Supporting Information

**Influence of Tris(trimethylsilyl)phosphite Additive on the Electrochemical Performance of Lithium-ion Batteries using Thin-film Ni-rich Cathodes**

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**S1. Additional Results and Discussion**

**S1.1. Core-level of Ni 2p, Co 2p, and Mn 2p on the surface of NCM622 thin-film electrodes with BE and with the addition of 1 wt% TMSPi after the 30th cycle.**

According to surface composition analysis of thin-film electrodes after the 30th cycle as shown in Fig. 3d in the manuscript, transition metals, including Ni, Mn, and Co only exhibited fairly little ratio with addition of 1 wt% TMSPi, due to the Li-rich organic artificial layer formation. To further understand the function of artificial layer, details on the core-level of Ni 2p, Co 2p, and Mn 2p are compared in Fig. S6. Based on the fitting results in Fig. S6a, two couples of split peaks of Ni 2p3/2 and Ni 2p1/2 can be identified on both of the electrodes at the 854.8, 872.1 eV (red line) and the 856, 873.5 eV (green line), with a characteristic spin-orbit energy of 17.3 eV (Ni2+) and 17.5 eV (Ni3+) respectively.1,2 Although signals from the artificial layer and the inner lattice structure could contribute to the difference in peak intensity, NCM622 thin-film electrode with an artificial layer showed a relatively higher Ni3+ component than that of the electrode with BE, implying an inhibited tendency of Ni reduction, such as rock-salt (NiO) structure with low Li+ conductivity. The spectra of Co 2p are displayed in Fig. S6b, in which a pair of split peaks at 780.4 eV and 795.4 eV, assigned to a typical binding energy of Co3+ in both of the electrodes.3‒5 However, additional peaks with high binding energy at 782.6 and 797.6 eV were observed with the TMSPi decomposition, which can be referred to the Co2+ formation, for instance Co‒O‒Si as reported by the previous literature.6,7In addition, the Mn 2p spectra are illustrated in Fig. S6c. Thin-film electrode with an artificial layer showed a pair of split peaks at 641.9 eV and 653.5 eV of Mn 2p3/2 and Mn 2p1/2, attributed to the layered NCM structure of Mn4+ with a typical split-orbit energy of 11.6 eV.8 In contrast, the thin-film electrode using pure electrolyte exhibited a shift to high energy at 642.7 eV of Mn 2p3/2, contributed by an additional peak at 643.5 eV, indicating the formation of spinel-like phase due to the structure degradation.9,10

**References**

1. W.Ahn, M. H. Seo, T. K. Pham, Q. H. Nguyen, V. T. Luu, Y. Cho, Y. W. Lee, N. Cho, and S. K. Jeong, *Front. Chem.*, **7**, 361 (2019).
2. S.-J. Sim, S.-H. Lee, B.-S. Jin, and H.-S. Kim, *J. Power Source*, **481**, 229037 (2021).
3. Y. Huang, X. Yao, X. Hu, Q. Han, S. Wang, L.-X. Ding, and H. Wang, *Appl. Surf. Sci.*, **489**, 913‒921 (2019).
4. R. Venkatkarthick, J. Niu, A. Srikhaow, C. Sriprachuabwong, S. Vasudevan, A. Tuantranont, and J. Qin, *ACS Appl. Energy Mater.*, **4**, 6520‒6530 (2021).
5. Z. Chen, X. Gong, H. Zhu, K. Cao, Q. Liu, J. Liu, L. Li, and J. Duan, *Front Chem.*, **6**, 643 (2018).
6. J. Pan, S. Li, F. Li, T. Yu, Y. Liu, L. Zhang, L. Ma, M. Sun, and X. Tian, *Colloids Surf. A: Physicochem. Eng. Asp.*, **609**, 125650 (2021).
7. Y. Zhang, C. Wang, H. Jiang, Q. Wang, J. Zheng, and C. Meng, *Chem. Eng. J.*, **375**, 121938 (2019).
8. L. Wang, L. Li, X. Zhang, F. Wu, and R. Chen, *ACS Appl. Mater. Interfaces*, **10**, 32120‒32127 (2018).
9. T. Kocak, L. Wu, J. Wang, U. Savaci, S. Turan, and X. Zhang, *J. Electroanal. Chem.*, **881**, 114926 (2021).
10. C. Pan, R. Zhang, R.G. Nuzzo, and A.A. Gewirth, *Adv. Energy Mater.*, **8**, 1800589 (2018).

**S2. Additional Figures:**

**Figure S1.** A schematic illustration of a three-electrode cell.



**Figure S2.** Charge-discharge curves of the 10th and 30th cycles of thin-film electrode with BE (dash line) and 1 wt% TMSPi (straight line).



**Figure S3.** Temperature dependences of Nyquist plots at the oxidation potential of NCM622 thin-film electrodes. (a) with BE and (b) with addition of 1 wt% TMSPi. Inset figures show the enlarged parts of the Nyquist plots at high-frequency region.



**Figure S4.** Core-level of Li 1s on the surface of NCM622 thin-film electrodes with BE and with the addition of 1 wt% TMSPi after the 30th cycle.



**Figure S5.** Core-level of (a) P 2p and (b) Si 2p on the surface of NCM622 thin-film electrodes with addition of 1 wt% TMSPi after the 30th cycle.



**Figure S6.** Core-level of (a) Ni 2p, (b) Co 2p, and (b) Mn 2p on the surface of NCM622 thin-film electrodes with BE and with addition of 1 wt% TMSPi after the 30th cycle.