Electronic supplementary information

Stimulative formation of truncated octahedral $LiMn_2O_4$ by Cr and Al co-doping for durable cycling Li-ion batteries

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The calculation of Li^+ diffusion coefficient(D_{Li+}):

The corresponding formula is as follows:[1]

$$Z'=R_s+R_{ct}+\delta_w\omega^{-0.5} \quad (1)$$

Further, the D_{Li+} can be calculated by the following formula:

$$D_{Li+}=R^2T^2/2S^2n^4F^4C^2\delta_w^2 \quad (2)$$

where the constant values of R and F are 8.314 J/K·mol and 96484.5 C/mol, respectively; the absolute temperature T is 298.15 K; S is the surface area of electrode which is 6.15(cm^2); the electron transfer number n is 1; C is the volume con-centration of Li^+ in the spinel $LiMn_2O_4$ 0.02378 mol/cm^3; δ_w is the slope of the line of $Z'\sim\omega^{-0.5}$(Figure. S10).

The calculation of the apparent activation energy(E_a):

The following formula is generally used to calculate the activation energy (E_a) depend on the EIS data at different temperatures:[2]

$$i_0=RT/nFR_{ct} \quad (3)$$

$$i_0=Aexp(-E_a/RT) \quad (4)$$

where i_0 means exchange current, the constant values of R and F are 8.314 J/K·mol and 96484.5 C/mol, respectively; the absolute temperature T is 298.15 K; A is an in-dependent coefficient of temperature; the insets in Figure. S11a and b show the Arrhenius plots of logi_0 as a function of 1/T. Based on Eq. (3) and (4), E_a can be expressed in the equation of E_a=-R$k$ln10(k is the slope of the fitting line in the insets of Figure. S11a and b), thus the activation energies can be further calculated.

References

1 Y. Liu, Z. Yang, J. Li, B. Niu, K. Yang and F. Kang, *J. Mater. Chem. A*, 2018, **6**, 13883-13893.

2 S. L. Chou, J. Z. Wang, J. Z. Sun, D. Wexler, M. Forsyth, H. K. Liu, D. R. MacFarlane, S. X. Dou, *Chem. Mater.*, 2008, **20**, 7044-7051.

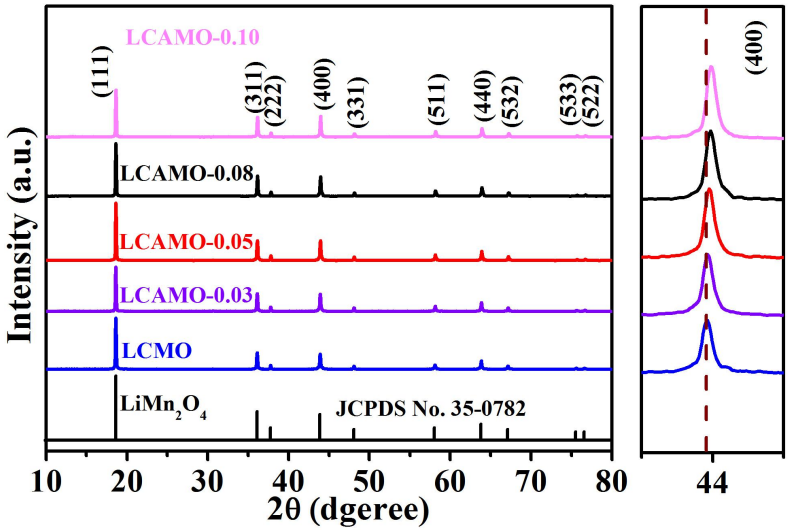

Fig. S1 XRD patterns of all samples along with locally enlarged (400)peaks.

