

Supplementary Information

**Operating Mechanisms of Electrolytes in Magnesium
Ion Batteries: Chemical Equilibrium, Magnesium
Deposition, and Electrolyte Oxidation**

SI-1

Gas-phase interaction energies [$\Delta G_{\text{int}} = G(\text{R}_n\text{Mg}) - nG(\text{R})$] of Mg complexes, calculated by sequential addition of R groups from $n = 1$ to $n = 3$ at the M062X/6-311+G** level (eV).

	$n = 1$	$n = 2$	$n = 3$
I	-19.60	-25.58	-28.14
II	-16.06	-24.26	-27.00
III	-15.51	-22.92	-25.63
IV	-13.87	-20.92	-23.19
Cl ⁻	-14.24	-22.77	-25.54

Gas-phase successive interaction energies [$\Delta\Delta G_{\text{int}} = G(\text{R}_n\text{Mg}) - G(\text{R}_{n-1}\text{Mg}) - G(\text{R})$] of Mg complexes, calculated by sequential addition of R groups from $n = 1$ to $n = 3$ at the M062X/6-311+G** level (eV).

	$n = 1$	$n = 2$	$n = 3$
I	-19.60	-5.98	-2.56
II	-16.06	-8.20	-2.74
III	-15.51	-7.40	-2.71
IV	-13.87	-7.04	-2.27
Cl ⁻	-14.24	-8.54	-2.77

Solvation energies (ΔG_{solv}) of R_2Mg , RMgCl , and RMg^+ in THF, calculated at the M062X/6-311+G** level (eV).

	I	II	III	IV	Cl ⁻
R_2Mg	-0.27	-1.23	-1.22	-1.93	-2.52
RMgCl	-1.48	-1.85	-1.96	-2.17	-2.52
MgR^+	-5.37	-6.07	-5.85	-6.97	-7.56

Solvent-coordination energies (ΔG_{coord}) of R_2Mg , RMgCl , and RMg^+ in THF, calculated at the M062X/6-311+G** level (eV).

	I	II	III	IV	Cl ⁻
R_2Mg	-0.04	-0.79	-0.81	-1.53	-1.97
RMgCl	-0.96	-1.31	-1.44	-1.69	-1.97
MgR^+	-4.01	-4.62	-4.44	-5.39	-6.11

SI-2

Relative energy profiles for eqs 1–13 in the gas phase at the M062X/6-311+G** level (eV).

	1	2	3	4	5	6	7	8	9	10	11	12	13
I	0.29	8.92	6.65	5.80	5.14	4.90	5.16	10.0 9	7.82	6.97	6.60	6.36	6.62
II	0.20	8.40	5.86	5.46	5.07	4.99	5.34	9.38	6.84	6.44	6.25	6.18	6.53
III	0.14	7.54	4.98	4.86	4.69	4.78	5.19	8.67	6.11	5.99	5.97	6.06	6.47
IV	0.05	7.09	4.87	5.01	5.05	5.28	5.78	7.63	5.41	5.55	5.64	5.87	6.37

Relative energy profiles for eqs 1–13 in the THF-coordinated phase at the M062X/6-311+G** level (eV).

	1	2	3	4	5	6	7	8	9	10	11	12	13
I	0.18	4.83	2.48	2.65	3.02	3.68	4.31	4.92	2.56	2.74	3.28	3.95	4.57
II	0.07	4.43	2.54	2.80	3.06	3.50	4.24	4.58	2.69	2.95	3.28	3.72	4.46
III	0.25	4.02	2.38	2.78	3.14	3.86	4.41	4.01	2.36	2.76	3.38	4.10	4.65
IV	– 0. 0 7	3.05	2.31	2.73	2.97	3.43	4.23	3.15	2.40	2.75	3.07	3.46	4.26

Relative energy profiles for eqs 1–13 in the THF phase at the M062X/6-311+G** level (eV).

