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SO 26 : Mixed La/Pr n = 3 Ruddlesden-Popper nickelates as stable and efficient oxygen electrodes for high temperature water electrolysis

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Due to their high ionic and electronic conductivities as well as electrocatalytic activity, $Ln_{n+1}Ni_nO_{3n+1\pm\delta}$ phases with Ruddlesden-Popper (RP) structure type ($n = 3$) are considered as oxygen electrode materials of substantial interest for SOFC & SOEC applications.¹ Such RP layered compounds present n - $LnNiO_3$ perovskite layers for one LnO rock-salt layer. The electronic conductivity, which is p-type, is ensured by the perovskite NiO_6 octahedra, while the anionic diffusion mainly takes place through oxygen interstitial sites in the rock-salt structure. Thus, the perovskite layers increasing with the n -value, the $n=3$ members present the highest electronic conductivity among the RP members. However, the lower rock-salt content leads to a decrease of ionic conductivity.¹⁻⁴

In the past, low- n RP materials have shown very promising properties. On one hand, $La_2NiO_{4+\delta}$ has shown a tremendous stability over time but a rather high polarization resistance at working temperatures^{5, 6}. On the other hand, $Pr_2NiO_{4+\delta}$ has demonstrated highly promising R_p values, but a crippling stability, decomposing into $Pr_4Ni_3O_{10+\delta}$, PrO_x and, NiO in a few weeks upon heating. Notwithstanding, after ageing, no increase of polarization resistance was observed⁷⁻¹⁰. Thus, two alternatives appear. First, to formulate mixed $\frac{3}{4}$ La, $\frac{1}{4}$ Pr oxides was brought as a solution to boost $La_2NiO_{4+\delta}$ performances, keeping a good stability. And second, to study the $n=3$ oxide: $Pr_4Ni_3O_{10+\delta}$ which shows impressive electrochemical performances in the SOFC mode while staying stable for long times.^{11, 12} However, the behavior of these materials concerning the area specific resistance and cell performances under SOEC conditions remains to be thoroughly investigated.

To this aim, in this study we focused on the $n=3$ RP $Ln_4Ni_3O_{10+\delta}$ ($Ln = La, Pr$) as well as the mixed La and Pr compounds with fixed La/Pr ratio of 3/1 and varying n : $La_{0.75(n+1)}Pr_{0.25(n+1)}Ni_nO_{3n+1}$ ($n=1$ and, 2). This is a preliminary investigation for SOEC alternative oxygen electrodes materials. The compounds were synthesized through the nitrate-citrate route, their structure and oxygen stoichiometry was characterized through Rietveld refinement and TGA analysis. Oxygen surface exchange coefficients on the powder samples was measured through the Pulsed Isotopic Exchange experiment, which confirms that these materials show fast kinetics compared to the state of the art LSCF material. Ionic and electronic conductivities as well as the polarization resistance at OCV are currently under investigation. This study paves the way for further investigation of high n member and mixed La/Pr rare earth nickelates as oxygen electrode in SOEC cells.

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