Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

On the surface modifications of high-voltage oxide cathodes for lithium-ion batteries: New insight and significant safety improvement

*Min-Sik Park, Jong-Won Lee, Wonchang Choi, Dongmin Im, Seok-Gwang Doo, and Kyu-Sung Park**

Battery Group, Samsung Advanced Institute of Technology, Yongin 446-712, Korea

*ks337.park@samsung.com, kspark37@gmail.com (K.-S. Park)

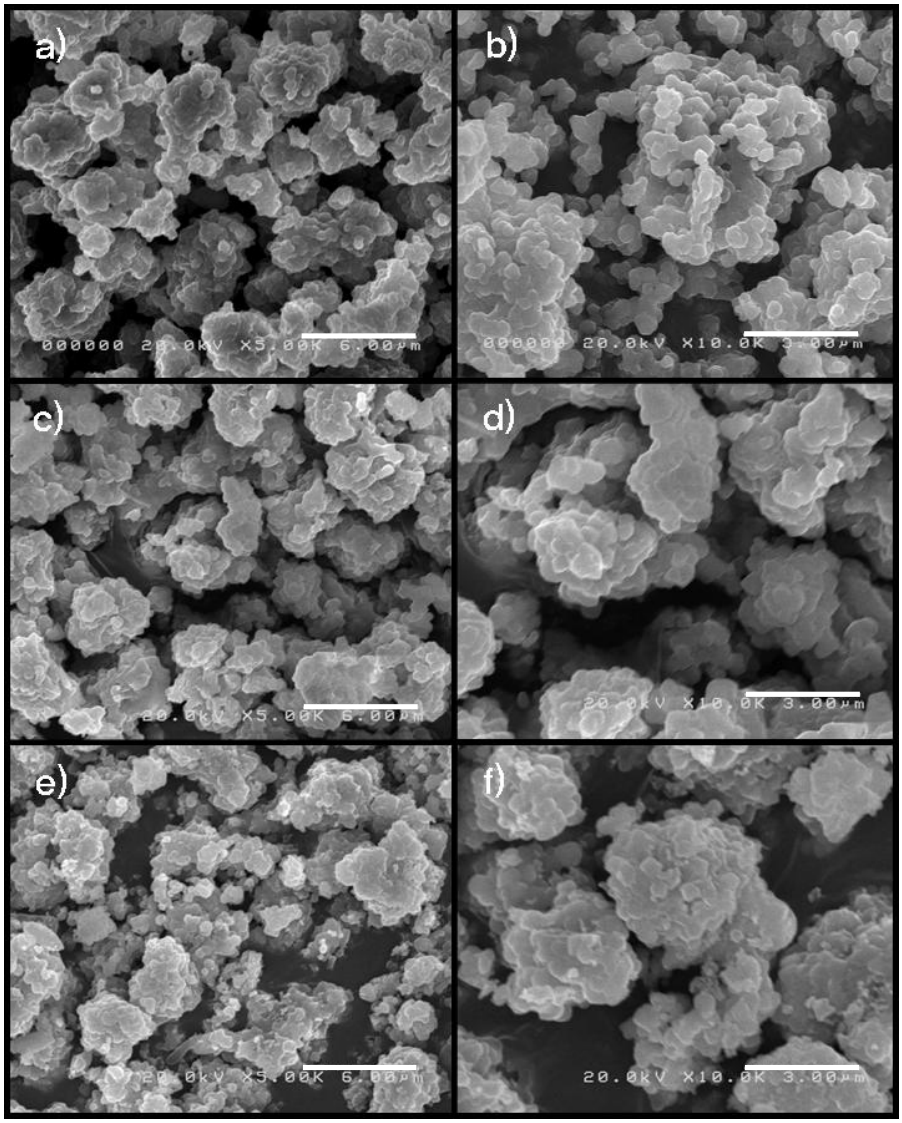


Fig. S1 FESEM images of (a) and (b) the pristine LNCMM, (c) and (d) the Al_2O_3 modified LNCMM, (e) and (f) the $AlPO_4$ modified LNCMM at different magnifications.

The morphologies of pristine and surface-modified LNCMM powders were characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4500) as displayed in Fig. S1. According to the comparison of FESEM images at different magnifications, there is no remarkable change in the morphology of LNCMM after the surface modification with Al_2O_3 and $AlPO_4$. It was difficult to confirm the existence of Al_2O_3 or $AlPO_4$ phase on the surface of LNCMM using FESEM in this work. However, the coated Al_2O_3 or $AlPO_4$ species were clearly observed in HRTEM images (Fig. 1).

