Electronic Supplementary Information

Effective management of passive layer using composite cathode in solid state magnesium battery

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Experimental Section:

Chemicals:

Aniline (Aldrich, 99%), phenothiazene (Aldrich, 98%), magnesium Chips (Aldrich, 4-30 mesh, 99.98%), iodine (resublimed, CDH chemical), diethyl ether (CDH chemical), ammonium peroxidisulphate (Fulka, 98%) sulphuric acid (RFCL Limited), Barium chloride (S.D. Fine Chemicals) were all of analytical-reagent grade. All the solutions were prepared in Milli-Q water (Millipore). Aniline was stored in refrigerator when not in use.

Re-crystallization of Phenothiazene:

Phenothiazene was re-crystallized prior to use. For this purpose excess of Phenothiazene(25 grams) was dissolved in excess of benzene (150-175 ml) by warming up to 30-40^{0}C on water bath. A pinch of charcoal was added to it and mixed well. Small volume of solution was transferred on filter paperconed placed in a funnel. Solidified phenothiazine on the filter paper was dissolved and passed by pouring hot benzene. The process was continued till whole solution was filtered.The filtrate was kept in refrigerator for about 12 hours followed by filtered and dried under ambient condition.

Preparation of charge transfer salt:

Mixed valence Phenothiazene-Iodine (Ptz-I_2) charge transfer salt was prepared in 2:3 molar ratio. The structure is given below. For this purpose 7.970 g of recrystallized Phenothiazine & 7.614 g of iodine was dissolved separately in excess of diethyl ether with the help of sonication and warming if required. After complete dissolution, both solutions were mixed properly and kept in refrigerator for few hours. The precipitate obtained was filtered under pressure in a Buchner funnel and dried at room temperature.

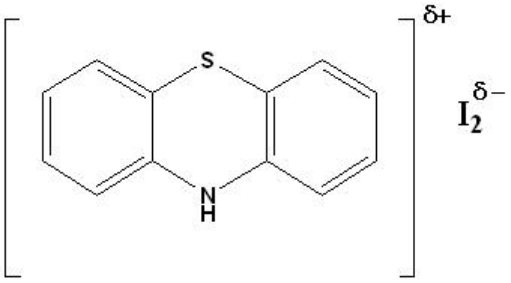


Figure S-1: Molecular structure of Phenothiazine-Iodine charge-transfer complex.

Polyaniline Monomer:

The aniline monomer was prepared in 0.5 M H_2SO_4. Aniline distilled under vacuum was added in required amount of H_2SO_4 to make 0.1 M monomer solution. The white precipitate was dissolved by sonication and stored in an air tight volumetric flask in ambient conditions.

Figure S-2: Protonation of aniline monomer.

Composite preparation:

The composites of Ptz-I_2 and polyaniline were prepared by adding aniline monomer to Ptz-I_2 charge transfer salt according to table-S-1. The suspension was stirred for 2-3 min using magnetic stirrer. To this, 0.1 M of oxidizing agent (ammonium peroxidisulphate solution) was added drop wise, as per table-S-1, under stirring condition and was kept in refrigerator (4-5^{0}C) for 12 hours. The polymerization reaction of protonated aniline monomer is given below. It was then filtered and washed thoroughly with milli-Q water till taking away of sulphate (filtrate was checked for sulphate ion using barium chloride).The precipitate was dried at room temperature and stored in an air tight container.

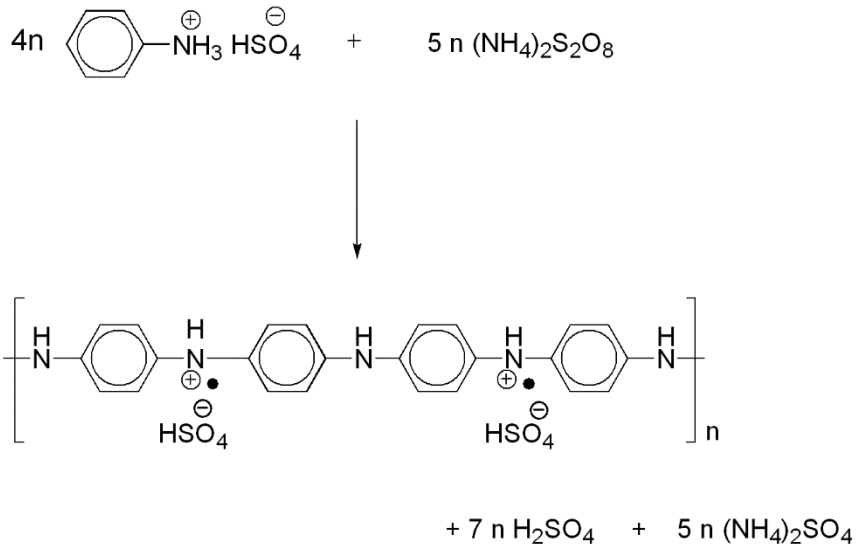


Figure S-3: Polymerization reaction of protonated aniline monomer.

