Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information for

Unraveling atomic-scale lithiation mechanisms in NiO thin film electrode

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Electrochemical tests

NiO nanoparticles (~100 nm) are purchase in Sigma-Aldrich co, LTD. and used without purification. Electrochemical tests were performed on CR2025 type coin cell assembled in a glove box full-filled with pure Ar gas. In the coin cell, lithium metal is used as counter electrode, Celgrad 2400 polymer film is used as separator, and 1 M $LiPF_6$ in EC-DMC (1:1 w/w) is served as electrolyte. As working electrode, NiO nanoparticle, acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1 were mixed into N-methyl-2-pyyrolidone (NMP) to form a slurry uniformly. Then, the slurry was coated on Cu foil evenly and then dried at 110 °C for 24 h in vacuum oven. After it is cool down to the room temperature, it was cut into a circular wafer with a diameter of 12 mm. Galvanostatic charge/discharge measurements were collected by using a battery testing system (LANHE CT2001A, P. R. China) in the potential range of 0.005-3.0 V. Cyclic voltammogram (CV) test were performed on an electrochemical workstation (Biologic EC-Lab SP-200) with a scan rate of 0.1mV/s in the potential range of 0.005 to 3 V.

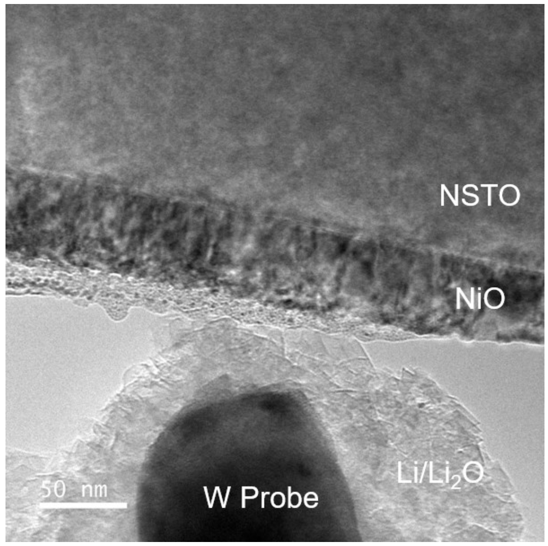

Figure S1. TEM image of the nanosized electrochemical cell configuration used in this study, consisting of a NiO thin-film working electrode, a metal Li counter electrode on a tungsten probe, and a solid electrolyte of Li_2O layer naturally grown on the surface of metal Li.

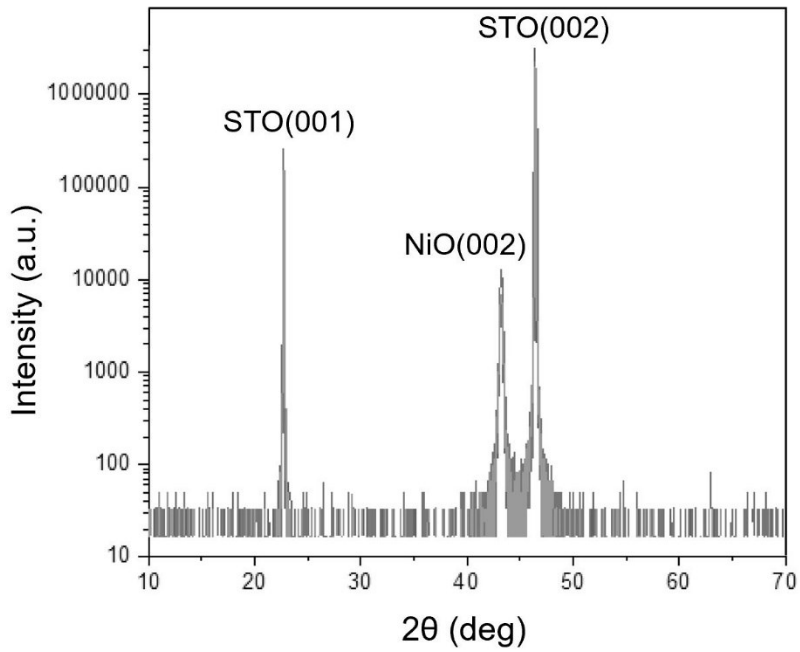

Figure S2. XRD results of NiO thin film grown on NSTO substrate.