Table. S1 Lattice parameters comparison of all samples

sample	lattice constants (Å)	cell volume(Å^3)	FWHM of (400) peak(°)
LCMO	8.23954	559.38	0.210
LCAMO-0.03	8.23700	558.86	0.206
LCAMO-0.05	8.23353	558.16	0.199
LCAMO-0.08	8.23057	557.56	0.197
LCAMO-0.10	8.22886	557.21	0.187

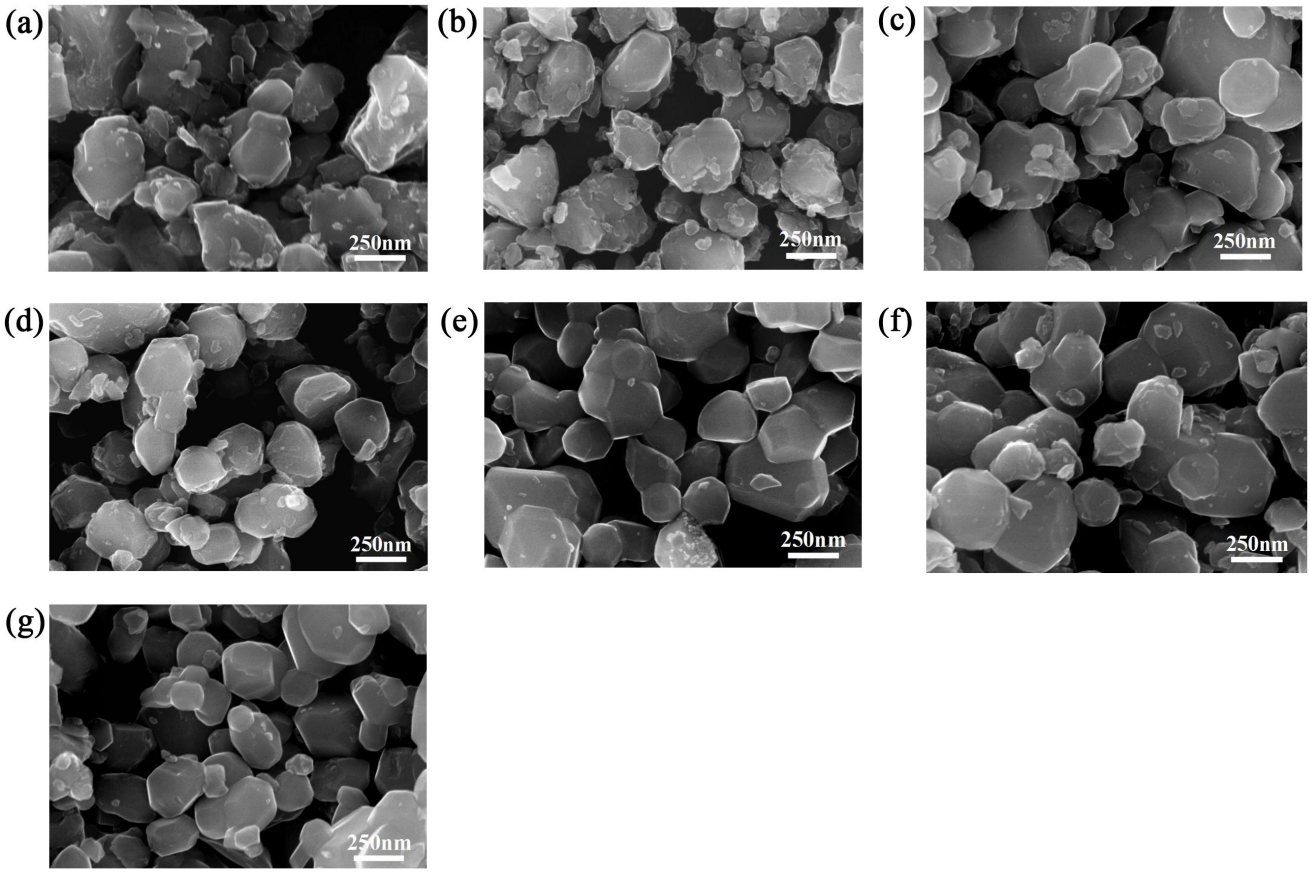

Fig. S2 SEM images of LMO (a), LCMO (b), LAMO (c), LCAMO-0.03 (d), LCAMO-0.05 (e), LCAMO-0.08 (f) and LCAMO-0.10 (g).

