Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI)

Fullerenes: Non-transition Metal Cluster For Rechargeable Magnesium Battery Cathode

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Materials, Methods and Characterization

i. Materials

Fullerene C_{60} (99%, Sigma), Carbon black (EC600-JD, Ketjen Black International Inc.), Magnesium foil(Mg, 0.004 in., 99.9995%, ESPI Metals), Tetrahydrofuran (THF, anhydrous, ≥99.9%, Sigma), Aluminium chloride($AlCl_3$, anhydrous, 99.99%, Sigma), Phenyl magnesium chloride (PhMgCl, 2M solution in THF, Sigma), Polytetrafluoroethylene (PTFE, Daikin). Graphite (TIMCAL KS4), Carbon nanotube (multiwall, ≥98, OD x ID x L 10±1nm x 4±0.5nm x 3~6 μm).

ii. Synthesis of C_{60}/carbon (C_{60}/C) black material

C_{60}/C was mechanically prepared using a Retsch PM100 ball milling machine. 1g C_{60} and 1g carbon black were sealed into a zirconia vial with eight ½' balls and twenty ¼' balls. The mechanical milling was performed for a total of 6 h.

iii. 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 by adding 8 ml THF. For the third step, 12 ml diluted PhMgCl-THF solution was added drop by drop to 8 ml $AlCl_3$-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 activities were performed under Ar in a glove box (<0.1 ppm of water and oxygen).

iv. Fabrication of C_{60}/C electrodes and cells

C_{60}/C electrodes were composed of 70 wt% as-prepared C_{60}/C material, 20 wt % Ketjen 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 C_{60}/C PTFE sheet was dried at 120 ^{o}C under vacuum overnight. C_{60}/C pellets were cut out from the sheet with 13 mm diameter (1.33 cm^2 area). The loading content of each electrode was about 10.6 mg. Each electrode pellet was tested in a customized Tomcell (TJ-AC Tomcell Japan[3]) using a 0.2 μm thick (28 mm diameter) standard glass filter (Sigma-Aldrich) as a separator and a Mg foil (19 mm diameter) as the counter and reference electrodes. Mg foil was polished by scraping each side of the foil with sandpaper and wiping clean with a Kimwipe (Kimberly-Clark). One glassy carbon dish was used as a current collector at the cathode side. All cells were assembled under Ar in a glove box (<0.1 ppm of water and oxygen).

v. Electrochemical cycling test

The cycling was performed in the voltage region between 0.8 and 2.25 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) in the main text), the cells were discharged and then charged at a constant current of 25 µA. Regarding the rate performance test, the cells were cycled at the desired current densities.

vi. Fabrication of C_{70}, carbon black, graphite and carbon nanotubes electrodes.

The C_{70} electrodes were prepared by sandwiching ~ 5 mg C_{70} particle in two pieces of 13ϕ mm carbon paper under 5 tons pressure. The electrodes were dried under vacuum over night at 120 ^{o}C.

Carbon black, graphite and carbon nanotubes electrodes were composed of 90 wt% those materials and 10 wt% of PTFE binder. The preparation method was described in part **iv**.

v. XRD, Raman, XPS and TEM characterization

Sample A shown in the main text Figure 1 is the C_{60}/C electrode as prepared. Samples B and C are the electrodes after discharge, 1 cycle at a constant current of 25 µA, respectively. The cells were disassembled under Ar in a glove box and the cathode electrodes were completely rinsed in THF and dried under vacuum at 25 ^{o}C for 1 hour in order to remove excess electrolyte bound to the surface.

The XRD patterns were obtained on a Rigaku Smartlab diffractometer using Cu Kά 1.54 radiation. Before the XRD scan, electrode pellets were sealed in an air-free Be window sample holder in the Ar glove box.

The Raman test (532 nm excitation laser) was carried out on the LabRam HR instrument (Horiba). The electrode pellets were sealed in customized air-free sample holder before Raman experiment.

Regarding the XPS characterization, all of the sample were sealed in a vacuum transfer vessel and then transferred to the XPS chamber. XPS experiments were carried out using a PHI5802 Multitechnique spectrometer.

TEM images data were obtained using JEOL JEM-2010 operated at 200 kV.