	1	2	3	4	5	6	7	8	9	10	11	12	13
I	0.44	1.63	0.06	0.04	0.41	1.36	0.95	1.66	0.09	0.08	0.88	1.83	1.43
II	0.16	1.35	0.08	0.12	0.54	0.94	0.82	1.52	0.24	0.29	0.87	1.27	1.14
III	0.32	1.04	0.01	0.24	0.54	1.28	1.00	1.02	0.00	0.22	0.84	1.58	1.30
IV	– 0.0 6	0.19	0.07	0.29	0.48	0.59	0.63	0.49	0.37	0.53	0.78	0.84	0.88

Equilibrium constant values of eqs 1–13 at 298 K.

	1	2	3	4	5	6	7	8	9	10	11	12	13
I	4.E-08	3.E-28	1.E-01	2.E-01	1.E-07	1.E-23	8.E-17	9.E-29	3.E-02	5.E-02	1.E-15	1.E-31	8.E-25
II	2.E-03	1.E-23	5.E-02	9.E-03	7.E-10	1.E-16	1.E-14	2.E-26	8.E-05	1.E-05	2.E-15	4.E-22	5.E-20
III	5.E-06	3.E-18	6.E-01	9.E-05	6.E-10	2.E-22	1.E-17	6.E-18	1.E+00	2.E-04	6.E-15	2.E-27	1.E-22
IV	9.E+00	6.E-04	6.E-02	1.E-05	8.E-09	1.E-10	2.E-11	4.E-09	5.E-07	1.E-09	6.E-14	7.E-15	2.E-15

SI-3

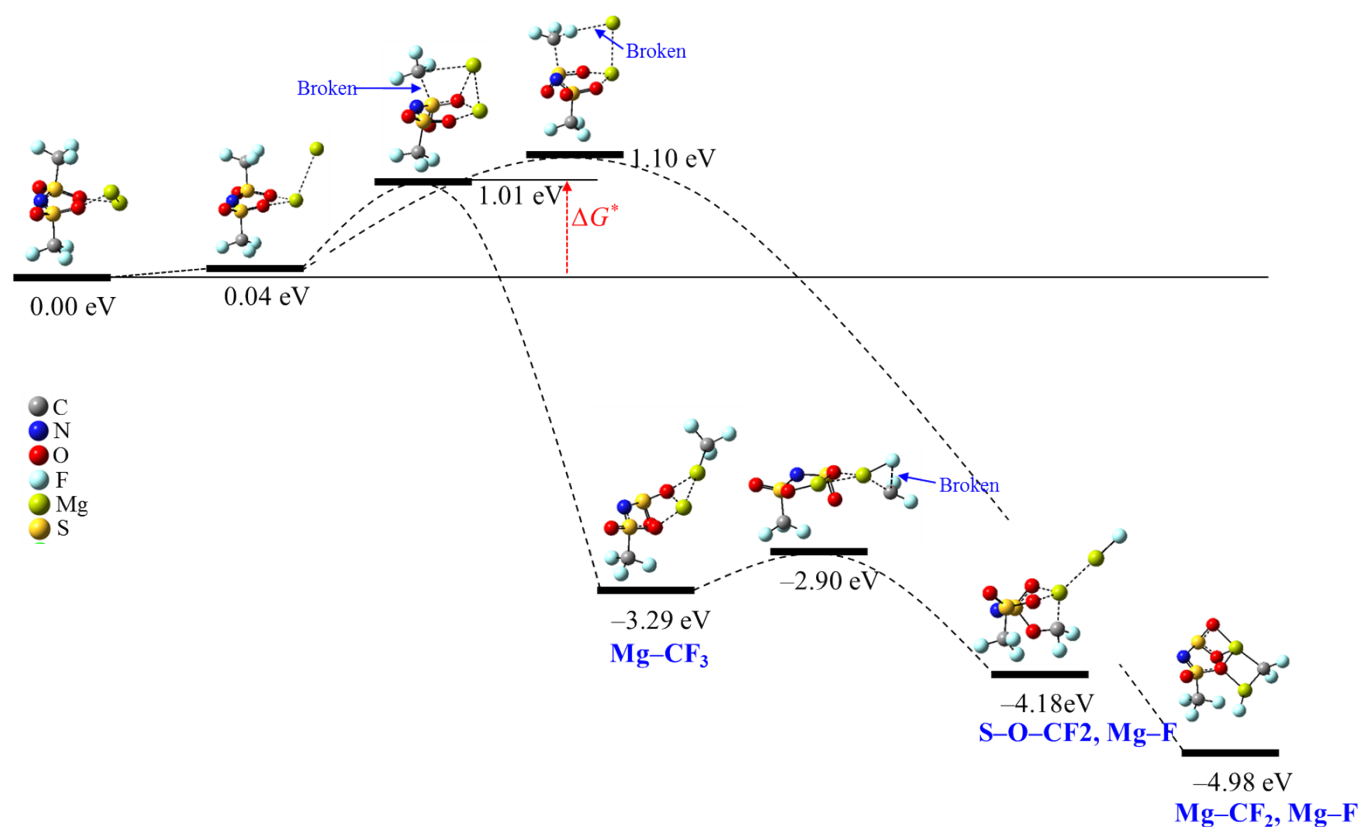
Comparisons of reduction energies ΔG_{red} of Paths 1–3 for **I–IV** at the M062X/6-311+G** level (eV).

