Supplementary Information (SI) For

Cubic $MnSe_2$ microcube enabling high-performance sulfur cathode for lithium-sulfur batteries

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Experimental and Methods

0.03 mol manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$, 99.9%, Aladdin) was first dissolved in a beaker with 180 mL deionized water. After that, 0.015 mol sodium selenite (Na_2SeO_3, 99.9%, Aladdin) was mixed in the solution. Meanwhile, 30 mL of hydrazine hydrate ($N_2H_4 \cdot H_2O$, 85%, Aladdin) was added into the beaker. After stirring for 5 minutes, the solution was transferred to several Teflon-lined hydrothermal synthesis reactors (50 mL of volume) and heated at 100°C for 24 hours. The reactors were cooled down to room temperature naturally. The chemical reaction of the preparation process is as follow:

$$Na_2SeO_3 + Mn^{2+} \rightarrow 2Na^+ + MnSeO_3 (\downarrow) \qquad (1)$$

$$MnSeO_3 \leftrightarrow Mn^{2+} + SeO_3^{2-} \qquad (2)$$

$$SeO_3^{2-} + N_2H_4 \rightarrow Se + N_2 + H_2O + 2OH^- \qquad (3)$$

$$3Se + 6OH^- \rightarrow 2Se^{2-} + SeO_3^{2-} + 3H_2O \qquad (4)$$

$$Se^{2-} + Se + Mn^{2+} \rightarrow MnSe_2 (\downarrow) \qquad (5)$$

The product was then transferred into 600 mL of citric acid (1 M) solution and stirred until $Mn(OH)_2$ precipitation dissolved. The sample was collected by filtration, washed with deionized water and absolute ethanol, and then dried at 70 °C in a vacuum oven.

To prepare Li_2S_6 polysulfide, 0.002 mol Li_2S was first dissolved in 10 mL Li-S electrolyte that mentioned in the text part. 0.01 mol S was then added into the solution and uniformly vibrated to form Li_2S_6. To conduct the adsorption comparison experiment, the as prepared polysulfide was diluted in Li-S electrolyte. The process was conducted in the argon-filled glove box ($O_2 \leq 0.2$ ppm, $H_2O \leq 0.5$ ppm).

Two kinds of cathode active materials were firstly prepared: 1) 70 wt % sulfur and 30 wt % Ketjenblack composite grinding for an hour under Argon atmosphere (denoted as SK), 2) 70 wt % sulfur, 20 wt % Ketjenblack and 10 wt % $MnSe_2$ composite grinding for an hour under Argon atmosphere (denoted as MSK). The active materials were then mixed with super-P carbon and poly (vinylidene fluoride) (PVdF) by a mass ratio of 8:1:1, separately, made into an N-methyl-2-pyrrolidone (NMP)-based slurry and coated onto aluminum foil. The cell was assembled in an argon-filled glove box ($O_2 \leq 0.2$ ppm, $H_2O \leq 0.5$ ppm). CR2032-type coin cells were assembled by sandwiching the polyethylene separator (Asahi ND 420) between the lithium anode and the sulfur-based cathode. For in situ XRD measurement, the CR2032-type coin cells with a window (3 mm) in the center for X-ray penetration. The window was sealed with polyimide tapes. The electrolyte consists of 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane (DME) (1:1 by volume) with 1% $LiNO_3$ additives.

The crystal structure of $MnSe_2$ was detected by Powder X-ray diffraction on an X-ray diffractometer (Bruker D8 Advance, Germany) with Cu-Kα radiation (λ = 0.1540 nm) at 40 kV, 40 mA. Scanning electron microscopy (SEM) was carried out by a field emission scanning electron microscope (FEI Quanta FEG 250). Cyclic voltammetry was conducted on a CHI660E electrochemical workstation (Shanghai Chenhua Instrument). The CV measurement was conducted between the potential range of 1.6-2.8 V in two-electrode coin cells, and the scanning rate was 0.1 mV/s. AC impedance was also conducted on the electrochemical workstation in the range of 2 mHz to 100 kHz with a voltage amplitude of 5 mV. The electrical tests were conducted in LAND CT-2001A electrochemical testing system. Valance state change of elements during the cycle was detected by X-ray photoelectron spectroscopic recorded on an ESCALAB210 electron using Al Kα radiation. Synchrotron-based time-resolved in situ XRD was performed on beamline BL02U2 (λ = 1.24 Å) at Shanghai Synchrotron Radiation Facility (SSRF). The UV-vis adsorption experiment was conducted by Daojin UV-3600.

