Supporting Information

**Preparation of SBA-15 silica**

This material was prepared according to a previously reported procedure. 1 4.0 g Pluronic P123 (EO20PO70EO20, MW =5800, Aldrich) was added to 120 mL 2.0 mol L⁻¹ HCl (36-38%, Sinopharm Chemical Reagent Co.) and 30 mL distilled water. After complete dissolution, the temperature of the solution was increased to 35 °C and 8.5 g tetraethyl orthosilicate (TEOS) (98.5%, Sinopharm Chemical Reagent Co.) was subsequently added to the solution and stirred for 24 hours. The mixture was transferred to a Teflon flask and sealed in an autoclave, then heated at 100 °C for 48 hours without stirring. The resulting precipitate was filtered and dried at 60 °C, and subsequently heated to 550 °C and maintained at this temperature for 6 hours.

**Preparation of KIT-6 silica**

This material was prepared according to a previously reported procedure. 2 5.595 g Pluronic P123 (EO20PO70EO20, MW =5800, Aldrich) was dissolved in 201.2 mL distilled water and 8.6 mL HCl (36-38%, Sinopharm Chemical Reagent Co.). After complete dissolution, 6.83 mL butanol (99%, Sinopharm Chemical Reagent Co.) was added and the mixture was stirred at 35 °C for 2 hours. Subsequently, 12 g tetraethoxysilane (TEOS) (98.5%, Sinopharm Chemical Reagent Co.) was added at 35 °C and the mixture was stirred for a further 24 hours. The mole ratio for TEOS:P123:HCl:H2O:BuOH in the mixture was 1:0.017:1.83:195:1.31. The mixture was transferred to a Teflon flask, then was sealed in an autoclave and heated at 100 °C for 72 hours without stirring. The resulting precipitate was centrifugated and dried at 60 °C, and subsequently heated to 550 °C and maintained at this temperature for 6 hours.

**Preparation of mesoporous Mg0.03Mn0.97SiO4**

Magnesium acetate tetrahydrate (Mn(CH3COO)2·4H2O, 99%, Sinopharm Chemical Reagent Co.) and manganese (II) acetate tetrahydrate (Mg(CH3COO)2·4H2O, 99%, Sinopharm Chemical Reagent Co.) was dissolved in ethanol (Sinopharm Chemical Reagent Co.) in a Teflon flask under continuous stirring at room temperature to obtain a homogeneous solution. Silicas KIT-6 or SBA-15 was subsequently added to the solution. The stoichiometric amounts for the precursors were accurately controlled with the molar ratio of 1.03:0.97:1 for Mg:Mn:Si. The mixture was stirred for 1 hour, then was sealed in an autoclave and heated at 120 °C for 24 hours without stirring. The resulting precipitate was centrifugated and dried at 60 °C, then pelleted and transferred to a tube furnace and heated in a reductive (Ar + 5 wt% H2) atmosphere at 550 °C for 6 hours, followed by final firing at 1000 °C at a rate of 2 °C/min for 24 hours, then cooling to room temperature naturally.

**Preparation of bulk Mg0.03Mn0.97SiO4**

Bulk Mg0.03Mn0.97SiO4 was prepared by a molten salt process. 3 KCl (melting point is 780 °C, 99.5%, Sinopharm Chemical Reagent Co.) was used as flux after drying for 3 hours at 150 °C under vacuum. The starting materials were magnesium oxide (MgO, ≥98.5%, Sinopharm Chemical Reagent Co.), manganese (II) carbonate (MnCO3, ≥95%, Sinopharm Chemical Reagent Co.), and silicon dioxide (SiO2, 15~20 nm, Sinopharm Chemical Reagent Co.) powders. The stoichiometric amounts for the precursors were accurately controlled with the molar ratio of 1.03:0.97:1 for Mg:Mn:Si. The mixture (flux/reactants = 4, by molar ratio) was hand-ground in a mortar by pestle for a few minutes, and was poured into a corundum crucible. Then, the powder mixture was dried at 120 °C for 5 hours under vacuum to minimize the water content in the mixture. After that, the mixture was immediately transferred to a tube furnace and heated in a reductive (Ar +
5 wt% H₂) atmosphere at 350 °C for 2 hours, followed by final firing at 1000 °C at a rate of 2 °C /min for 6 hours, then cooling to room temperature naturally. Finally, the product was washed for three times with deionized water to dissolve any remaining salt, separated by centrifugation, and dried under vacuum at 100 °C for 2 hours.

**Preparation of electrolyte**

The preparation procedure for electrolyte solution of 0.25 mol L⁻¹ Mg(AlCl₂EtBu)₂/THF has already been reported in detail and the experimental method is described briefly as follows: ⁴ proper amounts of MgBu₂ solution (1 mol L⁻¹ in hexane, Aldrich) and AlCl₂Et solution (0.9 mol L⁻¹ in heptane, Aldrich) in the ratio of 1:2 were mixed at room temperature, and a white solid precipitation formed immediately. After stirring for 48 hours, the hexane and heptane were completely evaporated, and a proper amount of high purity tetrahydrofuran (THF, distilled with benzophenone containing sodium chips under argon protection) was added to form the desired 0.25 mol L⁻¹ solution. All chemical preparations were carried out in an argon-filled glove box (Mbraun, Unilab, Germany).

**Material Characterization**

The Mg/Mn molar ratio (Si can not be tested) was analyzed by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) using Iris Advantagte 1000 spectroscope (Thermo Electron). The particle morphology was observed using scanning electron microscopy (SEM) on a JEOL field-emission microscope (JSM-7401F) and transmission electron microscopy (TEM) on a JEOL high-resolution electron microscope (JEM-2010). Small-angle and wide-angle XRD measurements were performed on a Rigaku diffractometer D/MAX-2200/PC equipped with Cu Kα radiation (λ=0.15418 nm). N₂ adsorption–desorption experiments were carried out at -196 °C on a ASAP 2010 M+C surface area and pore analyzer (Micromeritics, USA) after degassing of the samples at 200 °C for 3 hours.

**Electrochemical Measurements**

Electrode slurry was prepared by mixing 78 wt.% active material, 12 wt.% super-P carbon powder (Timcal) and 10 wt.% poly(vinylidene fluoride) (PVDF) dissolved in N-methyl-2-pyrrolidinone (Sinopharm Chemical Reagent Co.). The electrodes in diameter of Φ12.5 mm were formed by coating the slurry onto copper foil current collectors, drying at 80 °C for 1 hour, pressing at 2 MPa, and drying at 100 °C for 4 hours under vacuum. The active material loading was about 0.3-0.4 mg and the typical thickness of the active layer was 50 μm. Electrochemical behavior of the test materials was examined via CR2016 coin cells with magnesium ribbon (≥ 99.5%, Aldrich) counter electrode, Entek PE membrane separator and 0.25 mol L⁻¹ Mg(AlCl₂EtBu)₂/THF electrolyte. The cells were assembled in the argon-filled glove box. Cyclic voltammetry measurements were performed on a CHI650C Electrochemical Workstation (Shanghai, China). Galvanostatic charge-discharge measurements were conducted at ambient temperature on a Land battery measurement system (Wuhan, China) with the cut-off voltage of 2.1/1.5 V vs. Mg/Mg²⁺.

**References**