

REVERSIBLE WATER UPTAKE AND RELEASE OF PSEUDO-CUBIC TYPE $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ AT INTERMEDIATE TEMPERATURES

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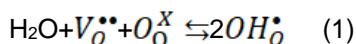
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Solid oxide fuel cells (SOFCs) based on oxide-ion conducting electrolytes possess several attractive advantages such as high energy conversion, low pollutant emission and fuel flexibility. However, SOFCs suffer from the high operating temperatures 800-1000 °C; such high temperature operations result in the increase of costs and lessened lifetimes of materials. Hence, there exists a strong demand to decrease the working temperature into intermediate temperature (IT) region below 600 °C. Proton conducting ceramic fuel cells (PCFCs) is a kind of promising IT-fuel cells operating at around 400-600 °C because of lower activation energies of proton conductivity than oxide-ion conductivity. Recently Choi et al [1] reported that PCFC with $\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3$ electrolyte exceeds 500 mW cm^{-2} at 500 °C, however, the performance still lags far behind the predicted values that is over 1.0 W cm^{-2} at 500°C. There are two major challenges, one is big ohm resistance of Zr-rich Ba(Zr, Ce, Y) O_3 (BZCY) electrolyte, and the other one is lack of highly efficient cathode specially designed for PCFCs [2]. Since most of the cobaltite base cathodes are oxide-ion conductors, the mismatch of main ionic carriers between cathode and electrolytes limits the efficient cathodic reaction area into cathode-electrolyte-gas triple boundaries. Hence, it is motivated to develop cathode catalysts which exhibit sufficient proton conductivity in order to extend the efficient reaction zone and thus reduce cathode overpotentials and finally increase reaction efficiency. The protonic defects are incorporated into oxides via hydration reaction, whereas, many oxides do not have enough large hydration enthalpy [3-5] and thus, the reaction is less-pronounced at elevated temperatures.

In this study, we report on the hydration behavior of cubic-perovskite-type $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ (LSMN, $x=0.0, 0.1$ and 0.3) in the intermediate temperature region. XRD patterns show that LSMN calcined at 800 °C (LSMN@800) is cubic (C) perovskite-type phase, while LSMN calcined at 1000 °C (LSMN@1000) is Rhombohedral (R) phase. Figure 1 (a) shows TG curves of C-type LSMN10 ($x=0$) at 415 °C with switching repeatedly between dry and wet Ar, indicating the mass abruptly increases by exposed to wet Ar while, conversely, the mass intermediately decreases with introducing dry Ar. These results confirm that C-type LSMN10 are capable of reversible H_2O uptake/intake at the temperatures by the following defect reaction.



The amount of proton defects for LSMN10 can be calculated to be $[\text{OH}]/[\text{LSMN}] \sim 0.12$. Meanwhile, R-type LSMN10@1000 does not exhibit reversible mass changes at the temperature shown in Figure 1 (b), indicating that this does not cause the hydration. Now more detail structural and compositional analysis has been carried out.

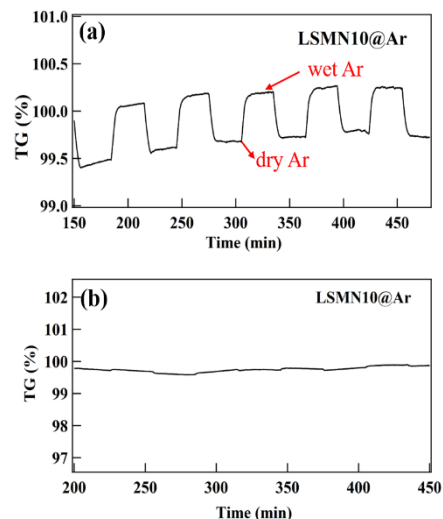


Figure 1 – Mass change of (a) PC-type LSMN and (b) R-type LSMN under dry and wet Ar at 415 °C

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