High-temperature characterization of oxygen-deficient K_2NiF_4-type $Nd_{2-x}Sr_xNiO_{4-\delta}$ (x = 1.0-1.6) for potential SOFC/SOEC applications

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Electronic supplementary information

S1. *Oxygen nonstoichiometry: kinetics of equilibration under oxidizing conditions*

All studied $Nd_{2-x}Sr_xNiO_{4-\delta}$ ceramics demonstrated very fast re-equilibration with a gas atmosphere on temperature cycling under oxidizing conditions (air and oxygen); several examples are illustrated in Fig.S1. Changing the temperature in a step-wise manner at 700-950°C resulted in an instant re-equilibration of the samples with a negligible weight drift during the iso-thermal steps (Fig.S1A). As a result, the difference between δ values obtained in dynamic mode (constant-rate cooling) and equilibrium values in this temperature range was less than 0.002 (Fig.S1B) which is comparable with the reproducibility error. Excellent reproducibility of oxygen nonstoichiometry values was also observed for powdered samples on temperature cycling with different rates as well as for sintered ceramics (Fig.S1C). No hysteresis was observed in heating/cooling cycles.

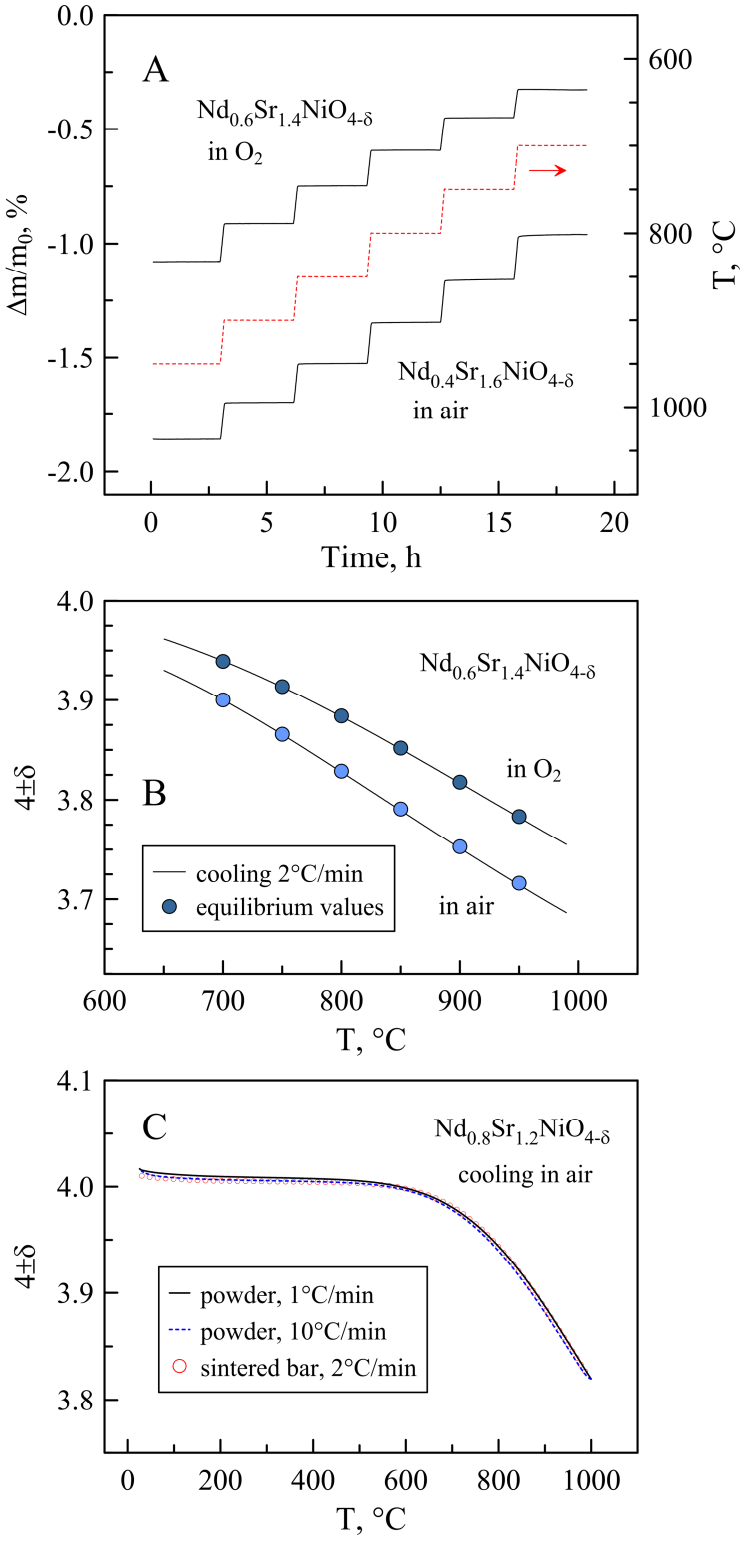

Figure S1. Illustration of equilibration kinetics under oxidizing conditions: (A) relative weight change on stepwise temperature cycling at 750-950°C; (B) comparison of oxygen nonstoichiometry values determined on constant-rate cooling with equilibrium values; (C) comparison of oxygen nonstoichiometric values obtained for powdered and bar-shaped ceramic samples at different cooling rates.

S2. *Oxygen nonstoichiometry: kinetics of equilibration under inert atmosphere*

Contrary to oxidizing conditions, $Nd_{2-x}Sr_xNiO_{4-\delta}$ samples demonstrated quite slow kinetics of equilibration in inert gas atmosphere (Fig.S2). At 700-950°C, 3-hours isothermal steps were far from enough for re-equilibration with the gas phase after temperature change. While on cooling such behavior can partly be explained by low concentration of oxygen in the gas flow, slow equilibration on heating implies that in fact this is associated with slow structural changes and that oxygen vacancy ordering is probably accompanied with ordering in cation sublattice as well.

