Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI)

A Conceptual Magnesium Battery with Ultrahigh Rate Capability

*Ruigang Zhang, Chen Ling and Fuminori Mizuno**

Toyota Research Institute of North America, 1555 Woodridge Avenue, Ann Arbor, MI 48105, USA

E-mail: fuminori.mizuno@tema.toyota.com

Materials, Methods and Characterization

i. Materials

Silver nitrate ($AgNO_3$, 99%, Sigma), Hydrochloric acid (HCl, 36.5-38%, Sigma), Lead(II) chloride ($PbCl_2$, 99.999%, Sigma), Copper(I) chloride (CuCl, 99.99%, Sigma), Copper(II) chloride ($CuCl_2$, 99.995%, Sigma), Nickel(II) chloride ($NiCl_2$, 99.99%, Sigma), Iron(II) chloride ($FeCl_2$, 99.9% Sigma), Chromium(III) chloride ($CrCl_3$, 99.99%, Sigma), Carbon black (EC600-JD, Ketjen Black International Inc.), Magnesium foil (Mg, 0.004 in., 99.9995%, ESPI Metals), Tetrahydrofuran (THF, anhydrous, $\geq$99.9%, Sigma), Aluminium trichloride($AlCl_3$, anhydrous, 99.99%, Sigma), Phenyl magnesium chloride (PhMgCl, 2M solution in THF, Sigma), Polytetrafluoroethylene (PTFE, Daikin).

ii. Synthesis of AgCl/C material

The AgCl/C composite was synthesized by a co-precipitation method. First, 1.69g of $AgNO_3$ was dissolved in 500 ml distilled water to form an aqueous solution, and then 1 g of carbon black was dispersed in the solution under stirring. Next, 20 ml of 5 M HCl was added to the above mixture at a rate of 2 ml/min to form AgCl precipitate under rigorous stirring. The mixture was stirred for two additional hours. The resulting precipitate was filtered and washed three times with distilled water to ensure that any residual impurities were completely removed. The prepared sample was dried at 80 ^{o}C under vacuum overnight.

iii. Synthesis of metal chloride and carbon composites

To obtain the preliminary results, composites of metal chlorides and carbon were prepared by mechanical mixing process using a Retsch PM100 apparatus. 1g of aforementioned metal chloride (except for AgCl) was mixed with 1g of carbon black, and then the mixture was set with a ZrO_2 container with ZrO_2 balls (4 balls in 1/2 inch and 8 balls in 1/4 inch). The milling process was done under a rotation speed of 400 rpm for 5h.

iv. Fabrication of MCl_x cathode

MCl_x cathode was composed of 70 wt% as-prepared MCl_x/C material, 20 wt% carbon black and 10 wt% PTFE. The mixture was ground using a mortar and pestle with the addition of 5 ml ethanol. After 30 minutes of grinding, the mixture became a soft block and was pressed into a 120 μm sheet via a press roller. The MCl_x/C/PTFE sheet was dried at 120 ^{o}C under vacuum overnight. The obtained cathode was cut out as shaped in the sheet with 13 mm diameter (1.33 cm^2 area). For example, the loading content of AgCl cathode was about 10.6 mg, which was calculated to be approximately 0.67 g/cc in apparent density. The real density of AgCl is reported to be 5.56 g/cc, suggesting that the prepared cathode is highly porous.

v. Preparation of electrolyte

The preparation of the electrolyte used in this study has been reported in previous papers[1-2] and was carried out in three steps. First, $AlCl_3$ was very slowly added to THF under vigorous stirring to form 0.5 M $AlCl_3$-THF solution. In the second step, 4 ml of 2 M PhMgCl-THF solution was diluted in 8 ml of THF. For the third step, 8 ml of $AlCl_3$-THF solution was added drop by drop in 12 ml of diluted PhMgCl-THF solution. The final solution was stirred at least 24 hours prior to use. It should be addressed that the previous three steps are exothermic reactions. A stirring stage with a cooling system is suggested to perform the mixing process. Since the electrolyte is moisture sensitive, all the processes were performed under Ar in a glove box (<0.1 ppm of water and oxygen).