Al_2O_3 (wt%)	*First cycle*			
	Charge capacity (mAh/g)	**Discharge capacity (mAh/g)**	**Irreversible capacity (mAh/g)**	**Efficiency (%)**
0	292.89	209.91	82.98	71.67
0.5	300.82	221.45	79.37	73.62
1.0	277.59	217.04	60.542	78.19
2.0	287.66	228.61	59.05	79.47
3.0	257.89	215.88	42.01	83.71
5.0	250.32	213.68	36.64	85.36

$AlPO_4$ (wt%)	*First cycle*			
	Charge capacity (mAh/g)	**Discharge capacity (mAh/g)**	**Irreversible capacity (mAh/g)**	**Efficiency (%)**
0	292.89	209.91	82.98	71.67
0.5	278.80	223.41	55.39	80.13
1.0	260.41	220.29	40.12	84.59
2.0	246.15	210.50	35.64	85.52
3.0	235.56	198.57	36.99	84.30
5.0	210.09	173.26	36.83	82.47

Table. S1 The electrochemical properties of the Al_2O_3-/$AlPO_4$-modified LNCMM within the voltage range from 2.0 to 4.55 V vs. Li/Li^+ at the rate of C/20.

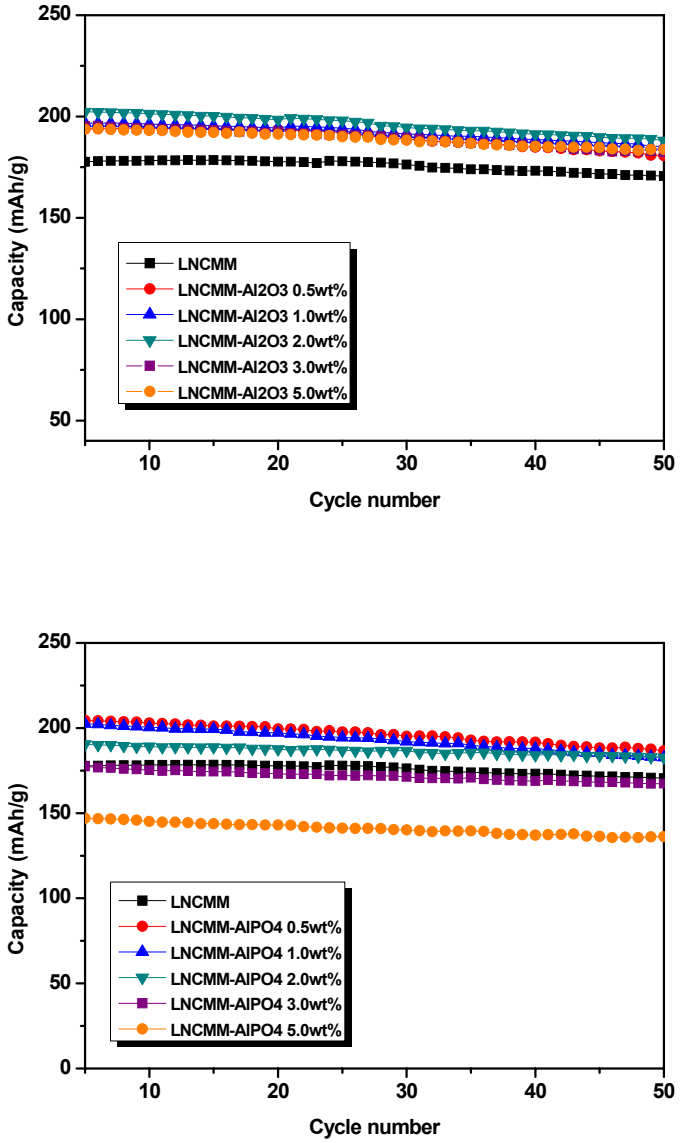
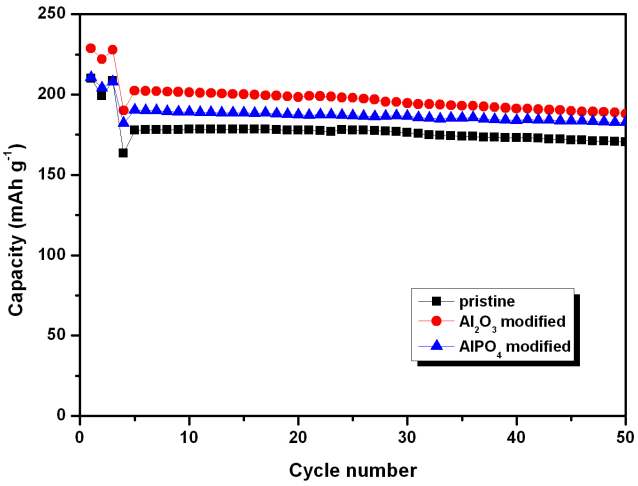
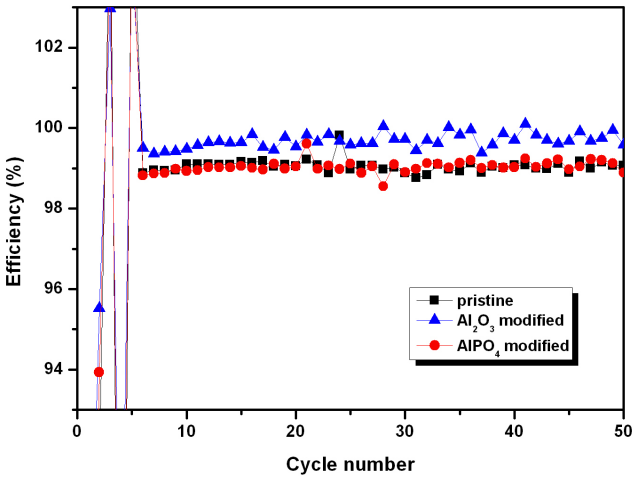