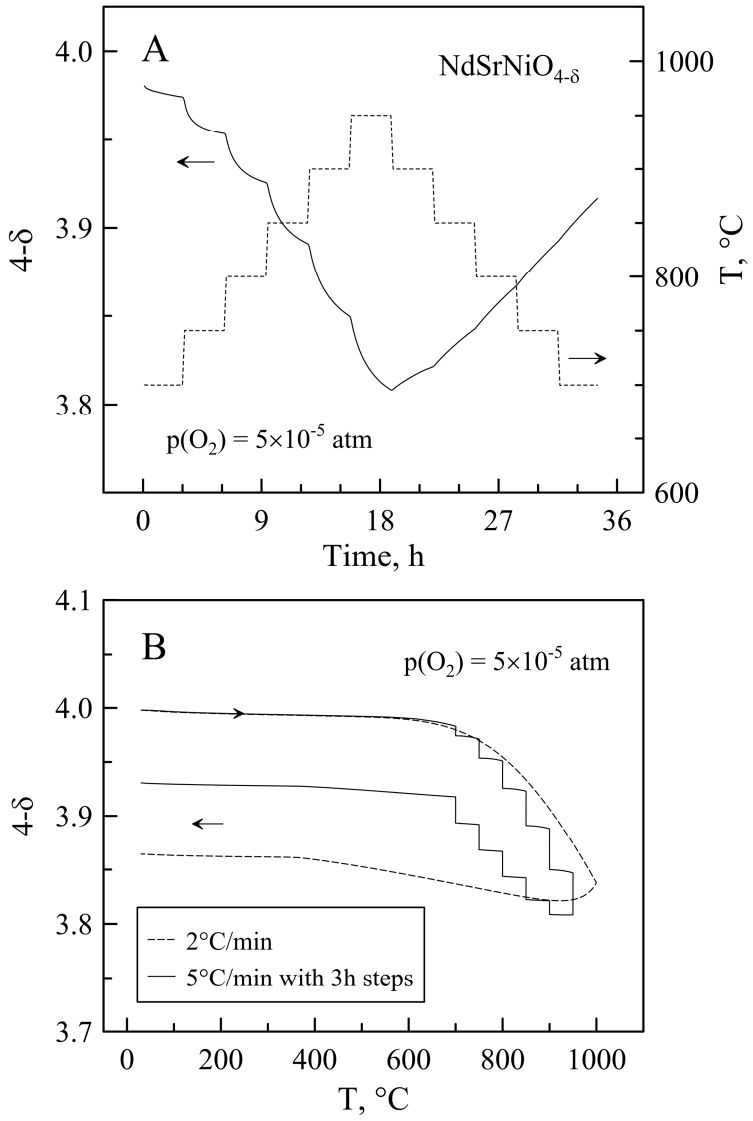

Figure S2. Kinetics of equilibration of $NdSrNiO_{4-\delta}$ ceramics under inert atmosphere: (A) changes of oxygen nonstoichiometry on stepwise temperature cycling at 700-950°C; (B) comparison of oxygen nonstoichiometry changes determined at constant-rate heating/cooling and on cycling with 3-hours equilibration steps at 700-950°C.

S3. *Thermal expansion: dimensional relaxation*

Dilatometric studies with isothermal equilibration steps at 700-950°C demonstrated that, even though ceramic samples