Table S-1: Table indicating amount of Ptz-I_2 charge transfer salt and aniline monomer to prepare various composites and the wt% of iodine available in the cathode.

Composite	Weight of Ptz-I_2 charge transfer salt (g)	Volume of Aniline monomer (mL)	Volume of oxidizing solution (mL)	Wt.% of iodine
Pristine CTC	2.0	---	---	48.86%
CTC:PANI (90:10)	1.8	21.475	5.0	43.97%
CTC:PANI (80:20)	1.6	42.950	10.0	39.08%
CTC:PANI (70:30)	1.4	64.424	15.0	34.20%
CTC:PANI (60:40)	1.2	88.900	20.0	29.31%

Pellets formation and cell assembly:

The pellets of the cathode and anode material were prepared by applying 10 tone pressure by a hydraulic press in a SS pellet die. Equal quantity of material (0.5 grams) was used every time to maintain the physical dimensions of the pellet [diameter 13 mm thickness 1.48 mm]. Similarly the pellets of the Mg chips was also prepared in the same manner. The chip was stored in an air tight container and exposed to the atmosphere for a limited time duration while fabrication of pellet [diameter 13 mm thickness 2.05 mm]. Cells were assembled in a spring loaded brass holder by holding cathode and anode in between two inert platinum electrodes (figure-S-5), followed by

they were transferred in to a moisture free airtight desiccator (fig. S-6), having electrical contacts, to study the cell performance.

The half-cell reactions:

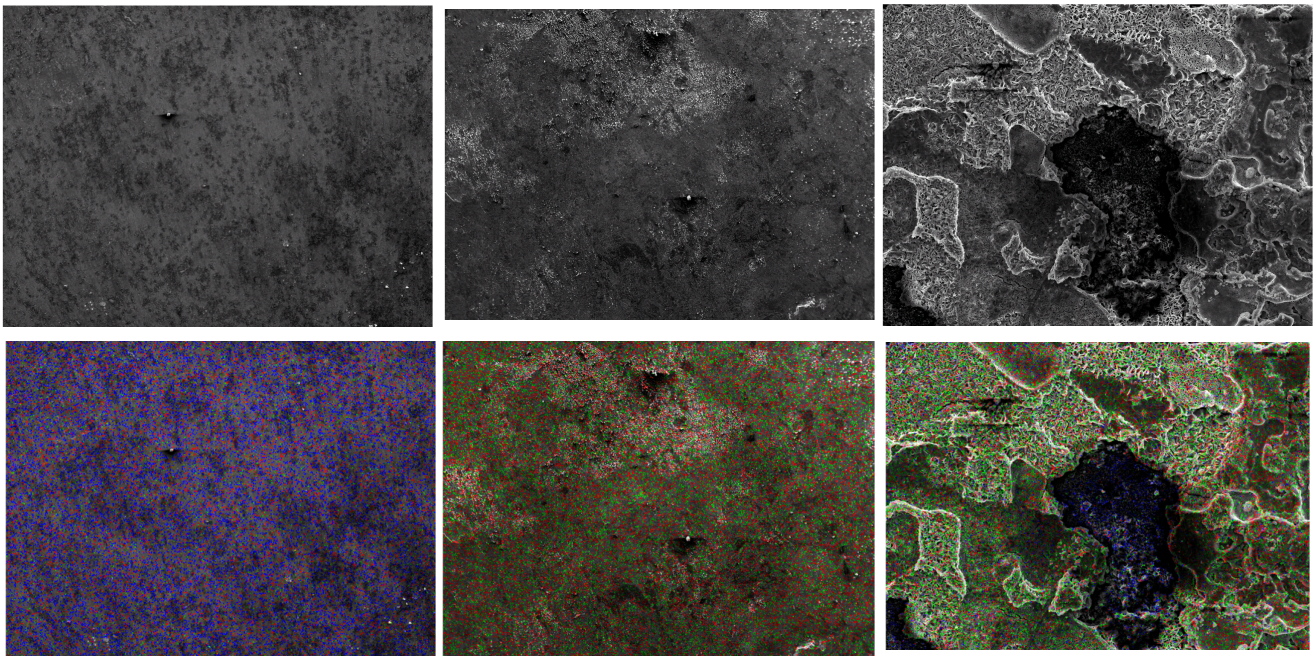
$Mg \longrightarrow Mg^{2+} + 2e^-$; E = 2.37 V

$I_2 + 2e^- \longrightarrow 2I^-$; E = 0.54 V

Therefore, theoretical EMF = 2.91 V.