vi. Mg battery assembly

Each electrode was tested in a customized Tomcell (TJ-AC Tomcell Japan[3]) using a 435 μm thick (28 mm diameter) standard glass filter (Sigma-Aldrich) as a separator, 250 μl of PhMgCl-AlCl3 in THF as the electrolyte and a Mg foil (19 mm diameter) as the anode. Mg foil was polished by scraping each side of the foil with sandpaper and wiping clean with a Kimwipe (Kimberly-Clark). To avoid any corrosion of a current collector at the cathode side completely, a specially-designed glassy carbon dish was set in the cell. All cells were assembled under Ar in a glove box (<0.1 ppm of water and oxygen).

vii. Electrochemical cycling test

The cycling was performed in the voltage region between 0.8 and 2.75 V vs. Mg/Mg^{2+} at a desired, constant current using a Bio-Logic potentiostat/galvanostat VMP battery testing system. All of the batteries were kept in an oven at constant temperature (25 ± 0.5 ^{o}C) during the test. For a proof of concept test (Figure.1 (a) in the main text), the cells were discharged and then charged at a rate of 0.05 C (9.4 mA/g). Regarding the rate performance test, the cells were cycled once at a constant current of 0.05 C before running at the desired C rates. This pre-cycling process at 0.05 C is called "activation" in this study. The C rate and capacity were calculated with the weight of AgCl in the cathode.

viii. Preparation of ex-situ XRD samples

Sample A shown in the main text Figure 1 (a) is the as-prepared AgCl electrode. Samples B, C and D are the electrodes after initial discharge, initial recharge and second discharge at a constant current of 0.05 C, respectively. The cells were disassembled under Ar in a glove box and the electrodes were repeatedly rinsed in THF and dried under vacuum at 25 ^{o}C overnight in order to remove excess electrolyte bound to the surface.

The ex-situ XRD for the anode side was prepared by replacing the Mg anode with stainless steel as a current collector. After completely discharging (electrochemical status B as shown in Figure

1 (a)), the cell was opened under Ar in a glove box and the Mg foil was taken out. One piece of clean and dried stainless steel plate with equal size was gently put in the cell. Next, 0.1 ml electrolyte was added to offset the electrolyte loss during this process. The charge-discharge profiles of this cell were similar to what is typically observed, indicating the replacement did not change the electrochemical reaction in the cell (Figure S6). The stainless steel foils were also soaked with THF and dried before taking XRD spectra.

ix. XRD, SEM and XPS analyses

All XRD characterization was carried out on a Rigaku Smartlab diffractometer using Cu Kά 1.54 radiation. During the XRD scan, electrode pellets were fixed with double-sided copper tape on the sample holder.

The SEM images were acquired in a JEOL JSM-7800F instrument with an acceleration voltage of 5 kV.

XPS experiments were carried out using a PHI5802 Multitechnique spectrometer and each spectrum was collected after 1 min Ar^+ sputtering. The cathode samples for XPS measurements were the same as the samples used in the ex-situ XRD scan.

All of the sampling processes were done under an inert gas condition. Also, all of the samples were sealed in either vacuum transfer vessel or gas-tight holder, and then transferred to each equipment.

x. Solubility measurement

The solubility of metal chlorides in the electrolyte was investigated with a PerkinElmer Optima 7000 DV ICP-optical inductive couple plasma-option emission spectrometer (ICP-OES).

Reference:

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

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

3. *Japan Pat.*, JP 4580751, 2010.

Supporting Figures

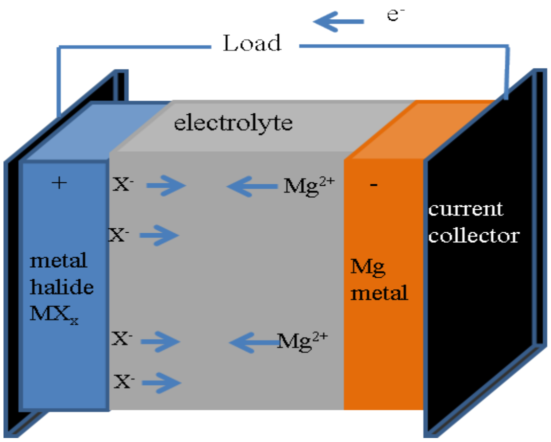

Figure S1 Schematic image of the architecture of a conceptual Mg battery.

