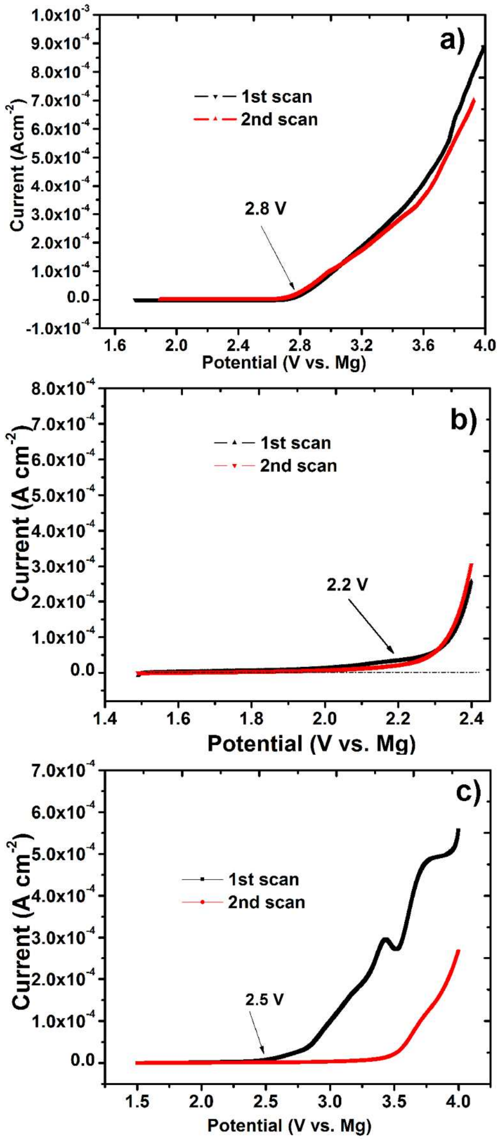

Figure 1. The first and second linear sweep voltammograms of Pt in electrolyte: (a) $(4\text{-}F\text{-}PhMgBr)_2$-$AlCl_3$/THF (OCP - 4.0 V (*vs.* Mg^{2+}/Mg)), (b) $MgBu_2(AlCl_2Et)_2$/THF (OCP -2.4 V), and (c) $(PhMgCl)_2$-$AlCl_3$/THF (OCP - 4.0 V) at the same voltage scan rate of 1 mVs^{-1}.

electrochemical window of 2.2 V, with no hysteresis between the first two scans.[22] In the case of $(PhMgCl)_2AlCl_3$/THF, despite its wide electrochemical window of 3.3 V in the second scan, hysteresis is observed between the first and second scans (Figure 1c). The discernible oxidation current of phenyl based electrolyte was also observed by Pour *et al*. in the voltage range of 2.7-2.9 V vs. Mg and was ascribed to the oxidation of electrolyte upon the anodic scan.[16]

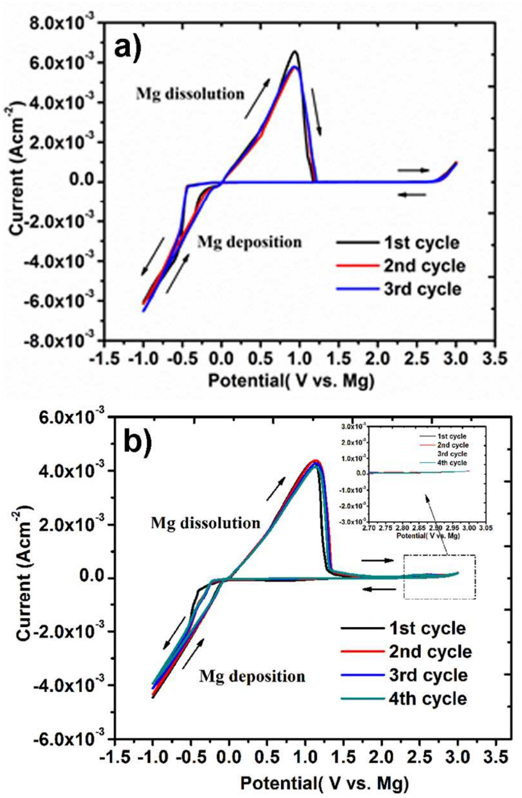

Figure 2. Cyclic voltammograms of $(4\text{-}F\text{-}PhMgBr)_2\text{-}AlCl_3$/THF electrolyte on (a) Pt electrode and (b) carbon paper electrode within the potential range of -1-3.0 V (*vs.* Mg^{2+}/Mg) collected at a voltage scan rate of 1 mVs^{-1}.

