

Supporting information for

**The sensitive surface chemistry of Co-free, Ni-rich layered oxides:  
identifying experimental conditions that influence characterization  
results**

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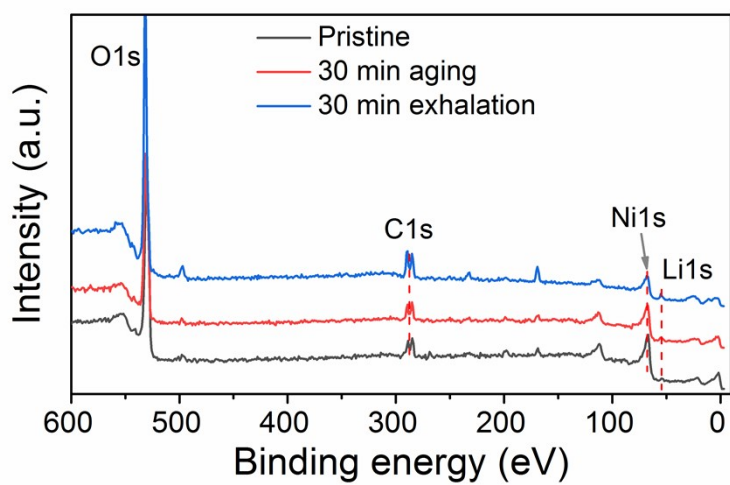
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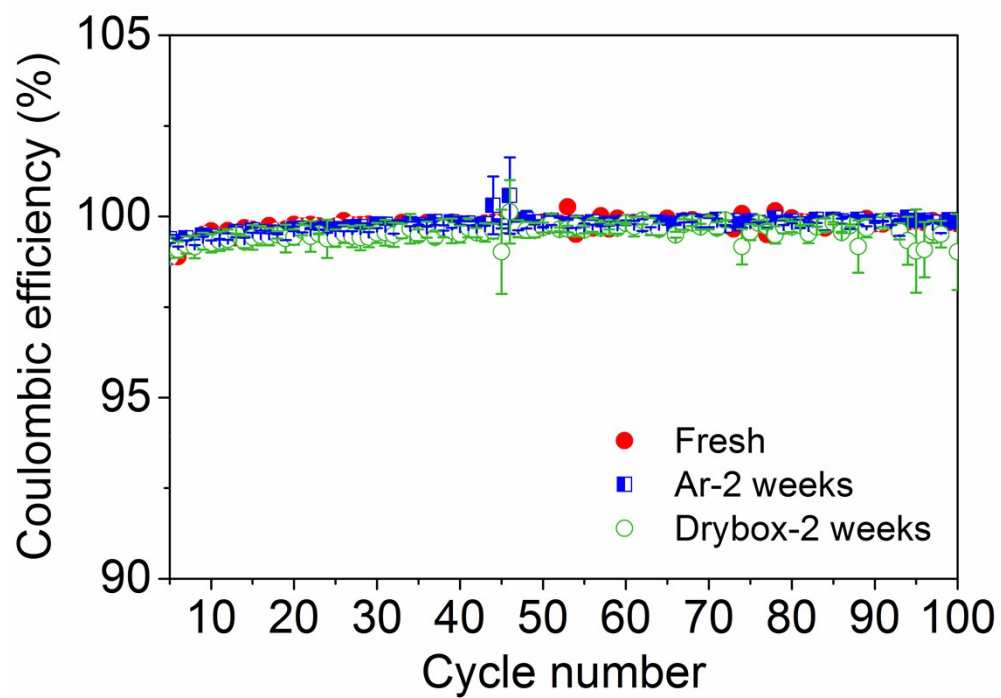
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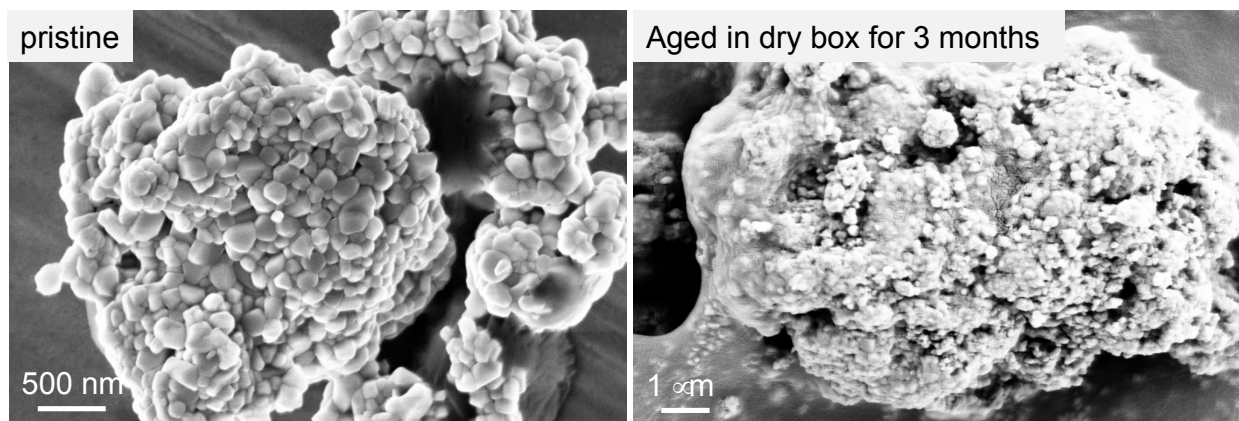
## Supporting Figures