	I	II	III	IV
1a	−4.81	−4.81	−4.81	−4.81
1b	−4.10	−4.11	−4.79	−5.06
2a	−5.67	−5.67	−5.67	−5.67
2b	−5.64	−5.51	−5.69	−5.37
2d	−5.17	−5.18	−5.39	−5.12
3a	−4.35	−4.35	−4.35	−4.35
3b	−4.86	−4.60	−4.78	−4.59
3c	−5.67	−5.18	−5.40	−4.91
3d	−4.83	−4.43	−4.80	−4.29
3e	−5.20	−4.85	−5.10	−4.66
3f	−5.62	−5.06	−5.64	−4.94

Comparisons of solvent reorganization energies λ_{solv} of Paths 1–3 for **I–IV** at the M062X/6-311+G** level (eV).

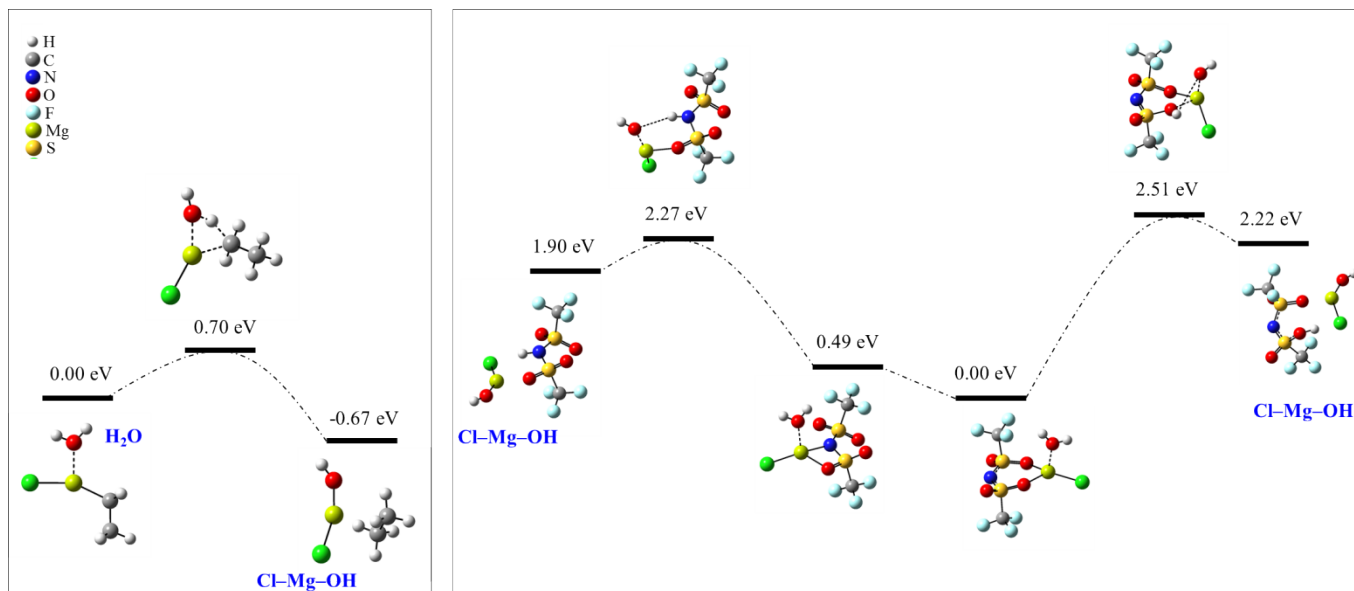
	I	II	III	IV
1a	4.93	4.93	4.93	4.93
1b	2.92	3.80	3.67	5.03
2a	12.60	12.60	12.60	12.60
2b	11.45	11.78	11.45	12.36
2d	10.47	10.92	10.47	12.02
3a	8.15	8.15	8.15	8.15
3b	7.10	7.63	7.67	8.09
3c	5.94	6.86	7.03	7.87
3d	5.95	6.81	6.52	7.85
3e	4.96	5.99	6.05	7.52
3f	3.97	5.60	5.53	7.43

