Improved conductivity of Ta and Ca doped $Li_7La_3Zr_2O_{12}$ (LLZO) for Li-S battery via modified solution method

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A modified solution method was designed to synthesize $Li_{7-x+y}Ca_yLa_{3-y}Zr_{2-x}Ta_xO_{12}$ ($0\leq x\leq 2$, $0\leq y\leq 0.05$) garnet electrolyte without producing toxic NO_x. Phase and conductivity of obtained $Li_{7-x+y}Ca_yLa_{3-y}Zr_{2-x}Ta_xO_{12}$ with different amount of substitution are presented in Table 1. Ta is helpful to stabilize the cubic phase at room temperature. As Ta:Zr ratio increased, the ionic conductivity offers upgrade firstly than descending latter tendency, which might be attributed to excessive Ta substitution that largely reduces lithium content in LLZO. The optimized Ta:Zr ratio is found to be 0.6:1.4 with peak conductivity of 1.95×10^{-4} S cm^{-1}. The incorporation of Ca increases the conducitivty of Ta-doped LLZO further to 4.03×10^{-4} S cm^{-1}, as the result of low vlance Ca^{2+} substitued for La^{3+} compensating the Li loss caused by Ta doping. The optimized solid electrolyte $Li_{6.45}La_{2.95}Ca_{0.05}Zr_{1.4}Ta_{0.6}O_{12}$ (LCLTZO) was applied as separator in Li-S cell in which pure sublimed sulfur acted as active cathode material. High Coulombic efficiency (nearly 100%) is achieved by cell with LCLTZO as shown in Fig.1a, whereas Coulombic efficiency of cell without solid electrolyte is extremely poor due to severe shuttle effect (Fig.1b).

Table 1 Lattice parameter and conductivity of LLZO with different composition

Composition	Phase	Conductivity (S cm^{-1})
$Li_7La_3Zr_2O_{12}$	tetragonal	7.83×10^{-6}
$Li_{6.8}La_3Zr_{1.8}Ta_{0.2}O_{12}$	cubic	6.54×10^{-5}
$Li_{6.6}La_3Zr_{1.6}Ta_{0.4}O_{12}$	cubic	7.85×10^{-5}
$Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$	cubic	1.95×10^{-4}
$Li_{6.0}La_3Zr_{1.0}Ta_{1.0}O_{12}$	cubic	8.30×10^{-5}
$Li_5La_3Ta_2O_{12}$	cubic	7.18×10^{-7}
$Li_{6.45}La_{2.95}Ca_{0.05}Zr_{1.4}Ta_{0.6}O_{12}$	cubic	4.03×10^{-4}

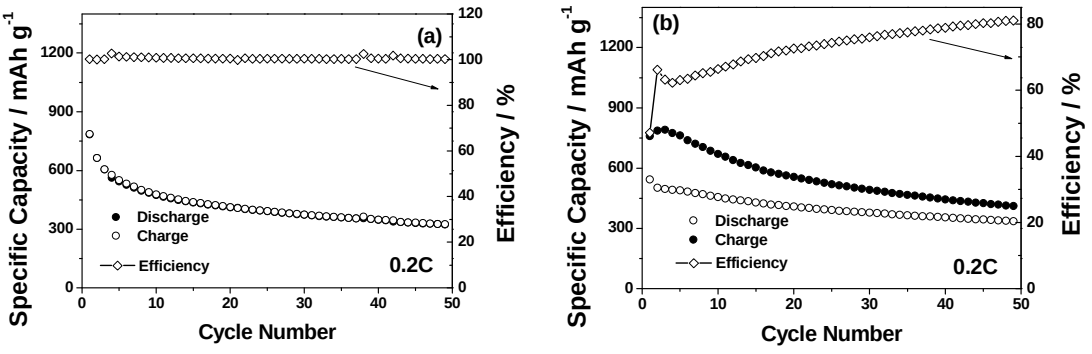

Fig.1 cycling performance profile of Li-S cell with (a) LCLTZO and (b) without LCLTZO