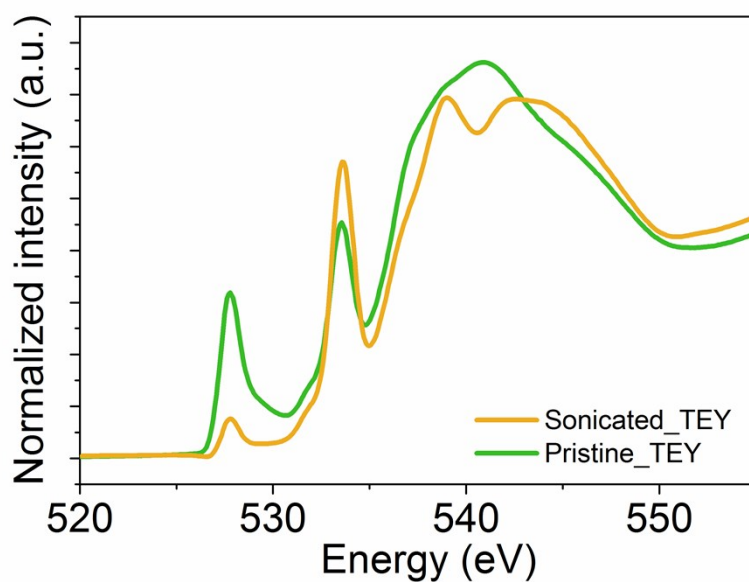
**Figure S1** Survey XPS spectra of the LiNiO<sub>2</sub> samples at different states, i.e., pristine, 30 min aging, and 30 min exhalation.



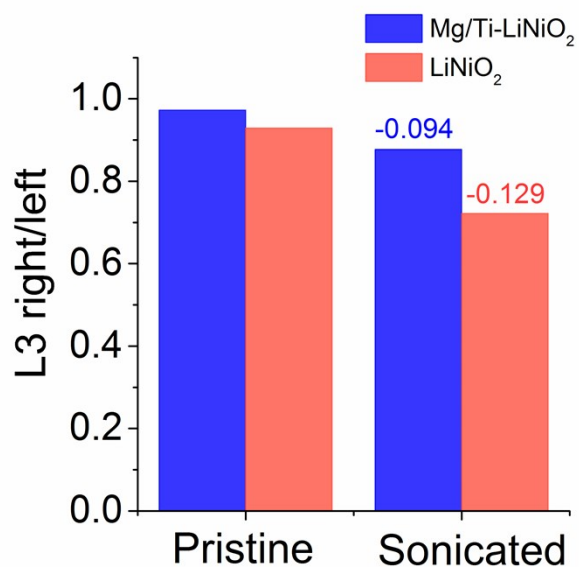
**Figure S2** Coulombic efficiency as a function of the cycle number, where the cells were cycled within 2.5–4.4 V vs Li/Li<sup>+</sup> at C/3 at 22 °C, and the error bars were created based on the standard deviation of three cells.