The first principle calculation is conducted in Cambridge Sequential Total Energy Package (CASTEP). Geometry optimization task is first conducted to achieve stable structures. The calculation quality was set to fine and the GGA-PBE functional was employed. The cutoff energy was 544 eV and on the flying ultra-soft pseudopotential was employed. Koelling-Hamon relativistic treatment was chosen to deal with heavy atoms like Mn and Se.[S1] For density of states (DOS) calculation, Monkhorst–Pack k-point mesh is 4 × 4 × 4, and Ueff value for Mn was 4.5 eV. For binding energy calculation, k-point mesh is 1 × 1 × 1 and density mixing electronic minimizer is employed. Self-consistent field calculations (SCF) were carried out until the SCF tolerance was below 1×10^{-6} eV/atom.

References

[S1] Y. Zhang, Y. Li, Y. Cao, J. Mol. Struc. Theochem. 864 (2008) 85-88.

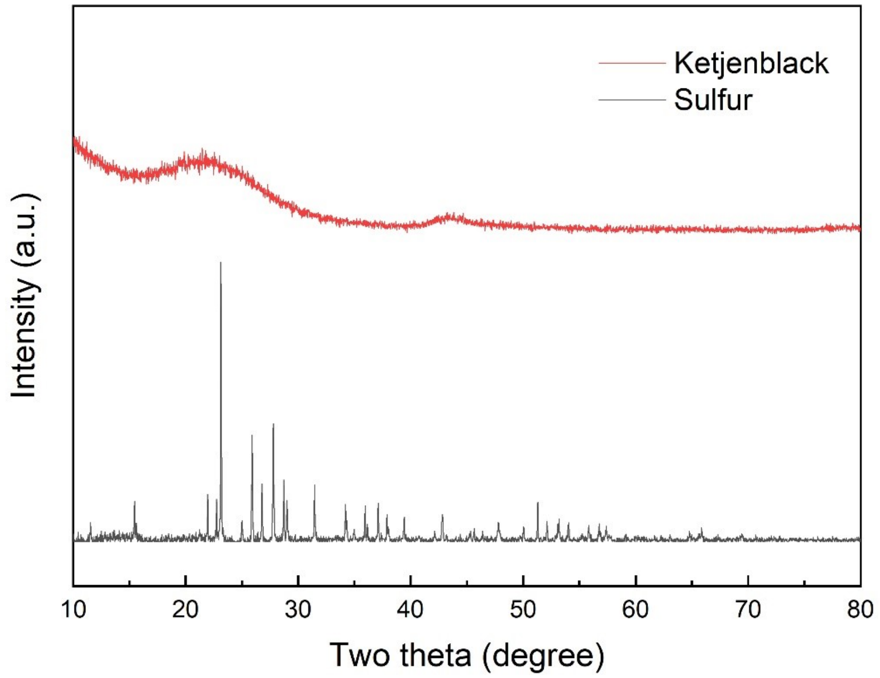

Fig. S1. XRD patterns of sulfur and Ketjenblack.

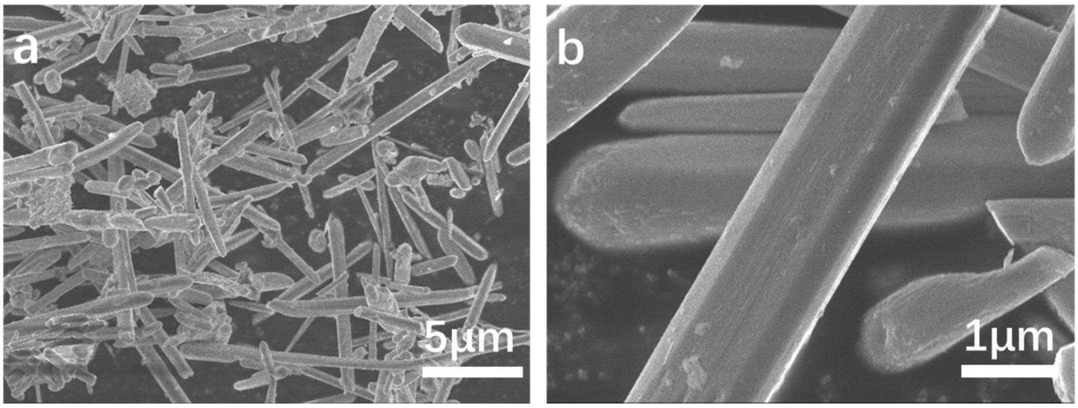

Fig. S2. (a, b) SEM images of $MnSe_2$ prepared with 50% N_2H_4.