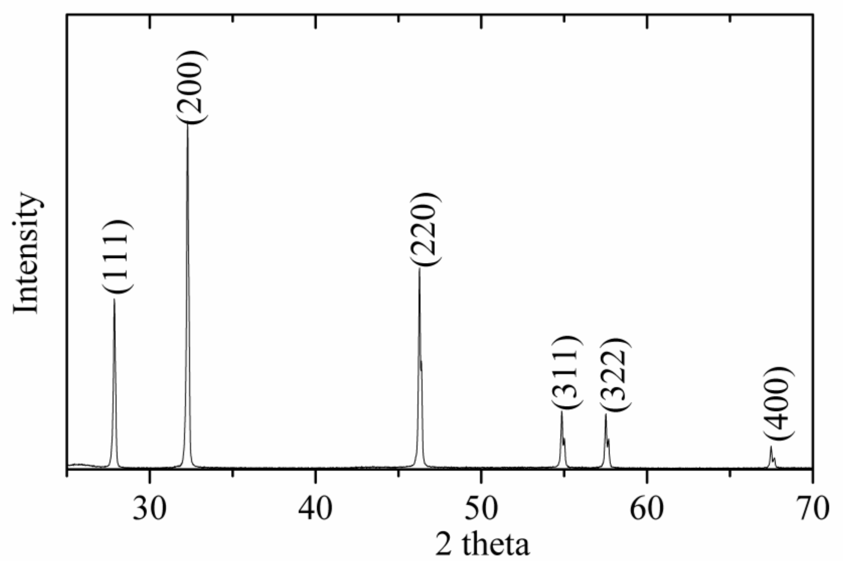

Figure S2 XRD pattern of the as-synthesized AgCl/C composite.

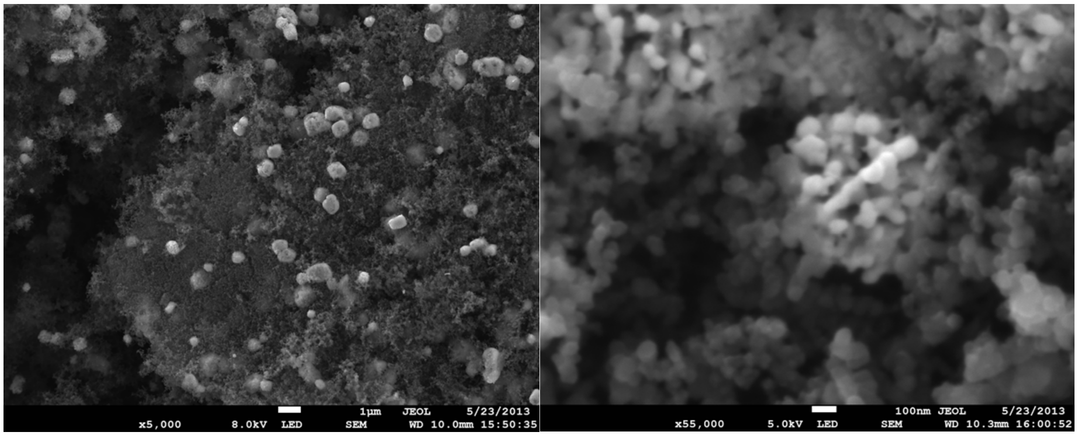

Figure S3 SEM images of the as-synthesized AgCl/C composite.

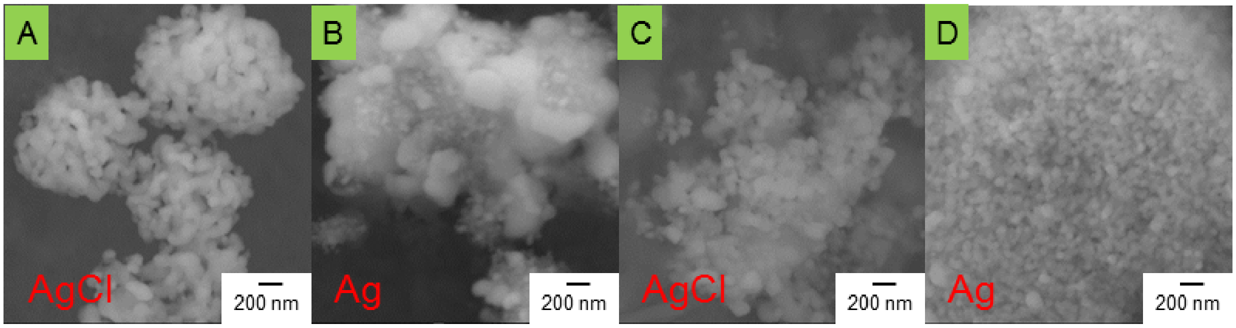

Figure S4 SEM images of the (A) pristine AgCl electrode, (B) first discharged electrode, (C) first recharged electrode and (D) second discharged electrode. The marks (A,B,C and D) represent the electrochemical states of the cathodes as described in Figure 1.