Equipments:

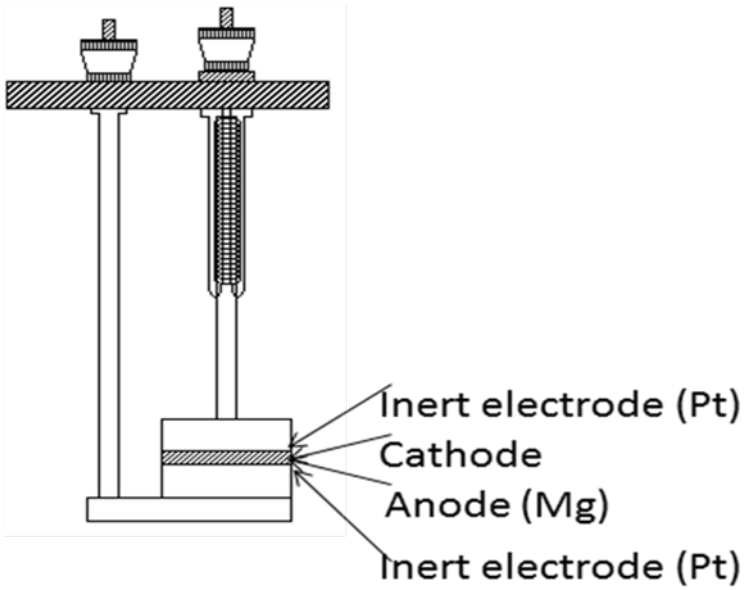
All the DC electrical measurements [potential (OCP), short circuit current (SCC)] were performed on source meter unit (Keithley 2635A System model). The AC electrical measurements were done on LCZ meter (Keithley 3330) in the frequency range from 40 Hz to 100 kHz. The impedance data were analyzed by using a CNLS software supplied by EG&G. Morphology of surface of cathodes and anodes were investigated by Scanning electron microscope (LEO 1430VP model) and elemental mapping were performed in conjugation with EDX (Oxford Instrument Inc. INCA X-sight). The SRI was carried out on scanning probe microscope (NT-MDT; Ntegra Aura).



[A] [B] [C]

Color code: **Red** – Iodine.;**Green** – Sulfur; **Blue** – Nitrogen. (For fig A & B)
Red – Mg; **Green** – Iodine; **Blue** – Sulfur.(For fig C)

Figure S-4: SEM image and SEM-EDX mapping of surface of A) Composite cathode; B) Pristine cathode; C) on dissembling.



Schematic diagram of pellet holder & cell assembly

Real optical image of the pellet holder & cell assembly

Figure S-5: Schematic diagram and real photograph of spring loaded brass pellet holder used for assembling cell.

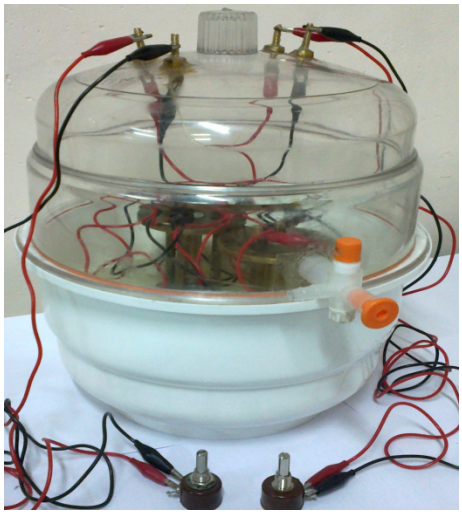


Figure S-6: Cell assembled in a spring loaded brass pellet holder secured in moisture free desiccators under ambient conditions.

Table S-2: Circuit parameter separated by AC impedance studies for:

A- The cell having composite cathode with Mg chips anode.

Time (Minutes)	Circuit Parameters						
	Bulk		Electrode		Grain Boundary		
	R (Ohms)	C (Farad)	R (Ohms)	C (Farad)	R (Ohms)	C (Farad)/ Q(Mho)	n
00	8.88×10^{2}	3.34×10^{-6}	2.40×10^{2}	3.52×10^{-7}	7.06×10^{3}	1.28×10^{-9}	0.73
23	8.22×10^{2}	3.89×10^{-6}	2.64×10^{2}	3.58×10^{-7}	7.21×10^{3}	1.84×10^{-9}	0.76
47	8.29×10^{2}	3.59×10^{-6}	2.54×10^{2}	4.06×10^{-7}	7.98×10^{3}	1.80×10^{-9}	0.71
52	8.11×10^{2}	3.90×10^{-6}	2.87×10^{2}	3.26×10^{-7}	7.69×10^{3}	1.20×10^{-9}	0.77
70	8.63×10^{2}	3.72×10^{-6}	3.09×10^{2}	3.88×10^{-7}	7.42×10^{3}	1.00×10^{-9}	0.76

B- The cell having pristine CTC with Mg chips anode.

Time (Minutes)	Circuit Parameters				
	Bulk		Electrode		
	R (Ohms)	C (Farad)	R (Ohms)	C (Farad)/ Q(Mho)	n
00	5.52×10^{2}	1.35×10^{-6}	1.73×10^{3}	5.28×10^{-6}	0.67
23	5.80×10^{2}	1.22×10^{-6}	3.68×10^{3}	5.33×10^{-6}	0.67
46	4.49×10^{2}	1.51×10^{-6}	7.30×10^{3}	7.69×10^{-6}	0.67
52	4.94×10^{2}	1.54×10^{-6}	9.37×10^{3}	8.09×10^{-6}	0.67
71	5.13×10^{2}	1.61×10^{-6}	1.37×10^{4}	1.02×10^{-5}	0.67