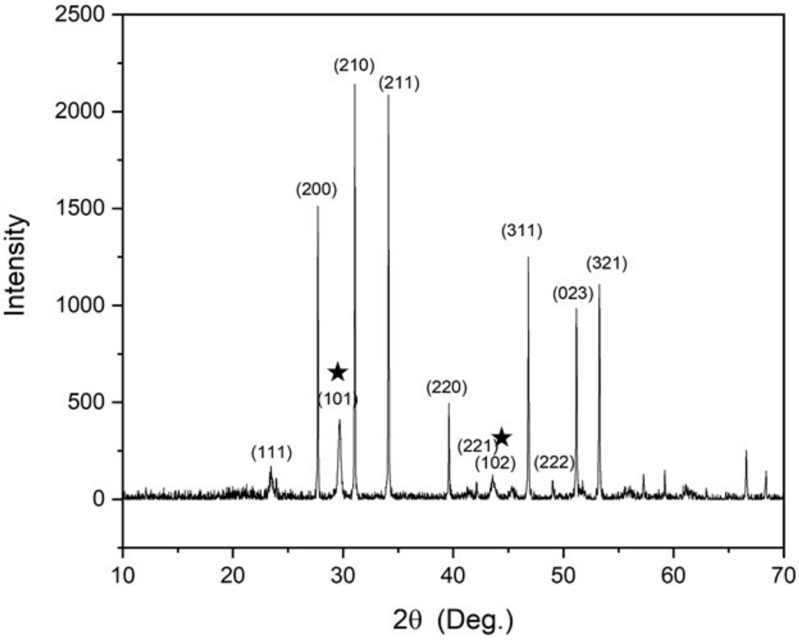

Fig. S3. XRD of $MnSe_2$ prepared with 50% N_2H_4.

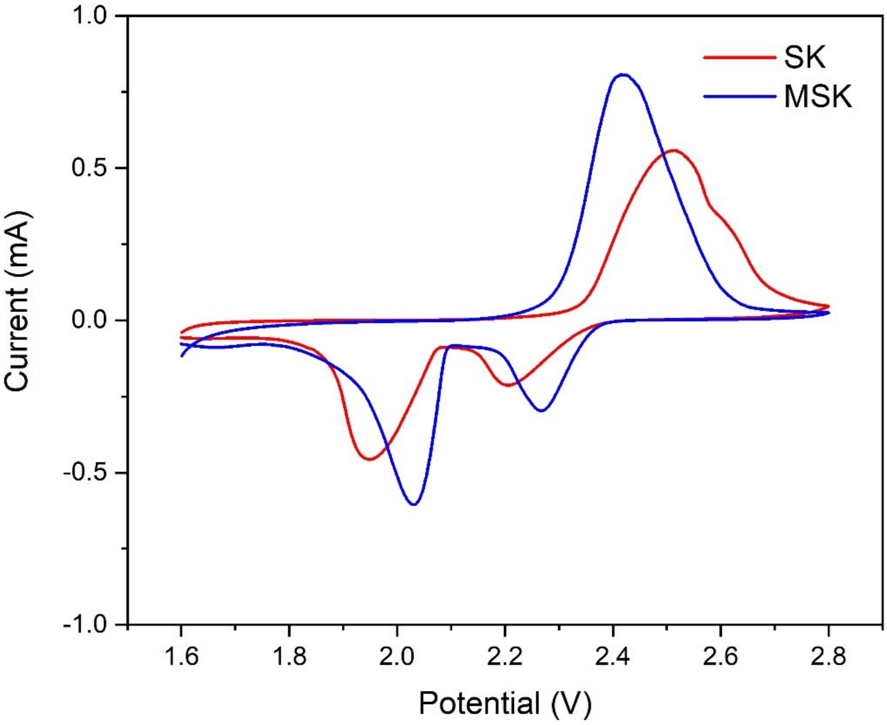

Fig. S4. CV profiles of SK and MSK electrodes in the first cycle.

