Rechargeable Mg-metal batteries have been focused as post Li-based batteries since Mg-metal has a higher volumetric energy density than Li-metal. For efficient use of Mg-metal as anode in batteries, its electrochemical deposition and dissolution with high reversibility should be realized. So far, ether-based electrolyte solutions including Grignard reagents have been investigated due to a high coulombic efficiency of the deposition and dissolution of Mg-metal. However, the ether-based electrolyte solutions are easily oxidized at around 1.5 V vs. Mg$^{2+}$/Mg. Therefore, new electrolyte systems with high oxidation stability are strongly required. The investigation of reaction mechanisms of Mg deposition and dissolution in current Grignard reagent systems is expected to provide insights into the design of such new electrolyte systems. In this study, the dynamic behavior of Grignard reagents in tetrahydrofuran (THF) during Mg deposition and dissolution was studied by in-situ FT-IR spectroscopy with an attenuated total reflection method, in which the behaviors of THF molecule coordinated with ethylmagnesium chloride (EtMgCl), phenylmagnesium chloride (PhMgCl) and ethylmagnesium bromide (EtMgBr) were mainly focused. In all the Grignard reagents, the solvation structure of THF molecule in the Mg deposition process was different from that in the dissolution process (Fig. 1), indicating that the solvated Mg$^{2+}$ ions play an important role in the deposition and dissolution processes. Based on this detail discussion on the reaction mechanism, new electrolyte with high oxidation stability should be considered to realize highly reversible Mg deposition and dissolution with low over-potentials.

Figure 1 Grignard reagent-based species formed during Mg deposition/dissolution processes.