SI-4



IV reacts with 2Mg *via* an activation barrier of 1.0 eV (ΔG^*), resulting in the formation of Mg-CF_2 and Mg-F bonds. Calculations were performed at the M062X/6-311+G** level in the gas phase. The rate constant k at 298 K is approximately $5 \times 10^{-5} \text{ s}^{-1}$, from transition-state theory [$k=(k_B T/h)\exp(-\Delta G^*/RT)$].

SI-5



H₂O reacts with **IMgCl** via an activation barrier of only 0.7 eV, resulting in the formation of **I-H** and Cl-Mg-OH. H₂O reacts with **IVMgCl** via an activation barrier of 2.3 eV, resulting in the formation of **IV-H** and Cl-Mg-OH. Calculations were performed at the M062X/6-311+G** level in the gas phase.

SI-6

Ab initio calculations were performed using the Gaussian 09 suite of programs. The geometries of stationary points were optimized, using density functional theory, with the M062X functional that includes dispersion energy and the 6-311+G** basis set. The parameterized, empirical exchange-correlation functional M062X was developed by Zhao and Truhlar, and it has been shown significant improvements over traditional density functionals to describe the non-covalent interactions. Frequency analysis was performed at the same level of theory. The zero point energy (ZPE) was then corrected and the M062X/6-311+G** relative energies were calculated. To investigate the more reliable solvation phase, the remaining sites on each Mg center of all Mg neutral and cationic species were coordinated through the O atoms of THF molecules, maintaining a coordination number of six. To search for low-lying energy structures, we extensively investigated many possible configurations. In the search for low-energy conformers, identification of non-THF-coordinated conformations was intuitive, but identification of THF-coordinated conformations required extensive investigation. In the present study, an extensive search for low-lying energy structures for the core solvation region was performed. We believe that the structures reported here would be the lowest-energy structures for each given cluster, because practically all possible topological isomers were investigated. For selected systems, determination of single-point energies of the coupled cluster theory with single, double, and perturbatively triple excitations [CCSD(T)] were carried out using the aug-cc-pVDZ basis set on the M062X/6-311+G** optimized geometries. The ZPE-corrected CCSD(T)/aug-cc-pVDZ relative energies were then calculated. To evaluate the energies in the condensed phase, single-point energy calculations were performed using self-consistent reaction field theory with the isodensity surface polarized model at the M062X/6-311+G** level. The dielectric constant used for THF was 7.58.