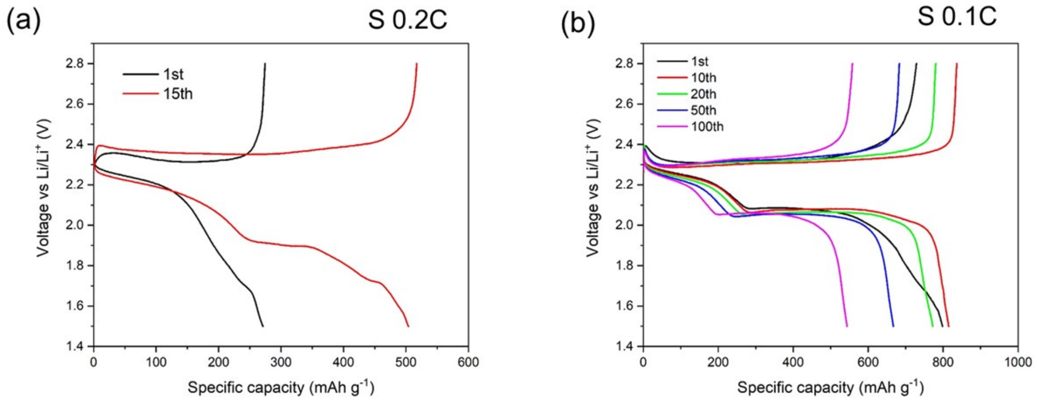

Fig. S5. Charge and discharge curves of the S electrode under (a) 0.2C and (b) 0.1C.

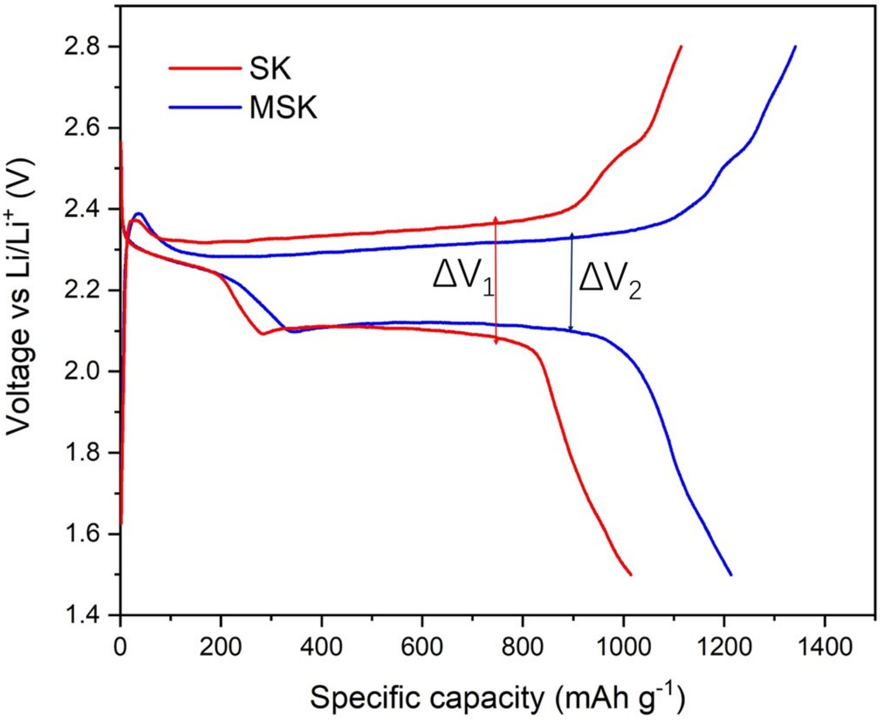

Fig. S6. The first discharge and charge curves of SK and MSK electrodes in LSBs.