Reversible Mg deposition/dissolution in the new $(4\text{-}F\text{-}PhMgBr)_2AlCl_3$/THF electrolyte was further examined by cyclic voltammetry (CV). As shown in Figure 2a, in the $(4\text{-}F\text{-}PhMgBr)_2\text{-}AlCl_3$/THF electrolyte, magnesium can be deposited and dissolved reversibly on a Pt electrode with a high efficiency of near 100%. Successful Mg deposition was observed and further confirmed by SEM and EDX analysis (Figure S1). The high reversibility and stability of the electrolyte during extended electrochemical reaction are proved by these well-overlapped CV curves. Furthermore, it is observed that, if carbon paper is used as the working electrode in the present electrolyte, the stable electrochemical window can be extended to 3.0 V. As shown in Figure 2b, on carbon paper, Mg can be deposited and dissolved with excellent efficiency between -1.0 and 3.0 V, which strongly indicates that $(4\text{-}F\text{-}PhMgBr)_2\text{-}AlCl_3$/THF can be a 3V electrolyte for Mg batteries.

It is crucial to understand the substitution mechanism underlying the improved electrochemical properties of the electrolyte. We hypothesize that the superior performance of $(4\text{-}F\text{-}PhMgBr)_2\text{-}AlCl_3$/THF is due to the fluorine substitution on the phenyl ring at the para-position. There, the fluorine acts as an electron-withdrawing functional group and affects the charge distribution along the whole phenyl ring, which may reduce the chance of electron loss from the Al-C bond. To support this hypothesis, we synthesized electrolyte with an electron-donating functional group on the phenyl ring, with a composition of $(2,6\text{-}methyl\text{-}PhMgBr)_2AlCl_3$. As shown in Figure S2, LSV indicates that substitution of electron-donating groups on the phenyl ring has an obvious negative effect on the anodic stability of the electrolyte, decreasing the stable electrochemical window to 2.0 V. This was further proved by LSV and CV analyses of a complex $(HexamethyleneMgBr)_2AlCl_3$/THF electrolyte, where the electron-donating hexamethylene group was used as the Lewis base (Figure S3). The above results suggest that substitution of electron-withdrawing functional groups instead of electron-donating ones on the phenyl ring have positive effects on the anodic stability of the electrolyte.

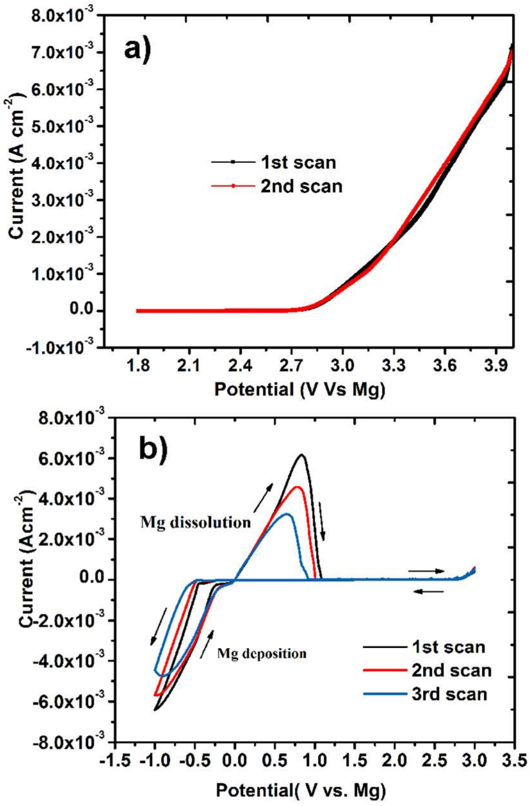

Figure 3. (a) The first and second LSV of Pt in $(3\text{-}F\text{-}PhMgBr)_2\text{-}AlCl_3$/THF electrolyte within the potential range between OCP and 4.0 V (*vs.* Mg^{2+}/Mg) and (b) corresponding previous three CV cycles between -1 and 3 V. (Both of the voltage scan rates are 1 mVs^{-1}).