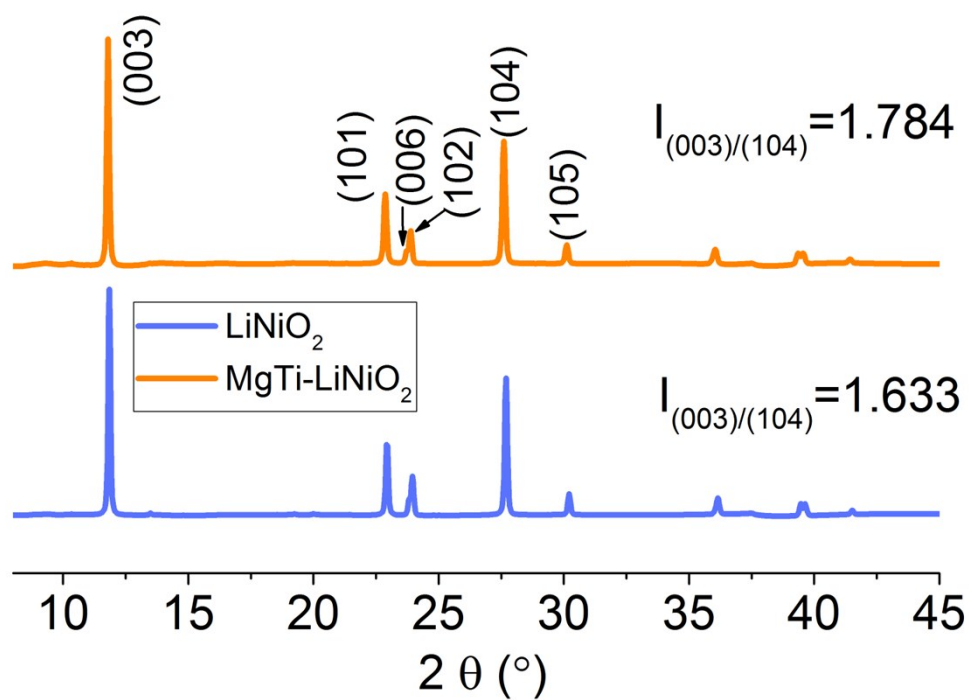
**Figure S3** Morphological evolution of the  $\text{LiNiO}_2$  after storing in the dry box for three months. The aged particles were surrounded by thick lithium residuals (likely  $\text{Li}_2\text{CO}_3$  and  $\text{LiOH}$ ).



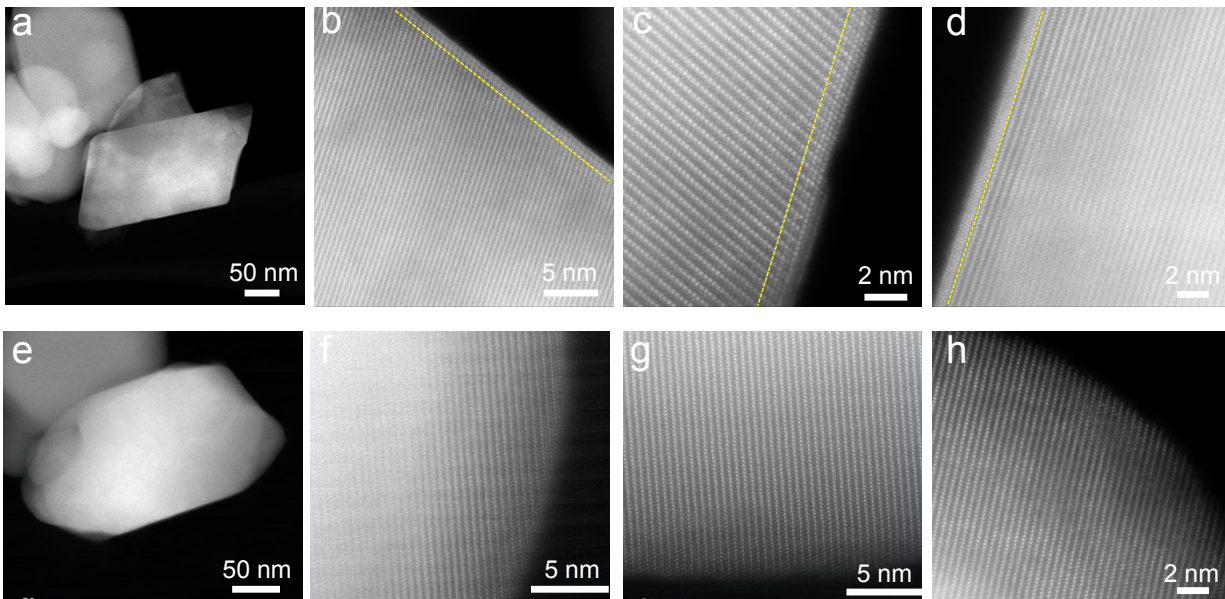
**Figure S4** Soft XAS O K-edge spectra in the TEY mode of the pristine Mg/Ti-LiNiO<sub>2</sub>, and the one sonicated in IPA for 30 min. The increased peak intensity located at ~534 eV, concurrently with the decreased hybridization of Ni<sup>3+</sup>-O peak (~528 eV), suggest the carbonate accumulation after the sample was sonicated in IPA for 30 min.