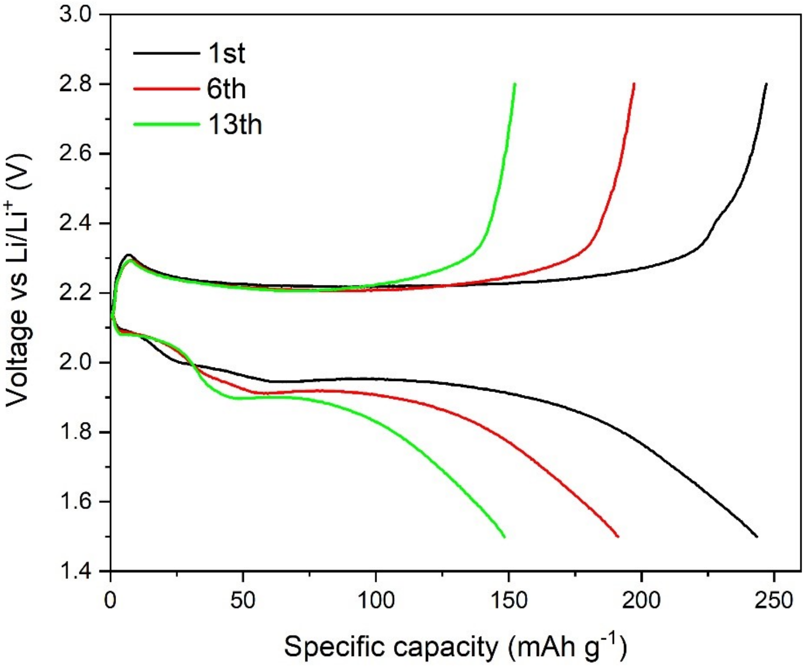

Fig. S7. Discharge and charge curves of $MnSe_2$ electrode in Li half cell.

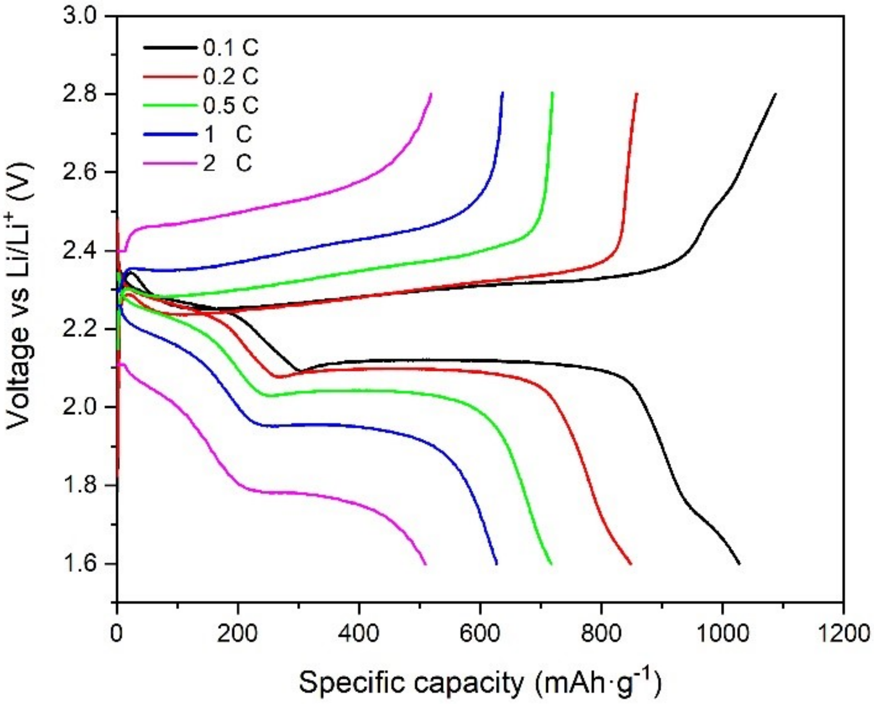

Fig. S8. Corresponding discharge and charge curves of MSK in the rate capability test (Fig. 2f).