Fig. S2 The charge/discharge cycle properties of the Al_2O_3-/$AlPO_4$-modified LNCMM within the voltage range from 2.0 to 4.55 V vs. Li/Li^+.



(a)



(b)

Fig. S3 Cycle performance and charge-discharge efficiency are compared for the pristine, Al_2O_3 and $AlPO_4$ modified LNCMM during 50 cycles in a voltage range of 2.0 to 4.55 V vs. Li/Li^+ at room temperature; (■) the pristine LNCMM, (▲) the Al_2O_3 (2 wt.%) modified LNCMM, (●) the $AlPO_4$ (2 wt.%) modified LNCMM.

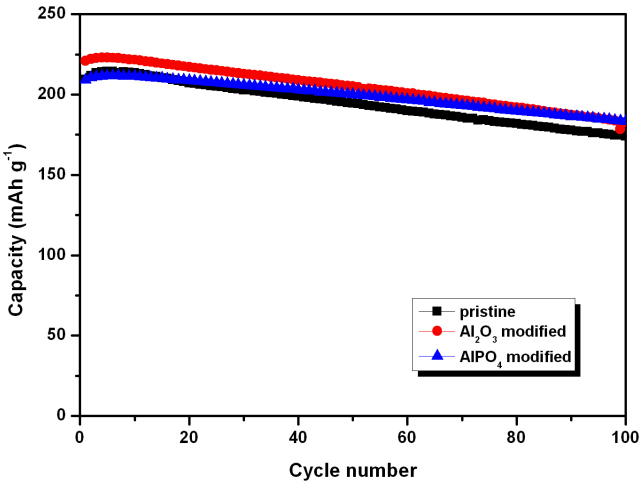
Table. S2 ICP composition analysis data for the Al_2O_3-/$AlPO_4$-modified LNCMM.

Samples	Li	Mn	Co	Ni	Mo	Al	P
LNCMM	8.98	27.90	5.92	14.44	3.60	-	-
Al_2O_3	8.75	27.24	5.80	14.16	3.43	1.06	-
$AlPO_4$	8.59	27.15	5.63	14.03	3.26	0.44	0.97