**Figure S5** Peak ratios of the nickel L3 right/left for the Mg/Ti-LiNiO<sub>2</sub> and LiNiO<sub>2</sub> samples before (pristine) and after sonication. They were derived from the soft XAS Ni L3-edge spectra in the TEY mode in Figure 3i. The values represent the decreased peak ratios from pristine state to after sonicated in IPA for 30 min. The larger decreased value of the LiNiO<sub>2</sub> after sonication indicate more nickel reduction.

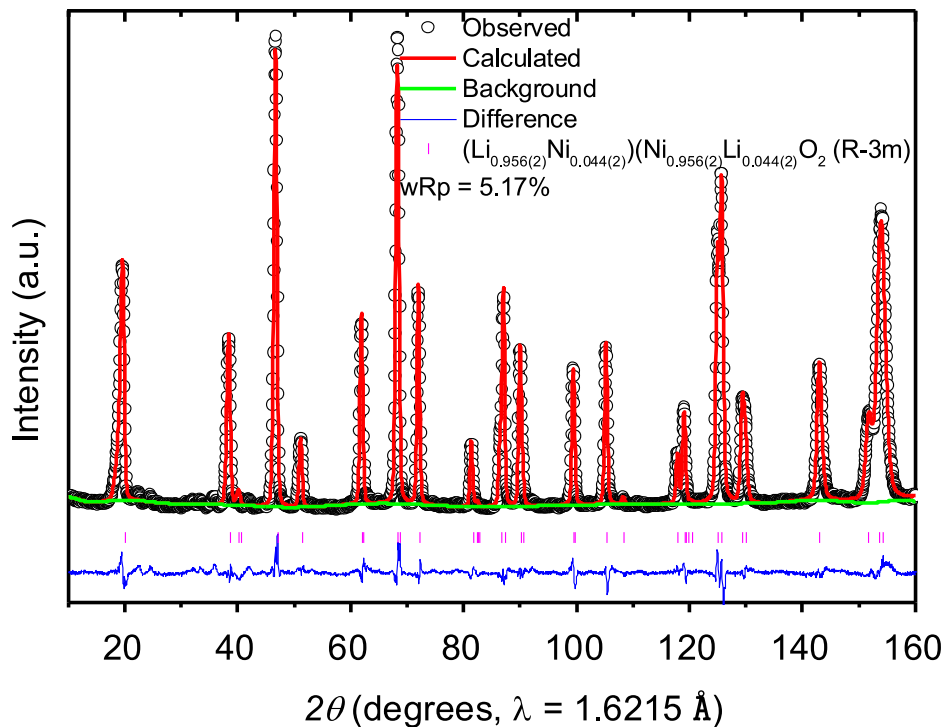


**Figure S6** Comparison of the global structures of the  $\text{LiNiO}_2$  and  $\text{Mg/Ti-LiNiO}_2$ . Synchrotron XRD patterns were collected from SLAC beam line 11-3, the wavelength of the X-ray was 0.976 Å.