To further understanding of the substitution effects of fluorine, electrolytes with different substitution positions and numbers of fluorine atoms on the phenyl ring were also synthesized. It is interesting to find that substitution position(s) and number of atoms have little effect on the anodic stability but a noticeable effect on the reversibility of Mg deposition/dissolution. As shown in Figure 3a, if fluorine is at the meta-position of phenyl, the obtained electrolyte (3-F-PhMgBr)$_2$AlCl$_3$/THF shows similar anodic stability to that of the para-substituted electrolyte. However, the reversibility of the Mg deposition/dissolution in that meta-substituted electrolyte is greatly decreased, as indicated by CV analysis (Figure 3b), which may be ascribed to the weakened stability upon reduction with fluorine meta-substitution and was proved by further theoretical calculation (*vide infra*).

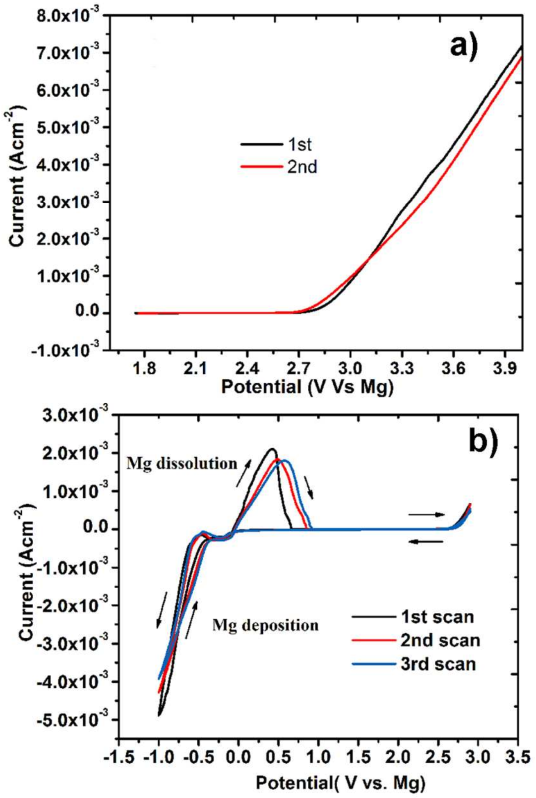

Figure 4. (a) The first and second LSV of Pt in (3,4-F-F-PhMgBr)$_2$-AlCl$_3$/THF electrolyte within the potential range between OCP and 4.0 V (*vs.* Mg^{2+}/Mg) and (b) corresponding previous three CV cycles between -1 and 3 V. (Both of the voltage scan rates are 1 mVs^{-1}).

Even worse reversibility was observed with double-fluorine substitution at both para and meta positions of phenyl ring ((3, 4-F-F-PhMgBr)$_2$AlCl$_3$/THF), as shown in Figure 4, although the anodic stability was similar to that of single meta- or para-substituted electrolytes. Besides the meta-substitution, which decreases the cathodic stability, the double-fluorine substitution may also increase the steric effects of the phenyl group and result in decreased π-π interaction in the phenyl ring, which is detrimental to the coulombic efficiency of the electrolyte.[19] The negative steric effect of the functionalized phenyl group on the electrochemical behaviors of the electrolyte is further demonstrated by introducing bigger size substitution groups onto the phenyl ring. For example, as shown in Figure S4, the electrolyte (3,5-bis(trifluoromethyl)PhMgBr)$_2$AlCl$_3$/THF exhibits much decreased anodic stability and very poor reversibility for Mg deposition/dissolution.