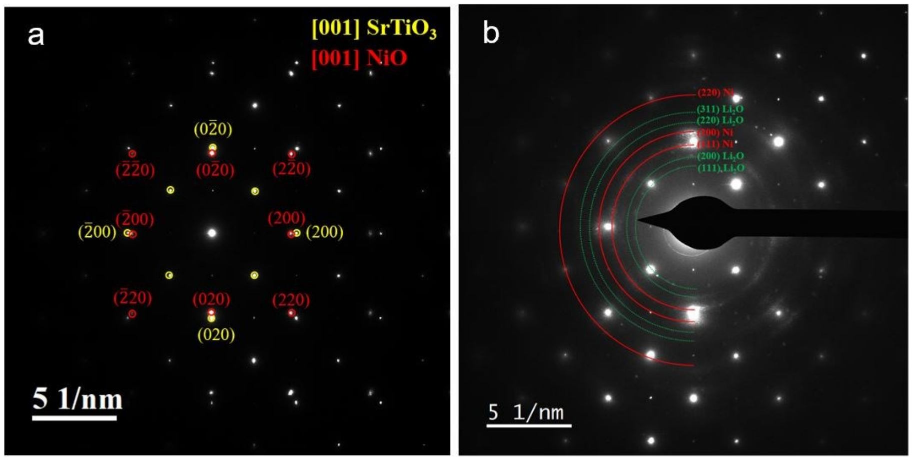

Figure S3. SAED patterns before and after lithiation of NiO thin film electrodes.

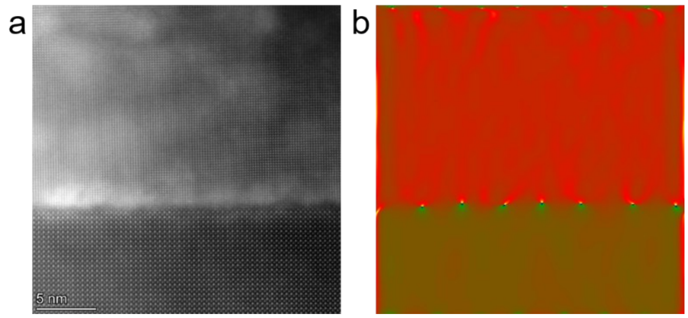

Figure S4. The periodic dislocations at the NiO/NSTO interface originate from lattice mismatch. (a) Cross-sectional HAADF-STEM image of pristine NiO thin film grown on NSTO substrate, viewing along [100]. (b) The corresponding geometric phase analysis (GPA) shows the periodic dislocations at the interface.