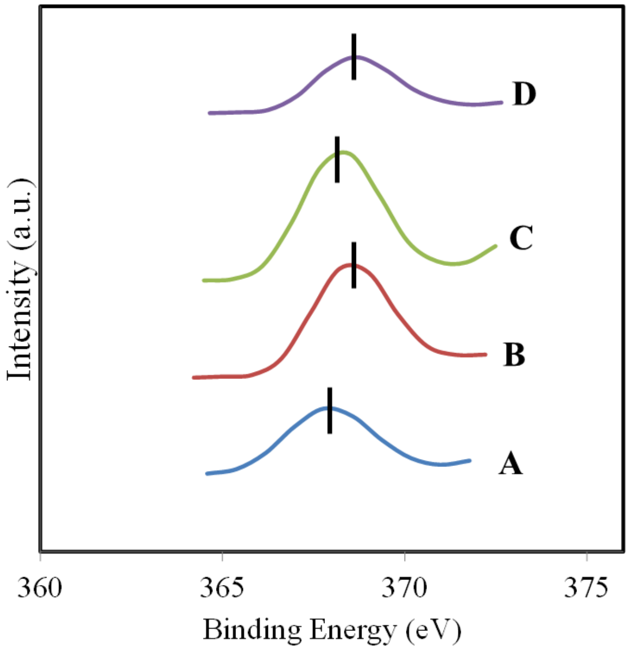

Figure S5 Ag $3d_{3/2}$ XPS spectra of the AgCl electrodes with different electrochemical states as labeled in the main text Figure 1(a).

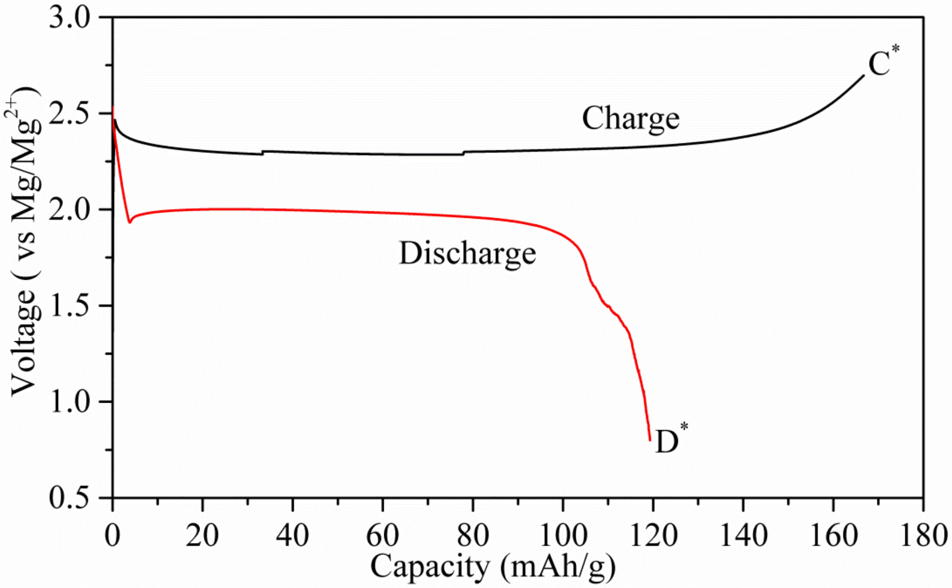

Figure S6 Galvanostatic cycling profiles of the Mg/AgCl battery after replacing the Mg anode with a stainless steel plate. The electrochemical states of C^* and D^* are the same as those of C and D shown in the main text Figure 1(a), respectively.