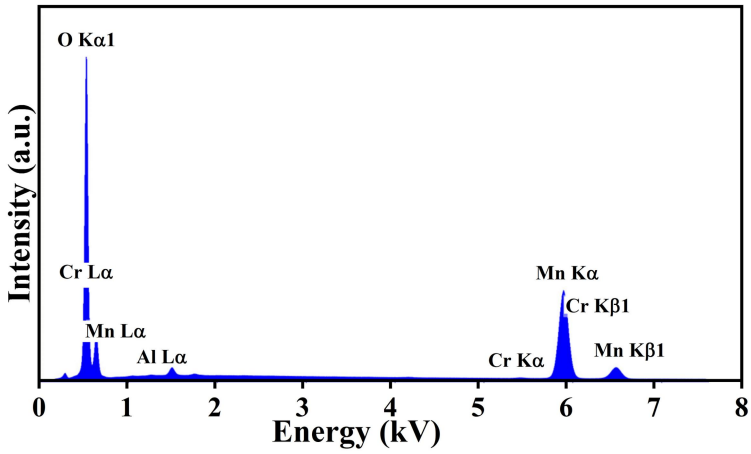

Fig. S3 EDS spectrum of the LCAMO-0.05.

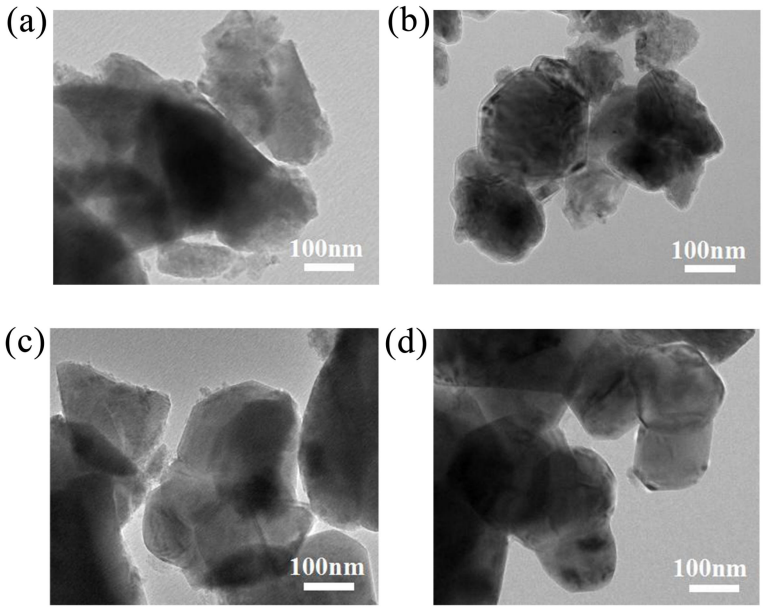

Fig. S4 TEM images of LMO (a), LCMO (b), LAMO (c) and LCAMO-0.05.