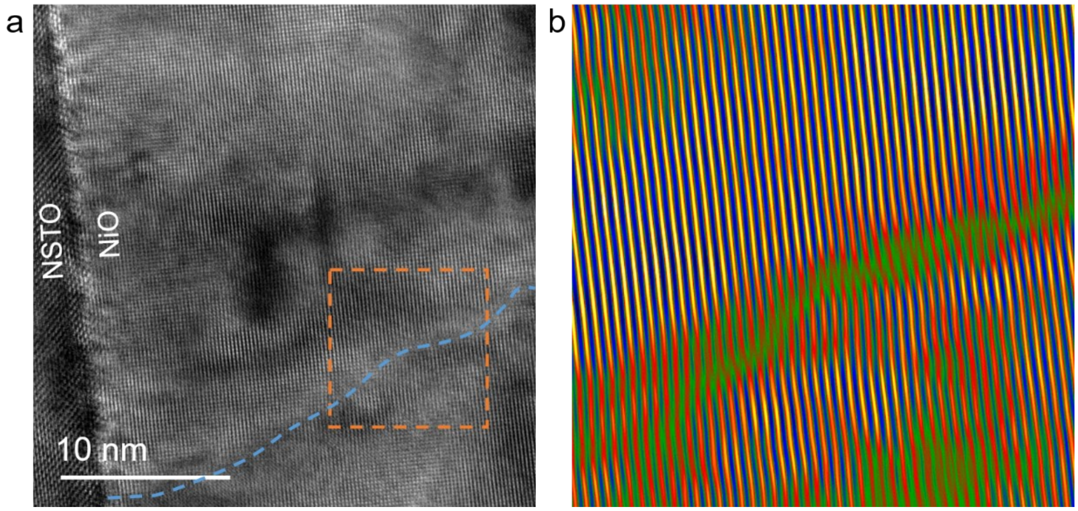

Figure S5. (a) High-resolution TEM image of a grain boundary marked by blue dashed line. (b) The corresponding FFT filtered image of the selected region marked by orange square in (a).

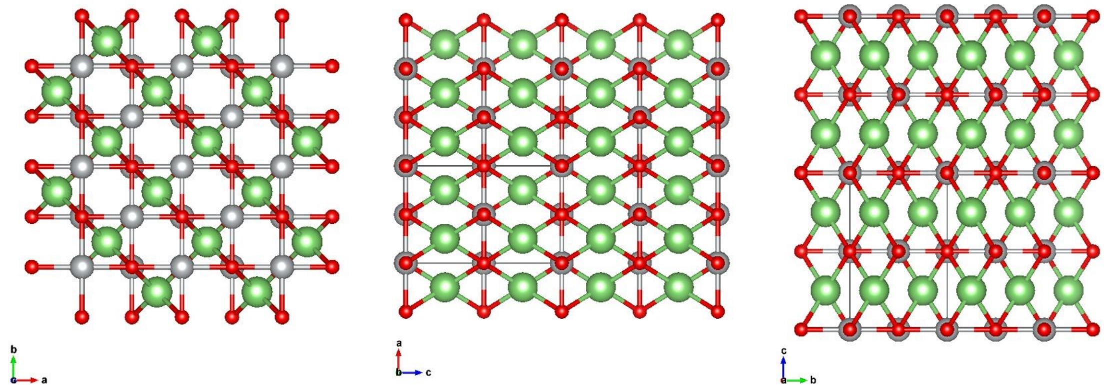

Figure S6. DFT calculated atomic model viewed along different directions.