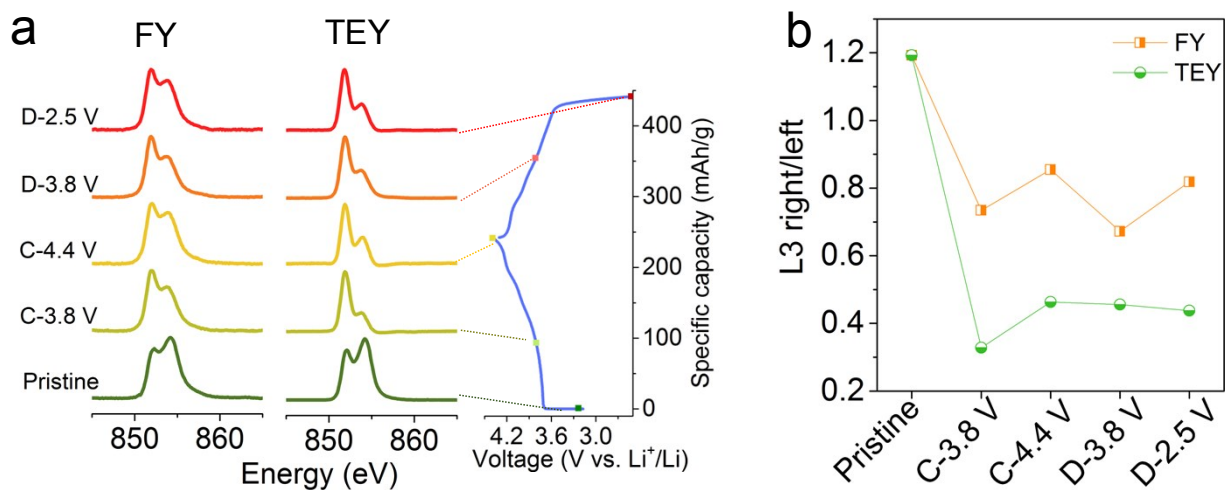


**Figure S7** Representative STEM images of the a-d)  $\text{LiNiO}_2$  and e-h)  $\text{Mg/Ti-LiNiO}_2$  primary particles.