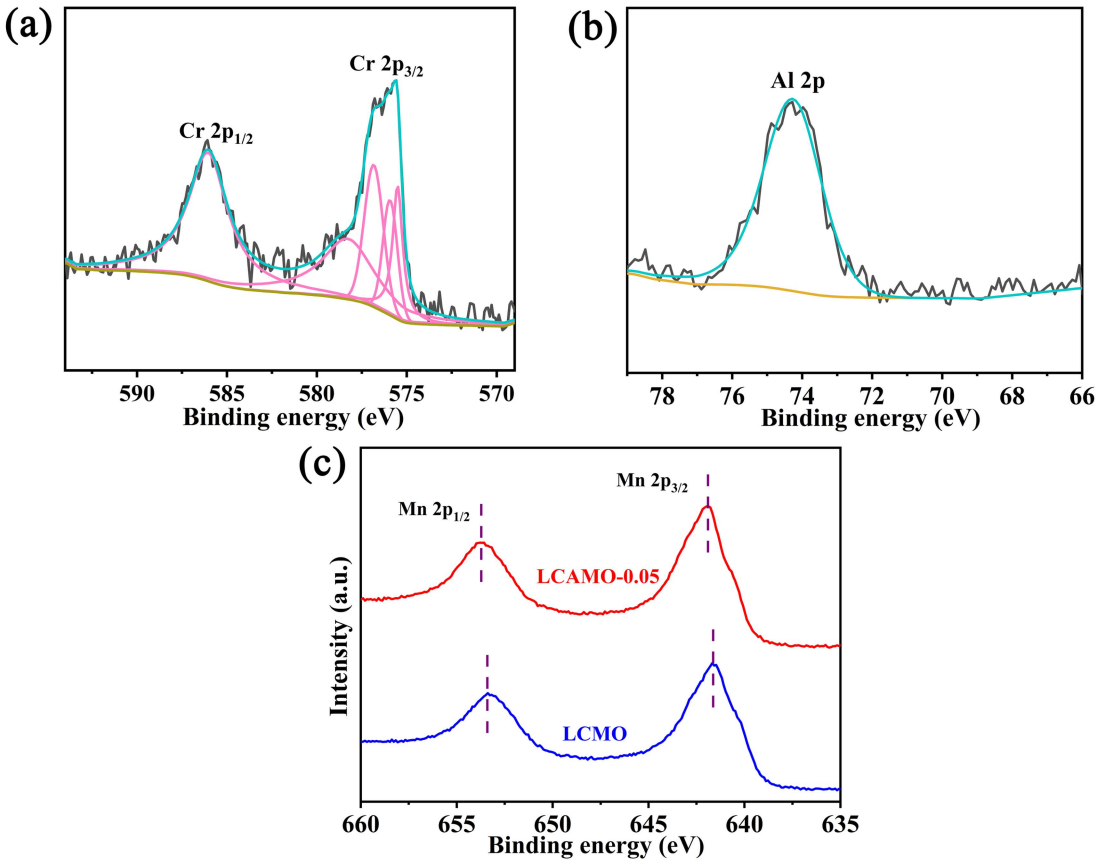

Fig. S5 The high resolution XPS spectra of (a) Cr2p and (b) Al2p of LCAMO-0.05, (c) Mn2p spectra of LCMO and LCAMO-0.05.

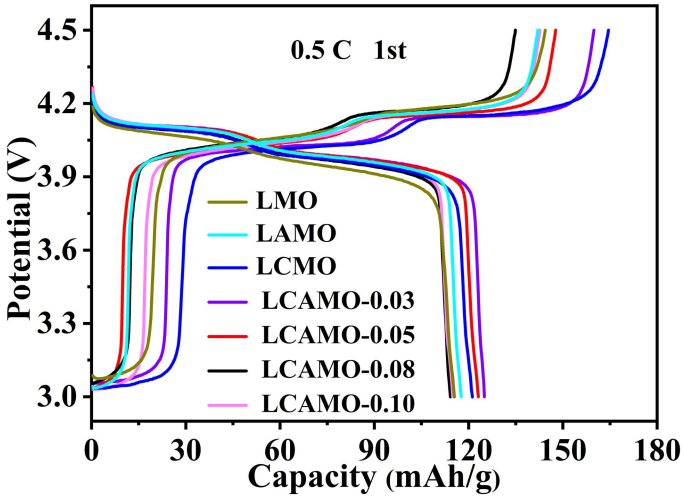

Fig. S6 Initial charge/discharge profiles of all samples at 0.5 C.

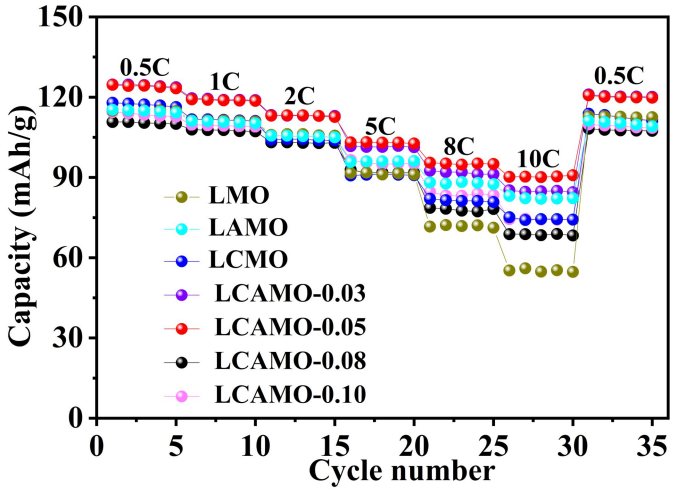

Fig. S7 Rate performances of all samples ranging from 0.5 to 10 C.