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

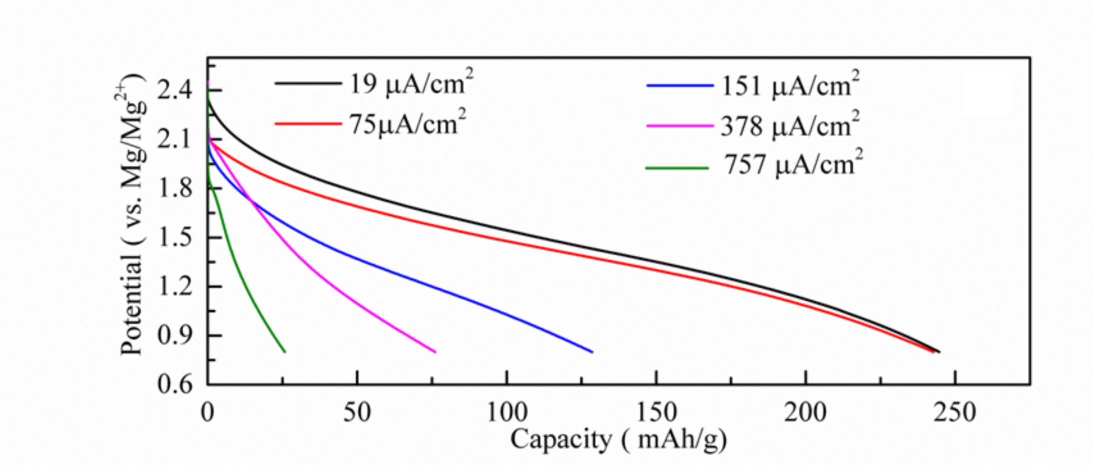

Figure S1 Galvanostatic discharge curves for the α-MnO_2 electrodes at different current density. α-MnO_2 (Erachem Comilog, Inc.) powder was used as active material for the cathode. The electrode preparation and electrochemical test were described in part **iv** and **v,** respectively.

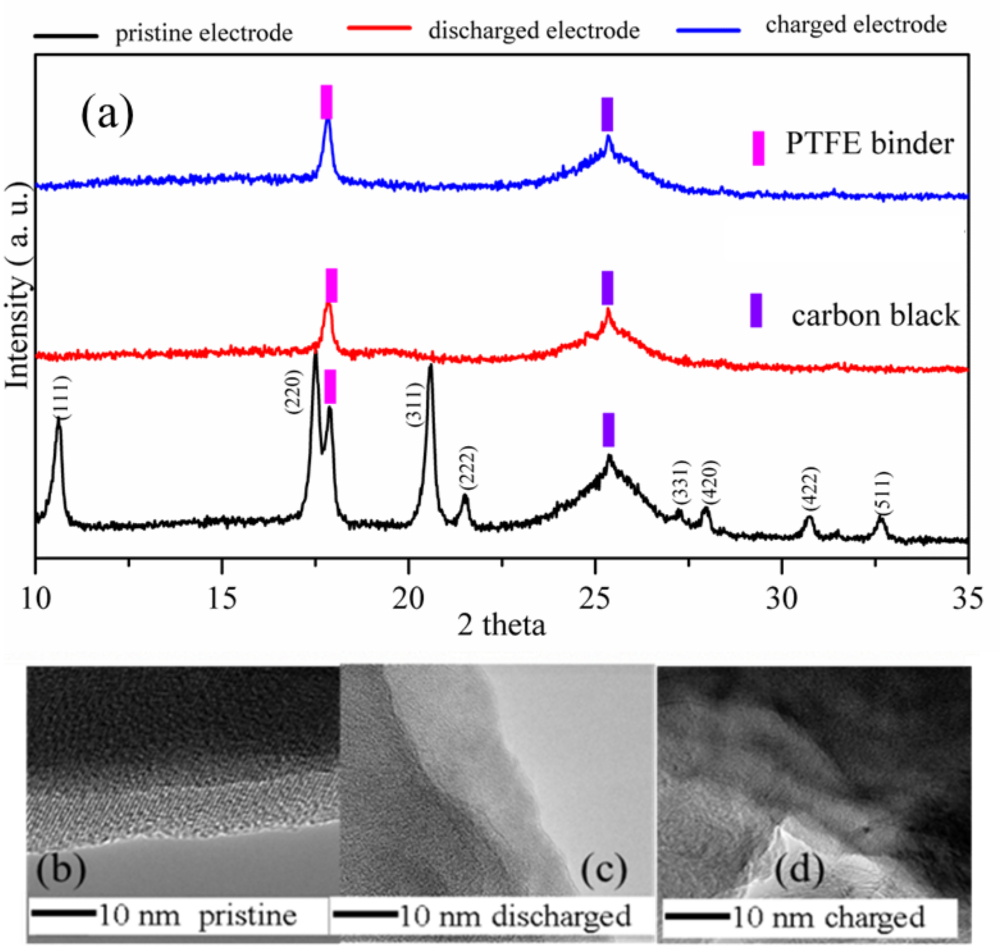

Figure S2 (a) XRD patterns of C_{60} electrodes at different electrochemical states and their TEM images ((b), (c) and (d)).