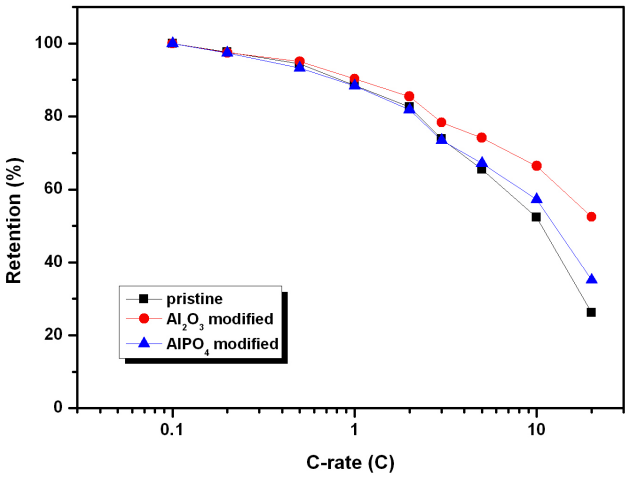
**All concentration values in wt.%*

The electrochemical tests for the pristine, 2 wt.% Al_2O_3- and $AlPO_4$-modified LNCMM were conducted to identify the effects of surface modification on the electrochemical performance. The coating amount was confirmed by ICP composition analysis. (Table S2) For Al_2O_3-modification, $Al(NO_3)_3 \cdot 9H_2O$ was dissolved in organic solvent (ethanol). In the case of $AlPO_4$-modification, $Al(NO_3)_3 \cdot 9H_2O$ and $(NH_4)H_2PO_4$ were dissolved in deionized water, and the pH value of the solution was measured to be *ca*. 3.5. When the LNCMM powders were added into the precursor solution, the pH value increased above neutral, and hence no dissolution of metal ions should occur.

Fig. S3 compares cycle performances and charge-discharge efficiencies of the pristine, Al_2O_3 modified and $AlPO_4$ modified LNCMM at room temperature. As shown in Fig. S2 and S3a, both surface-modified LNCMM cathodes show higher capacity retention compared to that of the pristine LNCMM during 50 cycles in a voltage range of 2.0 to 4.55 V vs. Li/Li^+. In particular, the reversible capacity of Al_2O_3 modified LNCMM can reach about 230 mAh g^{-1} at a current density of 12.5 mA g^{-1}. In addition, the charge-discharge efficiency of LNCMM also can be improved by treating the surface with Al_2O_3 or $AlPO_4$ as illustrated in Fig. S3b. The results reveal that overall electrochemical properties could be effectively improved by the surface modification.



(a)



(b)

Fig. S4 (a) Cycle performance of the pristine, Al_2O_3 and $AlPO_4$ modified LNCMM during 100 cycles at 45 °C. The applied current was fixed at 250 mA g^{-1} in a voltage range of 2.0 to 4.55 V vs. Li/Li^+, (b) Rate capabilities are compared at room temperature for (■) the pristine LNCMM, (▲) the Al_2O_3 (2 wt.%) modified LNCMM, (●) the $AlPO_4$ (2 wt.%) modified LNCMM.

Considering safety and stability issues, the electrochemical performance at high temperature was also examined in this work. Fig. S4a shows cycle performance of the pristine, Al_2O_3 and $AlPO_4$ modified LNCMM during 100 cycles in a voltage range of 2.0 to 4.55 V vs. Li/Li^+ with a current density of 250 mA g^{-1} at 45 °C. Interestingly, we found that surface-modified samples maintain higher reversible capacity during cycling when compared with the pristine cathode. In addition, it should be also noted that rate capability can be improved by the surface modification with Al_2O_3 and $AlPO_4$.

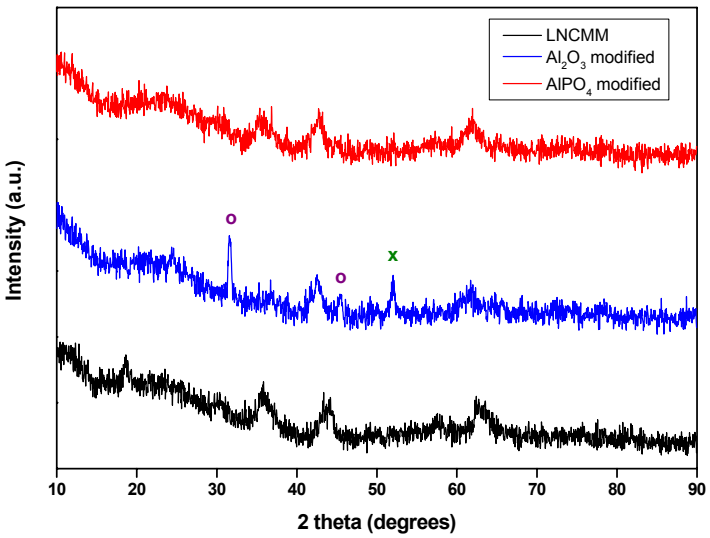


Fig. S5 XRD patterns of the pristine, Al_2O_3 and $AlPO_4$ modified LNCMM after DSC measurement (see Fig. 6).

The diffraction patterns were analyzed with X'Pert HighScore program (version 2.2a). After DSC thermal stability test, the active materials were completely decomposed in all cases. The diffraction peaks were able to be assigned to multiple phases which belong to the cubic symmetry. In the case of Al_2O_3-modified LNCMM, there are two aluminum oxide phases (o: JCPDS 01-075-0278 / x: JCPDS 01-075-0277) after phase decomposition.