Porous calcium manganese oxide for oxygen electrocatalysis and metal-air batteries

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Introduction
Efficient catalysis of oxygen electrochemistry plays an important role in various electrochemical energy storage and conversion devices including fuel cells and metal-air batteries. Precious metals (mainly Pt) are reported to be the best catalysts for the oxygen reduction reaction (ORR), but the high price and limited availability have hindered their widespread applications. In recent years, manganese oxides have been extensively investigated as alternative materials for oxygen electrocatalysis, because of low price, high abundance, environmental friendliness and considerable activity. In particular, composite manganese oxides adopting the perovskite structure that can provide more active sites and larger round-trip efficiency and larger discharge/charge capacity (Fig. 3). The intrinsically superior activity of CaMnO$_3$ towards ORR/OER and nanoporous structure that can provide more active sites and larger void for Li$_2$O$_2$ deposition are considered to contribute to the improved battery performance.

Experimental
Nanoporous CaMnO$_3$ was prepared through a citric acid-assisted sol-gel method. Typically, stoichiometric Ca(NO$_3$)$_2$ and Mn(NO$_3$)$_2$ was dissolved in water, in which citric acid and ethylene glycol were added. The mixture was evaporated to form a sol and dried in vacuum overnight. Oxide sample was obtained by first heating the dried gel at 400 °C for 2 h and then annealed at 900 °C for 3 h in air. For comparison, β-MnO$_2$ was synthesized via a hydrothermal route following previously reported procedures. Electrocatalytic properties were tested using a standard three-electrode cell with electrolyte of 0.1 M KOH. Lithium-air batteries were assembled with a Li foil anode, a glass fiber separator, an air cathode composed of different catalyst, and an electrolyte containing 1 M lithium bis(trifluoromethanesulfonyl)-imide (LiTFSI) in tetraethyleneglycol dimethyl ether (TEGDME).

Results and discussion
Fig. 1 shows the XRD pattern and SEM image of the synthesized sample. XRD results indicate high purity of prepared CaMnO$_3$ oxide, which coincides with standard JCPDS 76-1132. Typical SEM image (Fig. 1 inset) clearly reveals the interconnected porosity morphology of the synthesized perovskite CaMnO$_3$ that consists of secondary nanoparticles. Fig. 2 displays the linear sweeping voltammograms (LSVs) at 1600 round per minute (rpm) in O$_2$-saturated 0.1 M KOH solution. Compared with the benchmark Vulcan carbon XC-72 and β-MnO$_2$, CaMnO$_3$ exhibits enhanced oxygen reaction activity in terms of lower overpotential, higher half-wave potential, and larger reduction current.

In Li$_2$O$_2$ batteries, the CaMnO$_3$/C electrode exhibits a better electrochemical performance than that of β-MnO$_2$/C and carbon only-based electrodes, enabling higher round-trip efficiency and larger discharge/charge capacity (Fig. 3). The intrinsically superior activity of CaMnO$_3$ towards ORR/OER and nanoporous structure that can provide more active sites and larger void for Li$_2$O$_2$ deposition are considered to contribute to

References