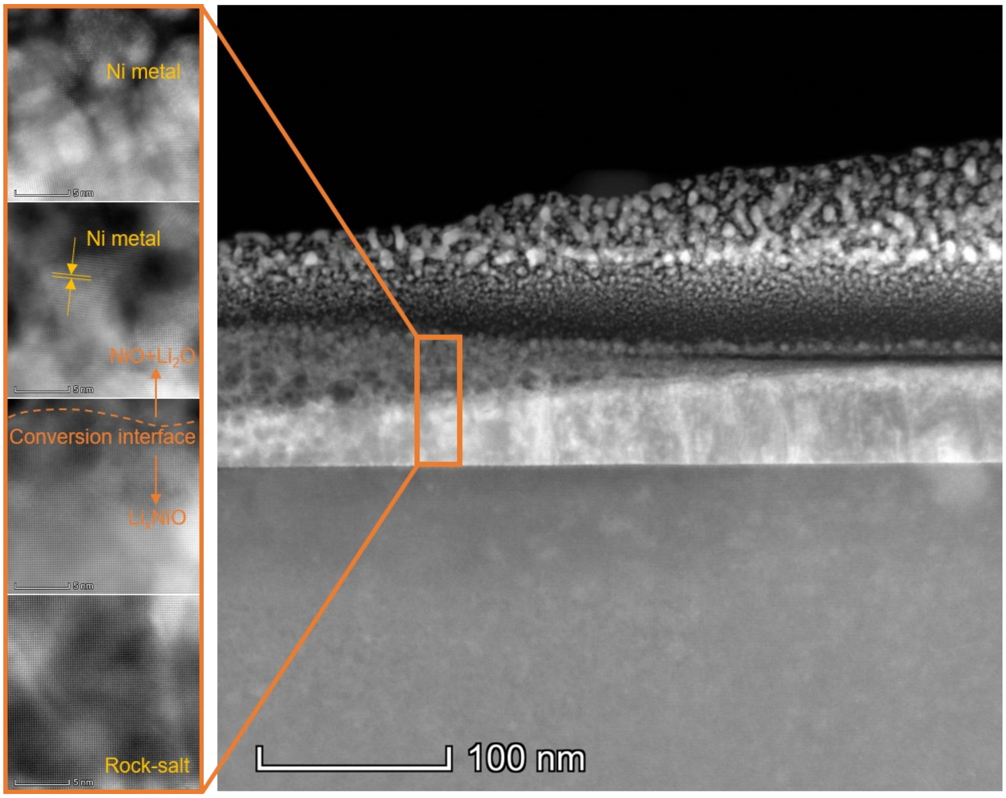

Figure S7. HAADF-STEM images showing the rock-salt crystal structure maintained in the transition valence region. The conversion interface is marked by orange dashed line in the left enlarged high-resolution HAADF-STEM image.

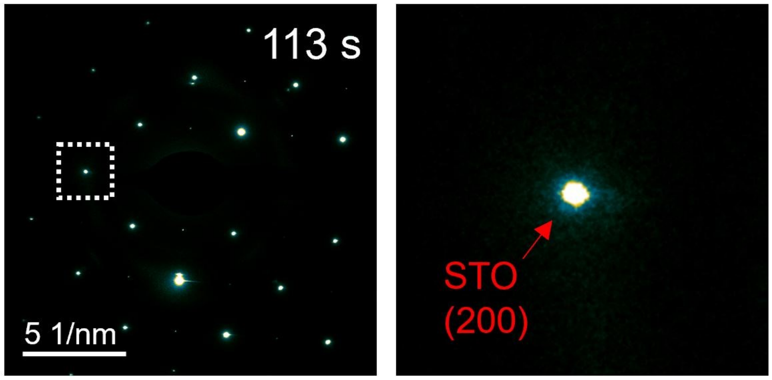

Figure S8. Time sequence of electron diffraction patterns captured from Movie S2. At 113s, the spot of NiO (200) completely disappeared.

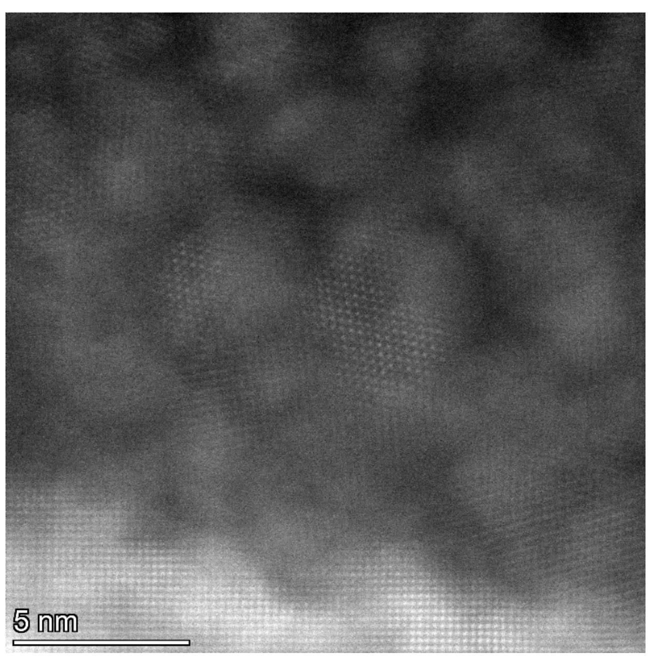

Figure S9. The corresponding raw HAADF-STEM image of Fig. 5g, showing the atomic structure of the reaction interface.