All these experimental results, especially the substitution effects of electron withdrawing/donating groups on the electrochemical properties of the electrolytes, have been compared with theoretical studies on these systems to estimate the relative durability of the complex solutions towards oxidation and reduction by analyzing their HOMO and LUMO energy levels, respectively. The oxidation reaction involves electron transfer from the complex's HOMO level whereas reduction reaction corresponds to electron transfer into the LUMO level. It is thus expected that complexes with higher HOMO and lower LUMO levels will have lower anodic and cathodic stability, as these will make electron transfer for oxidation and reduction reactions much easier, respectively. Table 2 lists the calculated HOMO and LUMO energy levels of various substituted complexes in THF solvent. The optimized structures of these complexes as well as the corresponding bond lengths and Mulliken charge populations are shown in Figure 5.

Table 2 Calculation results of LUMO and HOMO levels of the substituted phenyl complexes.

	Charge	LUMO (eV)	HOMO (eV)	Gap (eV)
[PhAl3]-	-1	0.213	-6.207	6.420
[(3-F-Ph)AlCl3]-	-1	0.019	-6.131	6.150
[(4-F-Ph)AlCl3]-	-1	0.235	-6.108	6.344
[(3,4-F-F-Ph)AlCl3]-	-1	0.046	-6.161	6.206
[(3,5-bis(trifluoromethyl)-Ph)AlCl3]-	-1	-0.617	-6.885	6.267
[(2,6-bismethyl-Ph)AlCl3]-	-1	0.123	-5.840	5.963

For electron-withdrawing-group-substituted products of [3-F-Ph-AlCl$_3$]$^-$, [4-F-Ph-AlCl$_3$]$^-$, and [3-4-F-F-Ph-AlCl$_3$]$^-$, it can be seen from Table 2 that their HOMO energy levels are close to each other with values around -6.1 eV, which indicates that their anodic stabilities are similar. This is consistent with their observed similar anodic stability as shown in Figures 1a, 3a, and 4a. Among their LUMO energy levels, the [4-F-Ph-AlCl$_3$]$^-$ has a value of 0.24 eV, which is much higher than those of [3-F-Ph-AlCl$_3$]$^-$ (0.02 eV) and [3-4-F-F-Ph-AlCl$_3$]$^-$ (0.05 eV). Such results demonstrate that the [4-F-Ph-AlCl$_3$]$^-$ should have a much higher reduction stability than [3-F-Ph-AlCl$_3$]$^-$ and [3-4-F-F-Ph-AlCl$_3$]$^-$, which is also supported by our experimental observations (Figure 2, 3a and 4a). Comparing the CV scans of these three fluorine-substituted electrolytes, shown in Figures 2-4, one can observe that (4-F-PhMgBr)$_2$-AlCl$_3$/THF (Figure 2) shows the best efficiency and reversibility for Mg deposition and dissolution, due to its higher LUMO level. In the case of (3-F-PhMgBr)$_2$-AlCl$_3$/THF (Figure 3b) and (3,4-F-F-PhMgBr)$_2$-AlCl$_3$/THF (Figure 4b), decreased efficiency and stability for Mg deposition/dissolution are observed and agree well with their relatively lower LUMO energy levels.

