Supplementary information

Noteworthy performance of $La_{1-x}Ca_xMnO_3$ perovskite oxides in generating H_2 and CO by the thermochemical splitting of H_2O and CO_2

Sunita Dey, B. S. Naidu, A. Govindaraj, C. N. R. Rao *
*E-mail: cnrrao@jncasr.ac.in

Experimental Section:

All LCM compounds were prepared by solid state reactions of stoichiometric amounts of La_2O_3, $CaCO_3$ and MnO_2. La_2O_3 was heated at 950°C for 12 hrs before weighing. Weighted precursors were mixed and ground well and the powders taken in a alumina crucible and fired at 1000°C for 2 hrs and 1450°C for 8hr. Intermediate grinding was carried out after every 4 hrs. For LSM compounds, $SrCO_3$ was used as a precursor instead of $CaCO_3$, keeping all the other reaction procedures same. LSM 35 ($La_{0.65}$ $Sr_{0.35}MnO_3$) and CeO_2 of commercial grade were purchased from Sigma-Aldrich. SmSM 50 ($Sm_{0.50}$ $Sr_{0.50}MnO_3$) was prepared by the same solid state reaction procedures using stoichiometric amounts of Sm_2O_3, $SrCO_3$ and MnO_2. Sm_2O_3 was also preheated like La_2O_3 before weighing. $La_{1-x}MnO_3$ (x=0.1, 0.2) and $La_{1-x}Fe_xO_3$ (x=0.3) was prepared by modified Pechini method. Stoichiometric amounts of nitrate precursors, $M^x(NO_3)_x.yH_2O$ were dissolved in water in the presence of excess citric acid and ethylene glycol. The gel was formed at 80°C, followed by drying at 200°C for 12 hrs. The product was heated at 800°C and 1200°C for 6 hrs each. Phase identification was performed by PXRD analysis with a Bruker D8 Advance diffractometer using Cu Kα radiation. The X-ray diffraction measurements were made in the range of 20-80°. Lebail fitting was carried out using Fullprof software in order to obtain the cell parameters of LCM 50, LSM 50, SmSM 50. FEI Nova Nanosem 600 was used to record the FESEM images and for Energy Dispersive X-Ray analysis (EDAX). X-ray photoelectron spectroscopy (XPS) was recorded with an Omicron nanotechnology spectrometer using Mg Kα (1253.6 eV) x-ray source.

Reactivity Tests:

Thermal reduction and CO_2 splitting experiments were carried out by thermo gravimetric analysis (TGA) using a Perkin-Elmer Pyris1 instrument. About 100 mg sample was introduced in a platinum crucible and placed inside the furnace chamber. The sample was heated to 1400°C with a heating rate of 20°C/min and maintained for 45 mins under continuous Ar (99.9999% grade) flow of 40 sccm. After cooling down to 1100°C, 40 % CO_2 mixed with Ar was injected to carry out the CO_2 splitting test. Total amount of O_2 evolved and CO produced was registered by calculating the change in mass. The water splitting activity of LSM 50 and LCM 50 was investigated using the experimental set up shown in Fig. 4. A known mass of the sample was kept in an alumina crucible and placed inside a tubular furnace. The sample temperature was ramped upto 1400 °C (rate

10°C/min) and maintained for 100 min under an inert atmosphere for complete reduction. The detection and measurement of O_2 released were carried out by a Gas chromatograph (PerkinElmer Clarus ARNEL 580) equipped with a TCD detector. For the H_2 generation step, the furnace was cooled down to 1000°C and steam injected along with a continuous flow of inert gas. The sample was maintained at 1000°C for 100 min for complete oxidation. Numerical integration of molar flow rate-time curves gives the total amount of O_2 evolved whereas total amount of H_2 was calculated by water displacement method.