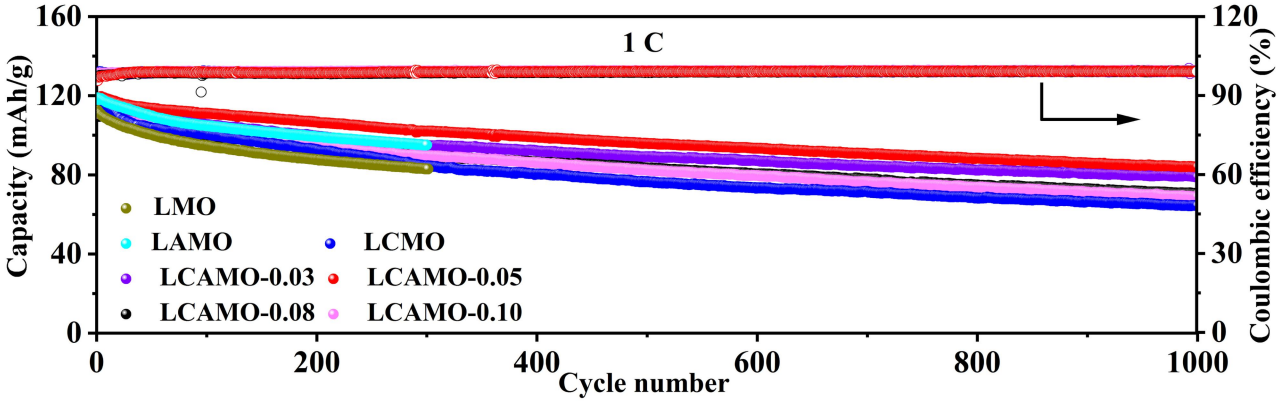

Fig. S8 Cycle performances of all samples at 1 C.

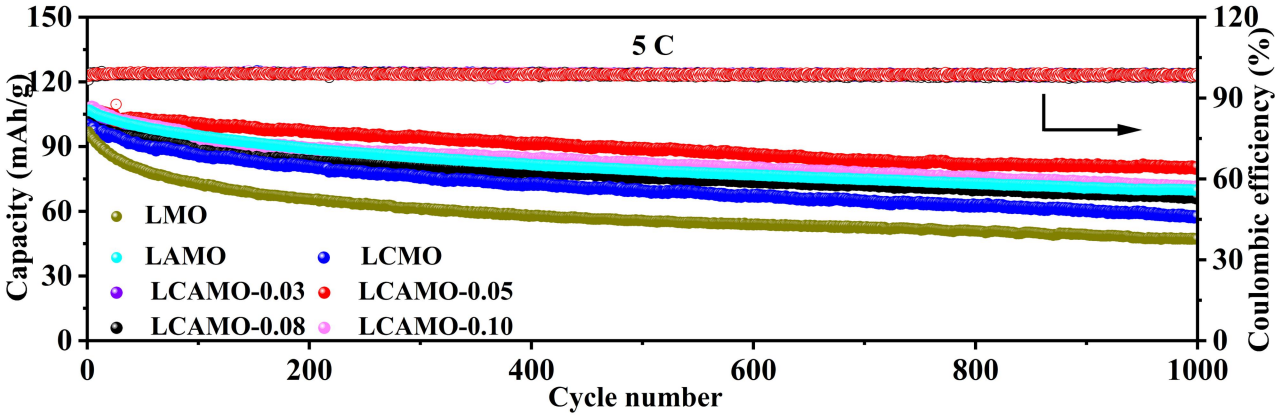

Fig. S9 Cycle performances of all samples at 5 C.