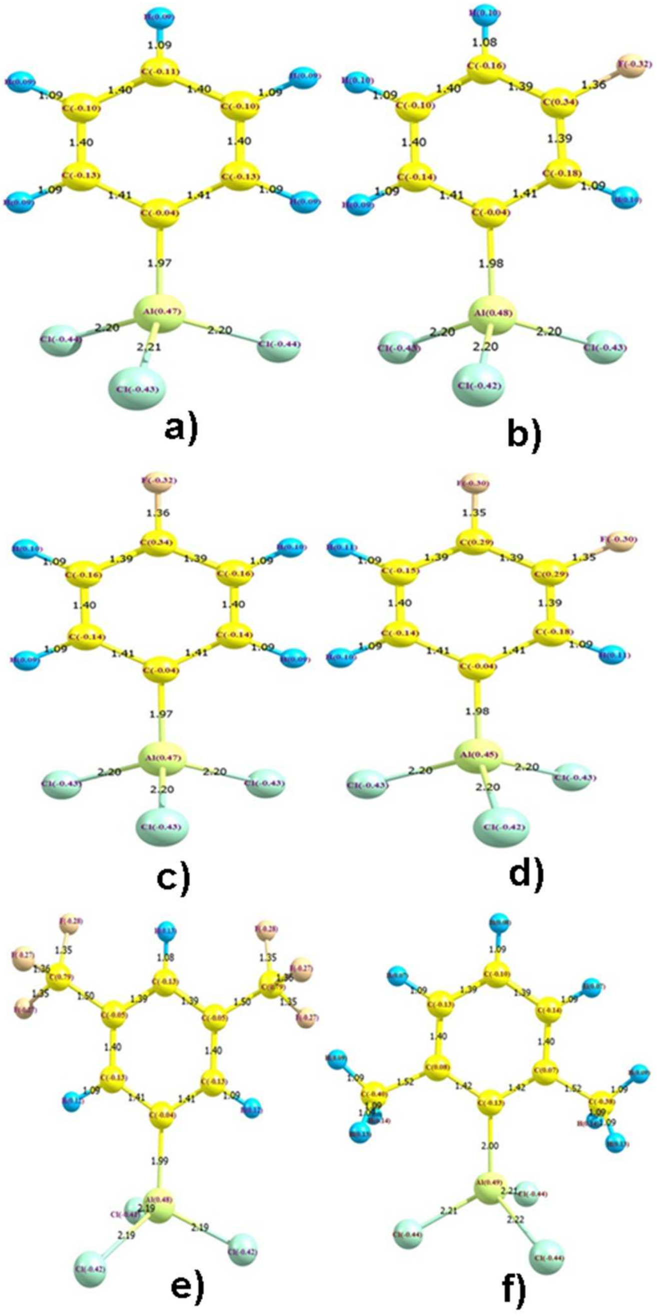

Figure 5. The molecular structures with bond length and Mulliken charge populations of the optimized complexes: (a) [PhAlCl$_3$]$^-$, (b) [(3-F-Ph)AlCl$_3$]$^-$, (c) [(4-F-Ph)AlCl$_3$]$^-$, (d) [(3,4-F-F-Ph)AlCl$_3$]$^-$, (e) [(3,5-bistrifluoromethyl-Ph)AlCl$_3$]$^-$ and (f) [(2,6-bismethyl-Ph)AlCl$_3$]$^-$.

Compared to the fluorine-substituted complexes, it is found that the base complex [Ph-AlCl$_3$]$^-$ is 0.1 eV lower in HOMO energy level than those of the fluorine substituted ones, and its energy gap (6.42 eV) is about 0.1~0.3 eV larger than those of fluorine substituted complexes. This difference is consistent with its 0.3 V wider electrochemical window. However, from Table 2 one can see that the LUMO energy level of the [Ph-AlCl$_3$]$^-$ is about 0.02 eV lower than that of the [4-F-Ph-AlCl$_3$]$^-$, which is the possible reason for the observed hysteresis between the first and second SLV scans, and may potentially lead to inferior cycling stability of the electrolyte when it is used in batteries. The complex [(3,5-bis(trifluoromethyl)-Ph)AlCl$_3$]$^-$ has a very low HOMO level of -6.88 eV and a fairly large energy gap of 6.27 eV, which may be ascribed to the substitution of the double trifluoromethyl groups. However, as shown in Figure S4 only a stable electrochemical window of *ca.* 1.3 V was achieved for this kind of electrolyte during experiment. This may be attributed to the large steric effects of the –CF$_3$, which decreases the π-π interaction in the phenyl ring. As one can see from Figure 5, the charge on the direct bonding carbon of phenyl ring with fluorine in fluorine substituted complexes are positive, while in the case of [(3,5-bis(trifluoromethyl)-Ph)AlCl$_3$]$^-$ the charge on the corresponding carbons are negative. At the same time, the calculated LUMO level of the [(3,5-bis(trifluoromethyl)-Ph)AlCl$_3$]$^-$ is as low as *ca*. -0.62 eV, indicating decreased stability upon reduction as proved experimentally by its poor performance during the CV scans. For the substitution from electron-donating groups, the calculated HOMO level of [(2,6-bismethyl-Ph)AlCl$_3$]$^-$ is -5.83 eV, which is much higher than that of fluorine substituted complexes and indicates decreased anodic stability upon oxidation. As shown in Figure S2, [(2,6-bismethyl-Ph)AlCl$_3$]$^-$ exhibits a stable electrochemical window of 2.0 V, which is lower than that of fluorine-substituted complexes and comparable to that of the alkyl-based Mg(AlCl$_2$EtBu)$_2$/THF electrolyte. This trend, *i.e.* electron–donating groups decrease the anodic stability of the electrolyte, is further proved by studying electrolyte solution of (HexamethyleneMgBr)$_2$AlCl$_3$/THF, which has an electron saturated hexatomic-ring structure and shows a typical 2.0 V stable electrochemical window of the alkyl-based electrolyte solutions (Figure S3).