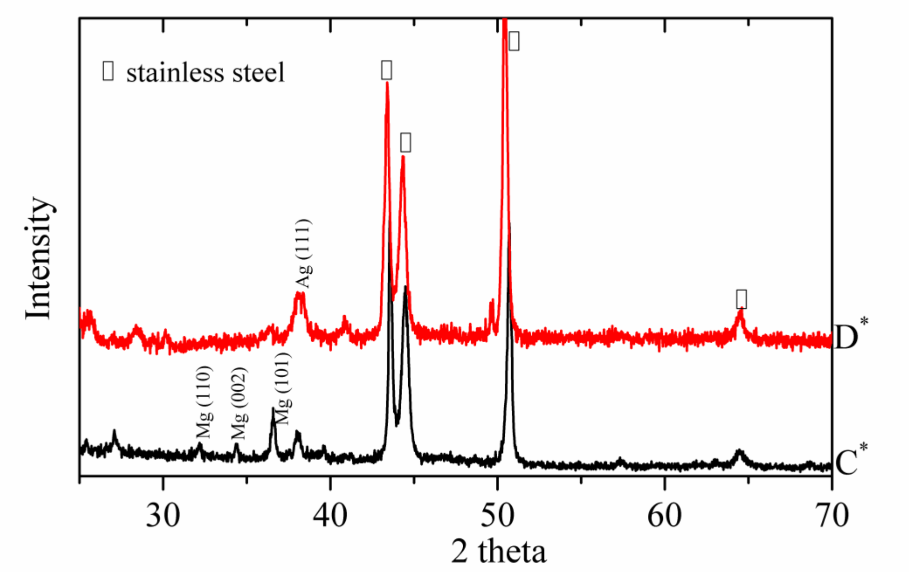

Figure S7 XRD patterns of the stainless steel electrode at the different electrochemical states C* and D*, which are labeled in Figure S6.

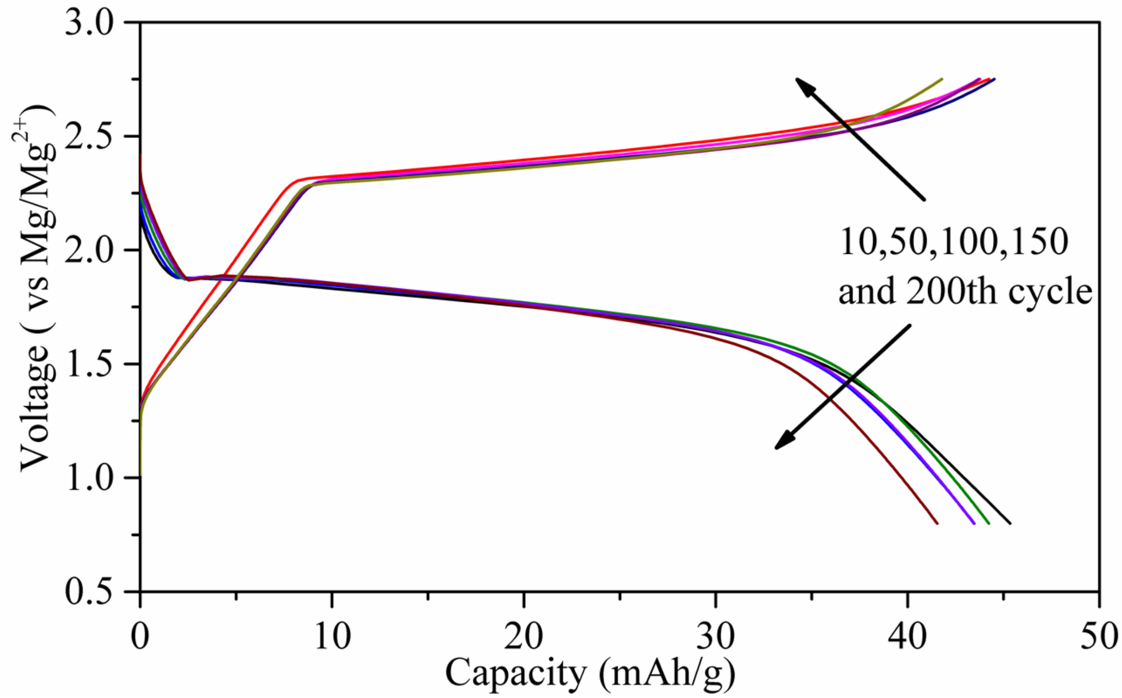

Figure S8 Galvanostatic cycling profiles of the Mg/AgCl battery operated at 10 C.