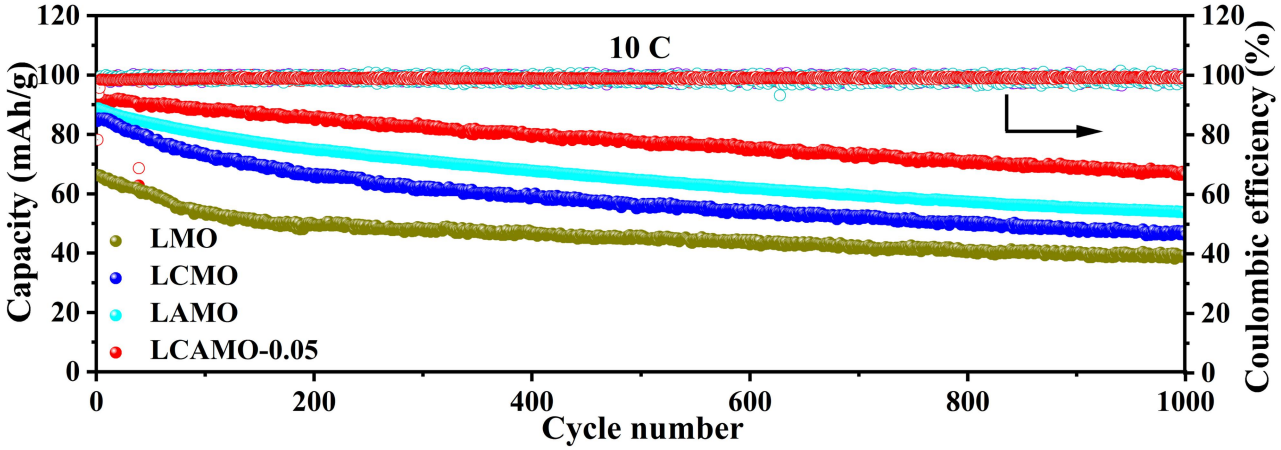

Fig. S10 Cycle performances of LMO, LCMO, LAMO and LCAMO-0.05 at 10 C.

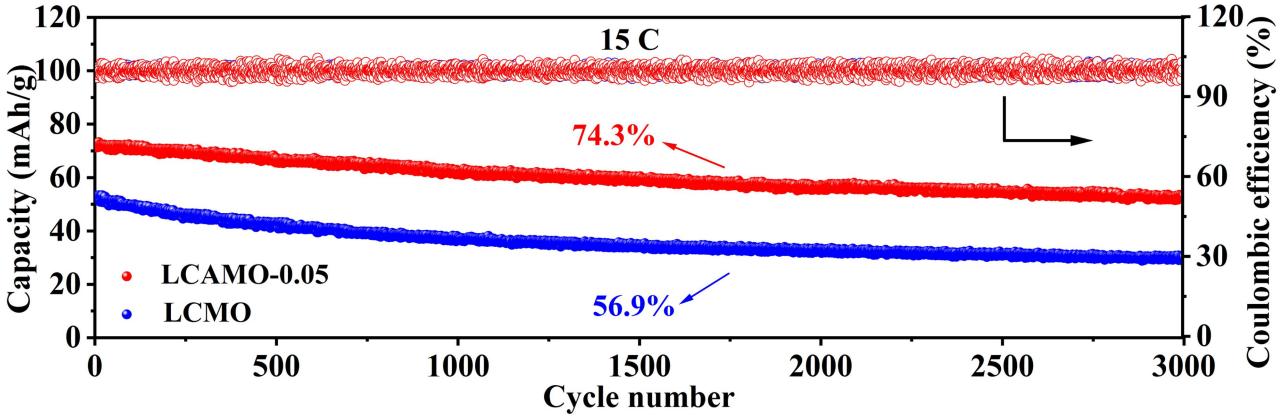

Fig. S11 Cycling performances of LCMO and LCAMO-0.05 at high rate of 15 C.