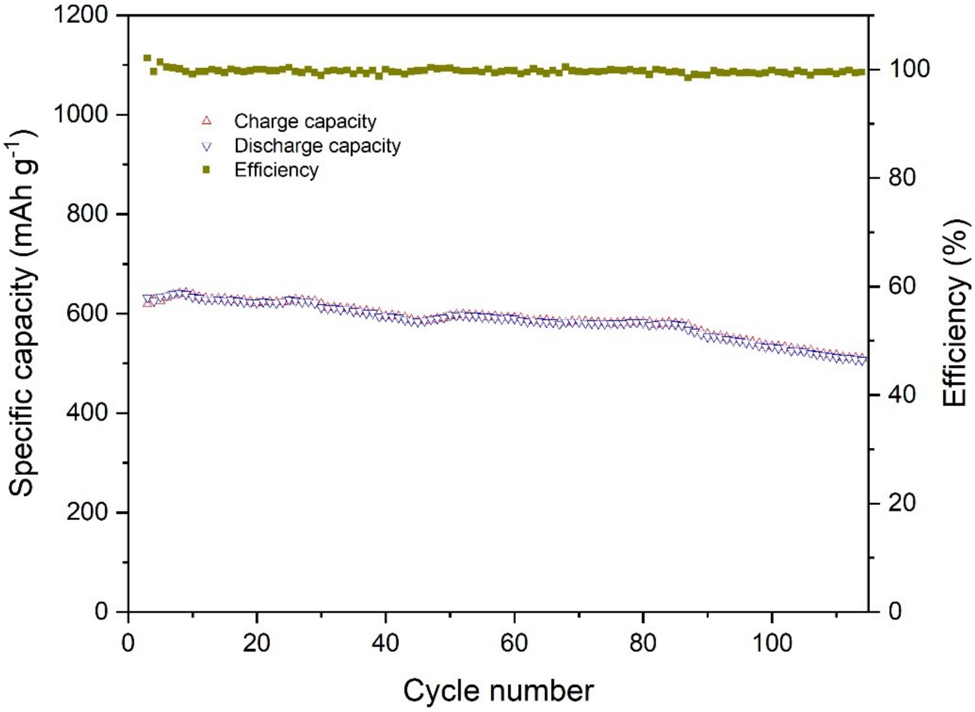

Fig. S9. Cycle performance of MSK electrodes under 1C current rate.

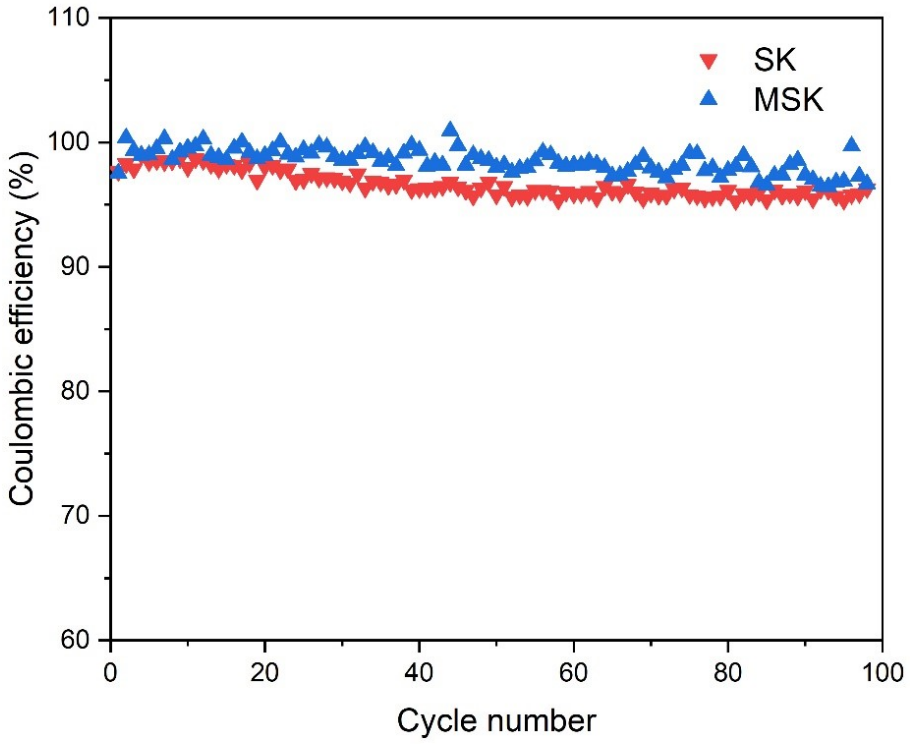

Fig. S10. Columbic efficiencies of MSK and SK electrodes at 1C current rate.