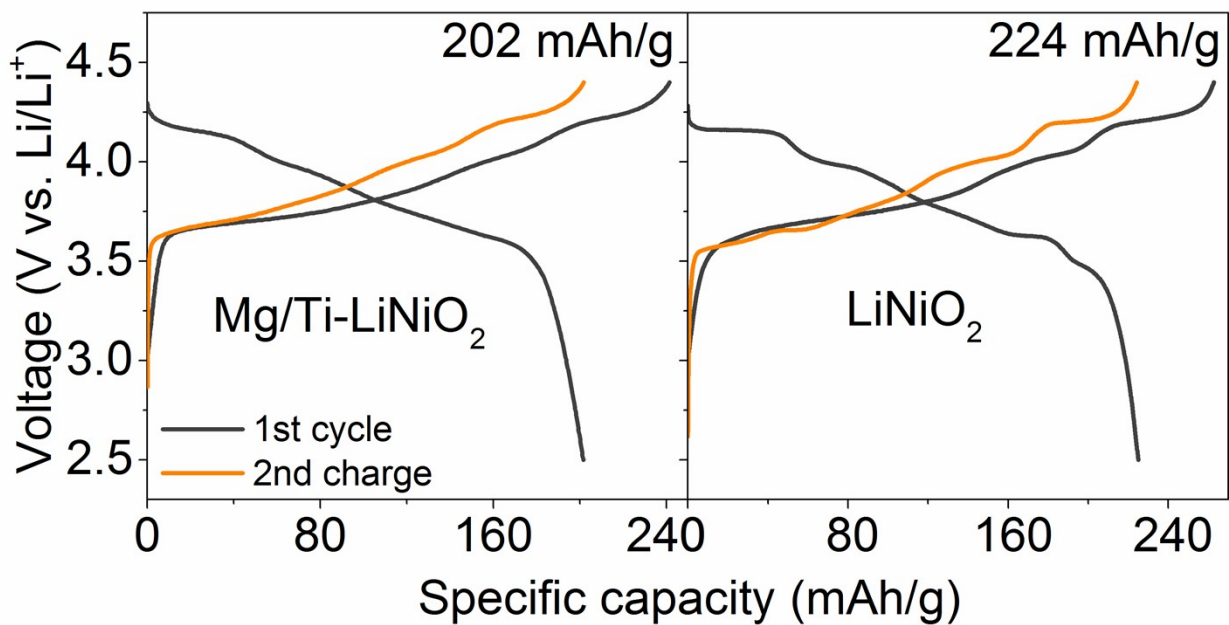




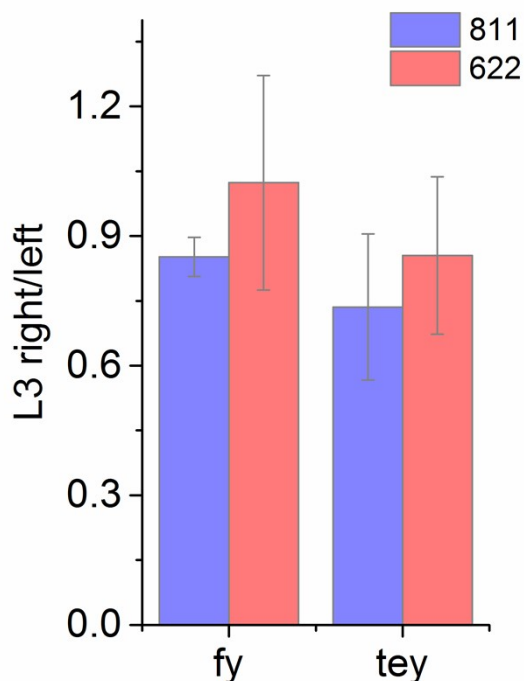
**Figure S8** Neutron diffraction pattern of the  $\text{LiNiO}_2$  powder with the Rietveld Refinement. The ND pattern of the Mg/Ti- $\text{LiNiO}_2$  can be referred to our previous study.<sup>1</sup> The refined structure formula was  $(\text{Li}_{0.962}\text{Ni}_{0.038})(\text{Ni}_{0.922}\text{Li}_{0.038}\text{Mg}_{0.02}\text{Ti}_{0.02})\text{O}_2$  for the Mg/Ti- $\text{LiNiO}_2$ , which has slightly lower cation mixing than  $\text{LiNiO}_2$  ( $(\text{Li}_{0.956}\text{Ni}_{0.044})(\text{Ni}_{0.956}\text{Li}_{0.044})\text{O}_2$ ).



**Figure S9** Surface characteristics of the Mg/Ti-LiNiO<sub>2</sub> at various charge/discharge states in the first cycle. (a) soft XAS Ni L3-edge spectra in the FY and TEY modes; (b) peak ratio of L3 right to left. The C and D represent charge and discharge.



**Figure S10** Charge/discharge profiles of the cells containing the Mg/Ti-LiNiO<sub>2</sub> and LiNiO<sub>2</sub> cathode cycled at C/5 within 2.5–4.4 V at 22 °C. The second charge capacity is labeled in the figure.



**Figure S11** Comparison of the peak ratios of the NMC811 ( $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ ) and NMC622 ( $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ ) electrodes at the charged 4.5 V, where the error bars were presented based on repeated measurements. We found inconsistency in the surface chemistry of other Ni-rich electrodes, including NMC811 and NMC622, upon charging to 4.5 V vs Li/Li<sup>+</sup>. In principle, NMC811 should possess higher Ni oxidation state than the NMC622 electrode. However, increased Ni oxidation states at deep delithiated state promote more surface instability. Due to the inherent surface reconstruction, decreased Ni oxidation states were observed in both TEY and FY modes. The direct comparison between NMC622 and NMC811 shows that a higher nickel content results in more surface instability, which can potentially complicate the state of charge assessment using the surface sensitive soft XAS technique.

1. Mu, L.; Zhang, R.; Kan, W. H.; Zhang, Y.; Li, L.; Kuai, C.; Zydlewski, B.; Rahman, M. M.; Sun, C.-J.; Sainio, S.; Avdeev, M.; Nordlund, D.; Xin, H. L.; Lin, F., Dopant Distribution in Co-Free High-Energy Layered Cathode Materials. *Chemistry of Materials* **2019**, *31* (23), 9769-9776.