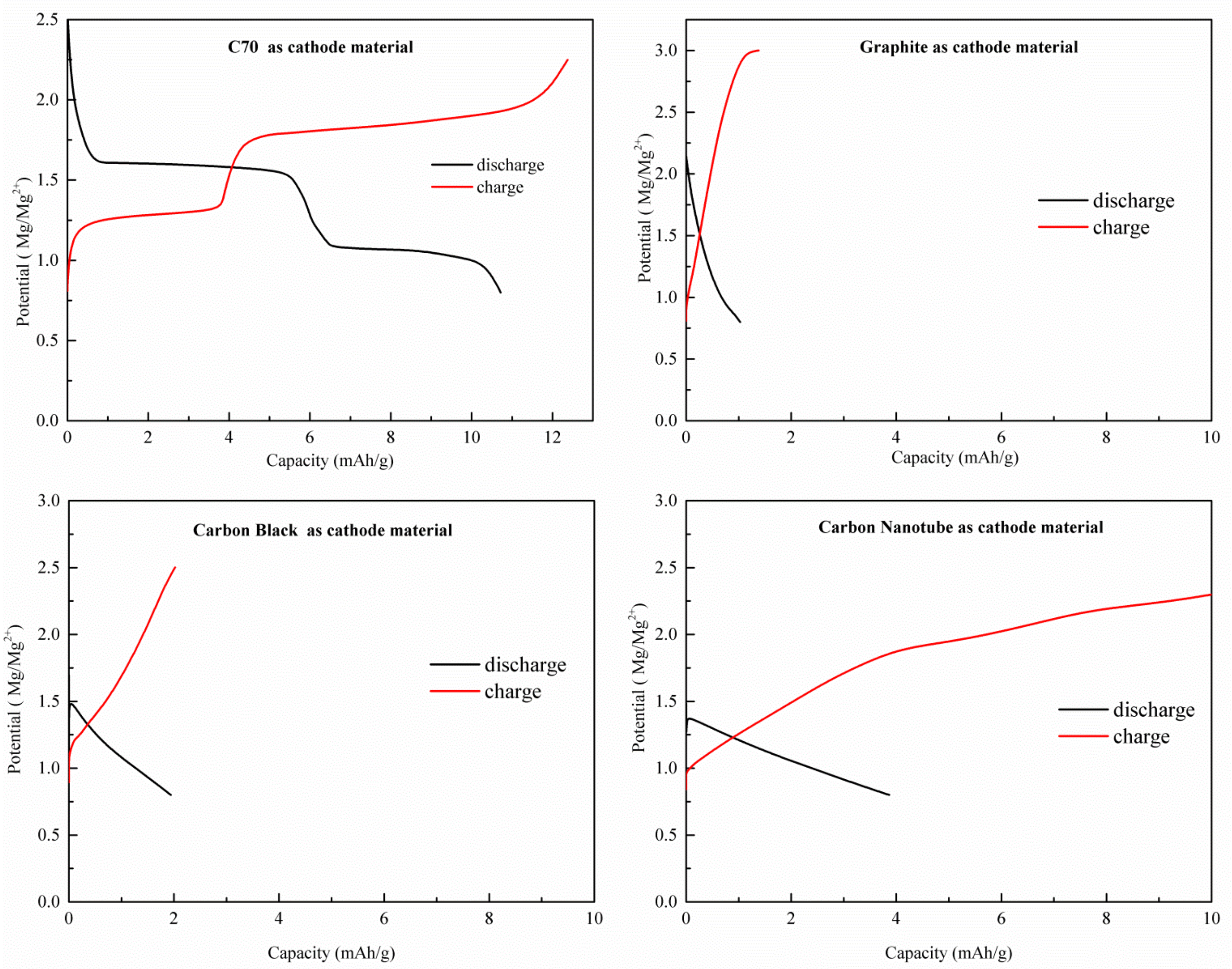

Figure S3 Galvanostatic discharge-charge curves for (a) C_{70}, (b) graphite, (c) carbon black and (d) carbon nanotubes at a current density of 19 uA/cm^2.