From the optimized structures shown in Figure 5, one can find that the type, position, and number of the substitution groups have profound effects on the charge distribution on the atoms and on the Al-C bond lengths. For example, the [4-F-Ph-AlCl$_3$]$^-$ has the shortest Al-C bond length and least charge on the Al and C atoms among these fluorine substituted complexes, which indicates strong covalent bonding between Al and C and is therefore consistent with its best performance in these electrolyte solutions. As for the electron-donating group substituted complex, the [(2,6-bismethyl-Ph)AlCl$_3$]$^-$ has a Al-C bond length of 2.0 Å, which is longer than that of fluorine substituted ones and agrees well with its poor anodic stability as an electrolyte.

The experimental results and theoretical calculations indicate that electron-withdrawing functional groups with small size on the phenyl ring increase the anodic stability of the electrolyte solution and the reversibility and efficiency of Mg depositon/dissolution by decreasing HOMO and increasing LUMO energy levels, respectively. On the contrary, an inverse trend is observed for the electron-donating groups, which increase HOMO energy level of the complexes and have detrimental influences on the anodic stability of the electrolyte. This study provides valuable information for electrolyte structural design with improved electrochemical performance and demonstrates that it is crucial to increase the LUMO energy level and decrease the HOMO energy level of the complexes by introducing functional groups into the complexes for Mg electrolyte with both high anodic stability and high efficiency for Mg deposition and dissolution.

Conclusions

Introduction of functional substitution groups into a complex structure is a straightforward but effective strategy to tune the electronic structure and electrochemical properties of $(PhMgCl)_2AlCl_3$)/THF electrolyte for Mg batteries. It is found in this study that substitution of electron-withdrawing functional groups and small steric effects on the phenyl ring improves anodic stability and reversibility for Mg deposition/dissolution; while electron-donating groups or those with large steric effects have profound negative effects. In this view, the fluorine substituted $(4\text{-F-PhMgBr})_2\text{-AlCl}_3$/THF is a stable 3 V electrolyte for Mg batteries with high Mg deposition/dissolution efficiency. Furthermore, this study demonstrates that the substitution effects of fluorine on the phenyl ring vary with the type, position, and number of substitution groups, which is attributed to differences in the molecular orbital energy level, charge distribution on the atoms, and Al-C bond lengths of complexes. The calculated results from DFT theoretical studies are consistent with our experimental observations and indicate that electron-withdrawing groups with small steric effects on phenyl rings are beneficial to the improvement of electrolyte by decreasing HOMO and increasing LUMO energy levels of the complex component, while electron-donating groups show the reverse effect. This study provides usefully guidance in structure design of high performance Mg battery electrolytes with both high anodic stability and high efficiency for Mg deposition and dissolution.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

References

1 J. M. Tarascon; M. Armand, *Nature*, 2001, **414**, 359.

2 D. Aurbach; Z. Lu; A. Schechter; Y. Gofer; H. Gizbar; R. Turgeman; Y. Cohen; M. Moshkovich; E. Levi, *Nature*, 2000, **407**, 724.