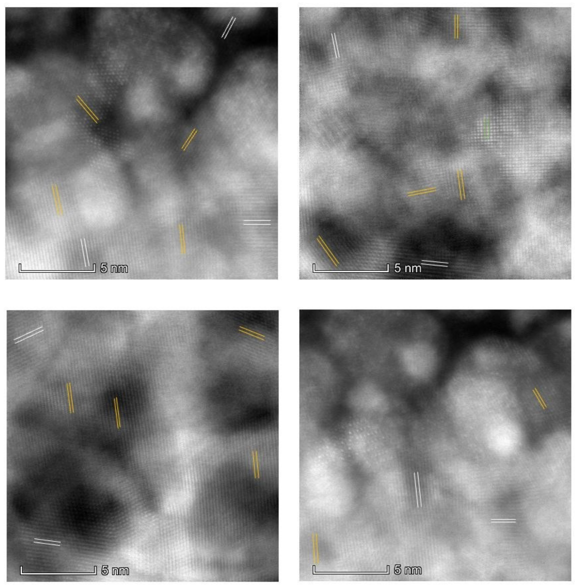

Figure S10. Atomic resolution HAADF-STEM images of conversion regions. Ni (111) lattices marked by yellow double lines. Li_2O lattices marked by white double lines.

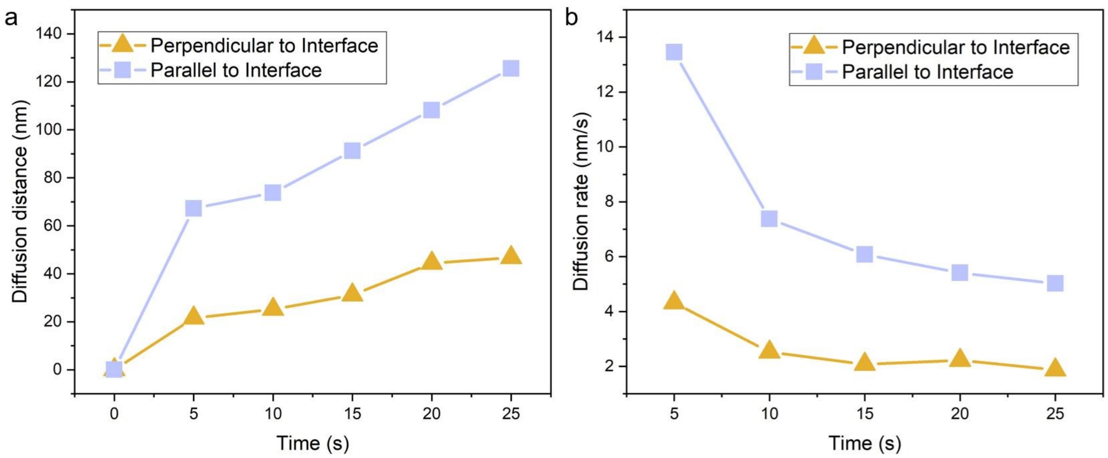

Figure S11. Plot of diffusion distance (a) and diffusion rate (b) in two directions showing in Fig. 2a.

Movie S1 (Corresponding to Fig. 1f-h) *In situ* observation of the lithiation process of NiO thin film with a grain boundary.

Movie S2 (Corresponding to Fig. 5 a-f) *In situ* electron diffraction patterns showing the phase transition of NiO thin film during lithiation process.

Movie S3 (Corresponding to Fig. 6a) *In situ* observation of the lithiation process when the Li tip contact the top surface of thin film.

Movie S4 (Corresponding to Fig. 6c) *In situ* observation of the lithiation process when the Li tip contact the side of NiO thin film. The video is 5 times fast as actual time.

Movie S5 *In situ* observation of the electron beam irradiation on NiO thin film. The electron beam has no effect on the phase transition during lithiation process of NiO thin film.