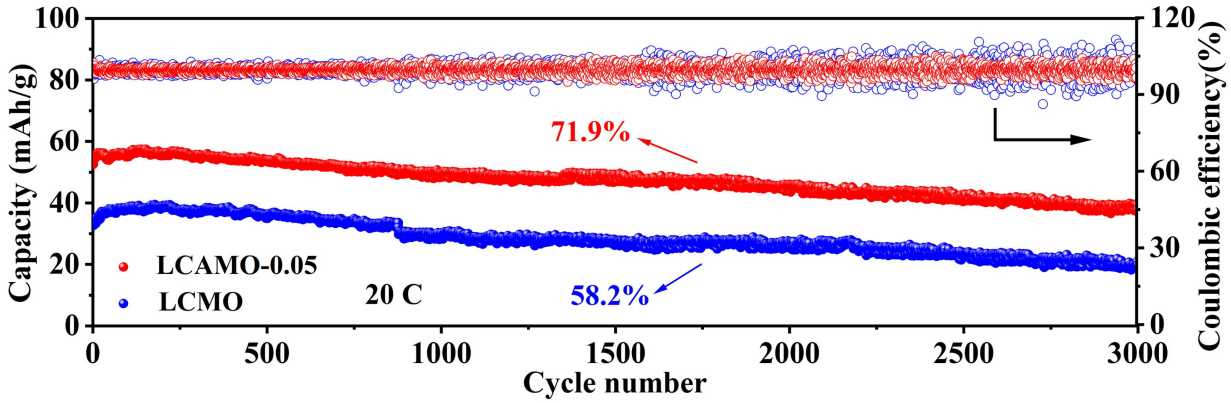

Fig. S12 Cycling performances of LCMO and LCAMO-0.05 at high rate of 20 C.

Table. S2 The charge transfer resistance(R_{ct}), electrolyte resistance(R_s) and ΔR_{ct} [R_{ct}(before cycle)-R_{ct}(after cycles)] values of LCMO and LCAMO-0.05 based on the EIS data before and after 1000 cycles at 5 C

sample		R_s/Ω	R_{ct}/Ω	$\Delta R_{ct}/\Omega$
LCMO	before cycle	1.82	170.6	169.4
	after cycles	3.78	340.0	
LCAMO-0.05	before cycle	1.50	151.3	70.3
	after cycles	3.73	222.0	

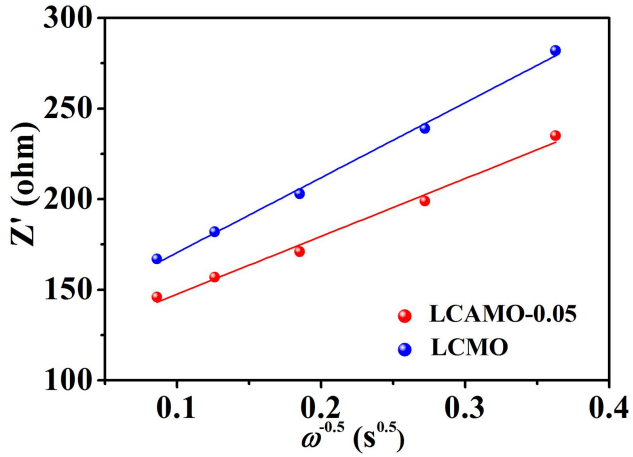

Fig. S13 Fitting curves of the real parts of complex impedance Z' and the $\omega^{-0.5}$

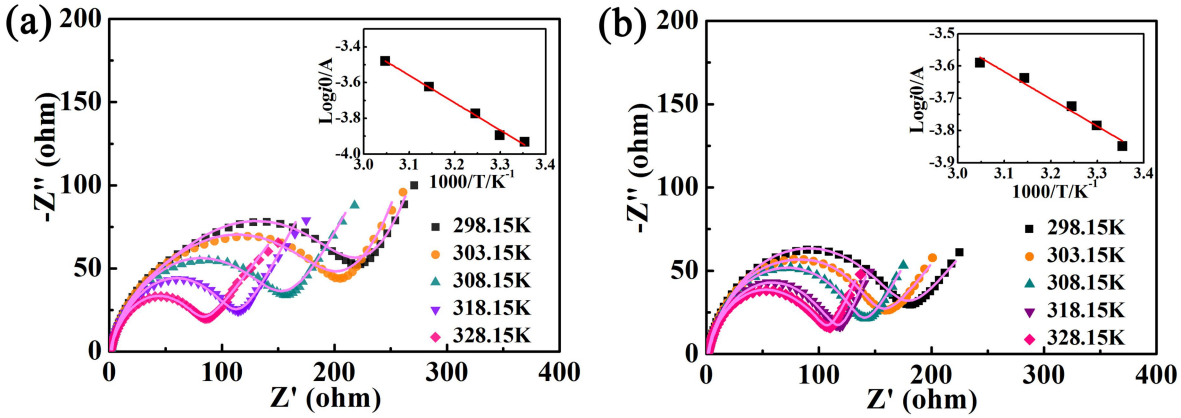

Fig. S14 EIS spectra at different temperatures(25-55℃) of LCMO (a) and LCAMO-0.05 (b), the insets are the corresponding Arrhenius plots of logi_0 vs. 1000/T.