3 H. S. Kim; T. S. Arthur; G. D. Allred; J. Zajicek; J. G. Newman; A. E. Rodnyansky; A. G. Oliver; W. C. Boggess; J. Muldoon, *Nat. Commun.*, 2011, **2**.

4 B. Peng; J. Liang; Z. Tao; J. Chen, *J. Mater. Chem.*, 2009, **19**, 2877.

5 Y. Nuli; Z. P. Guo; H. K. Liu; J. Yang, *Electrochem. Commun.*, 2007, **9**, 1913.

6 W. Y. Li; C. S. Li; C. Y. Zhou; H. Ma; J. Chen, *Angew. Chem., Int. Ed.*, 2006, **45**, 6009.

7 D. Aurbach; Y. Gofer; O. Chusid; E. Levi; M. D. Levi; Y. Vestfrid; H. Gizbar; E. Lancry, *Indian Journal of Chemistry Section a-Inorganic Bio-Inorganic Physical Theoretical & Analytical Chemistry*, 2005, **44**, 875.

8 D. Aurbach; G. S. Suresh; E. Levi; A. Mitelman; O. Mizrahi; O. Chusid; M. Brunelli, *Adv. Mater.*, 2007, **19**, 4260.

9 J. Muldoon; C. B. Bucur; A. G. Oliver; T. Sugimoto; M. Matsui; H. S. Kim; G. D. Allred; J. Zajicek; Y. Kotani, *Energy Environ. Sci.*, 2012, **5**, 5941.

10 Y. Shao; T. Liu; G. Li; M. Gu; Z. Nie; M. Engelhard; J. Xiao; D. Lv; C. Wang; J.-G. Zhang; J. Liu, *Scientific reports*, 2013, **3**, 3130.

11 D. Lv; T. Xu; P. Saha; M. K. Datta; M. L. Gordin; A. Manivannan; P. N. Kumta; D. Wang, *J. Electrochem. Soc.*, 2013, **160**, A351.

12 E. Levi; Y. Gofer; D. Aurbach, *Chem. Mater.*, 2010, **22**, 860.

13 C. Liebenow; Z. Yang; P. Lobitz, *Electrochem. Commun.*, 2000, **2**, 641.

14 T. D. Gregory; R. J. Hoffman; R. C. Winterton, *J. Electrochem. Soc.*, 1990, **137**, 775.

15 D. Aurbach; I. Weissman; Y. Gofer; E. Levi, *Chem. Rec.*, 2003, **3**, 61.

16 N. Pour; Y. Gofer; D. T. Major; D. Aurbach, *J. Am. Chem. Soc.*, 2011, **133**, 6270.

17 Y. Gofer; O. Chusid; H. Gizbar; Y. Viestfrid; H. E. Gottlieb; V. Marks; D. Aurbach, *Electrochem. Solid-State Lett.*, 2006, **9**, A257.

18 O. Mizrahi; N. Amir; E. Pollak; O. Chusid; V. Marks; H. Gottlieb; L. Larush; E. Zinigrad; D. Aurbach, *J. Electrochem. Soc.*, 2008, **155**, A103.

19 Y.-s. Guo; F. Zhang; J. Yang; F.-f. Wang; Y. NuLi; S.-i. Hirano, *Energy Environ. Sci.*, 2012, **5**, 9100.

20 Y. S. Guo; J. Yang; Y. N. NuLi; J. L. Wang, *Electrochem. Commun.*, 2010, **12**, 1671.

21 E. Cances; B. Mennucci; J. Tomasi, *J. Chem. Phys.*, 1997, **107**, 3032.

22 D. Aurbach; H. Gizbar; A. Schechter; O. Chusid; H. E. Gottlieb; Y. Gofer; I. Goldberg, *J. Electrochem. Soc.*, 2002, **149**, A115.