show some minor dimensional relaxation during isothermal treatments, these changes are negligible, and the overall shape of dilatometric curves and thermal hysteresis are maintained.

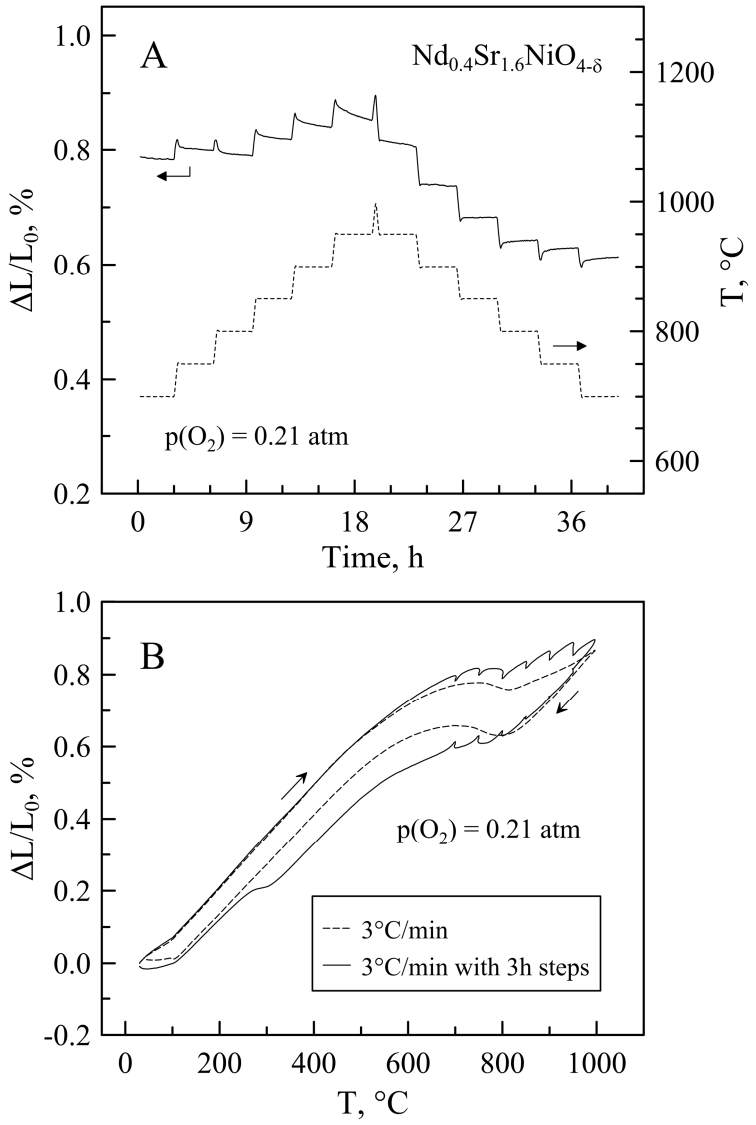

Figure S3. Dilatometric data for $Nd_{0.4}Sr_{1.6}NiO_{4-\delta}$ ceramics in air: (A) relaxation of sample length on stepwise temperature cycling at 700-1000°C; (B) comparison on dilatometric curves recorded on constant-rate heating/cooling and on temperature cycling with 3-hours isothermal steps at 700-950°C.