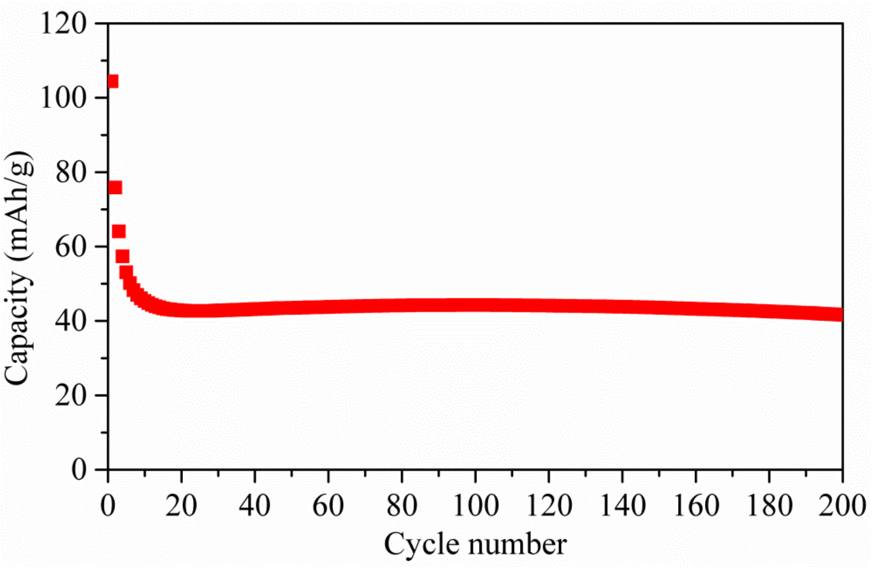

Figure S9 Cycling performance of the Mg/AgCl battery operated at 10 C.

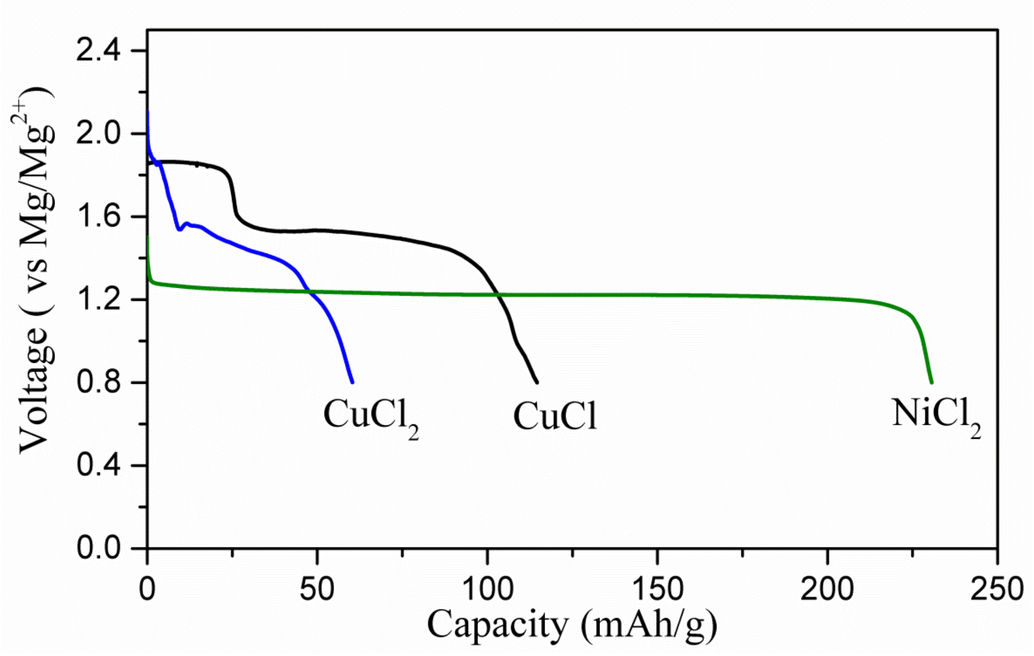

Figure S10 Initial discharge curves of metal chlorides in Mg batteries operated at 0.05 C.