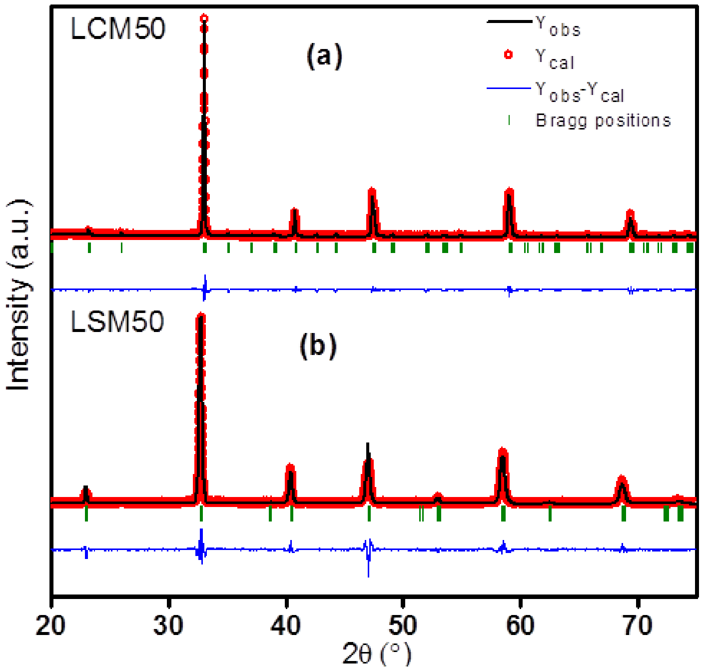

Fig. S1 XRD patterns of (a) $La_{0.5}Ca_{0.5}MnO_3$ (LCM 50) and (b) $La_{0.5}Sr_{0.5}MnO_3$ (LSM 50). The cell parameters obtained by fitting the Powder XRD patterns of LCM50 (space group Pnma) and LSM50 (space group R-3c) are a= 5.4228(2) Å, c= 7.6424(3) Å and a= 5.4683(3) Å, c= 13.3773 (9) Å respectively.

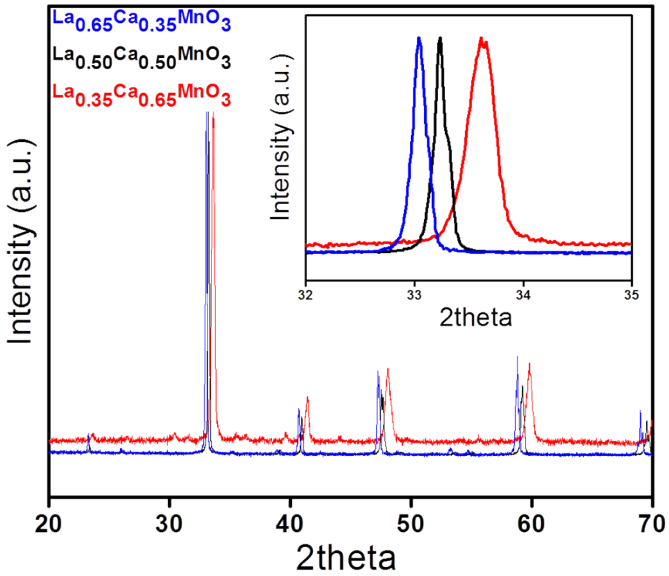

Fig. S2 Powder XRD of $La_{1-x}Ca_xMnO_3$ (x= 0.35, 0.5, 0.65) perovskites phases. Inset highlights magnified view of the (200) reflections.

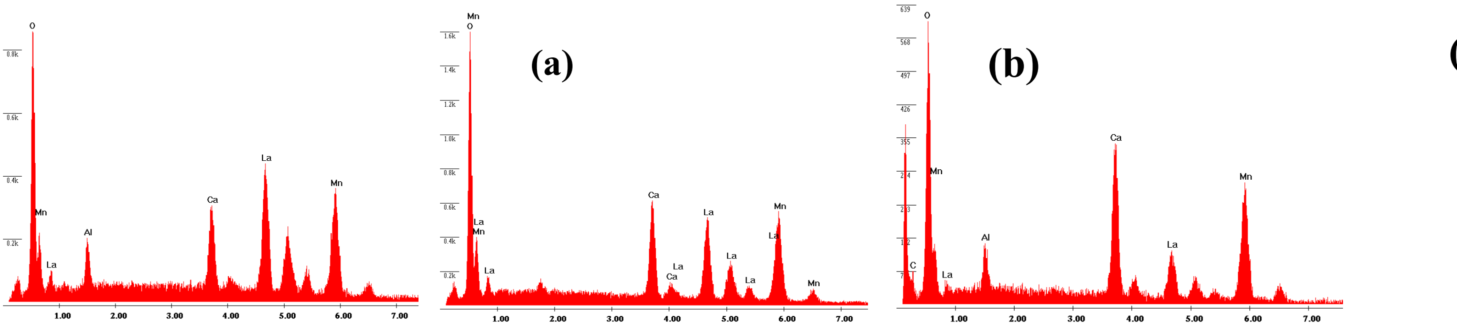

Fig. S3 EDS (X and Y axis are Energy in KeV and counts respectively) of (a) LCM 35, (b) LCM 50 and (c) LCM 65

Table S1. Atomic % of La, Ca and Mn present in LCMs as calculated from EDS analysis.

	LCM 35	LCM 50	LCM 65
Element	Atomic %	Atomic %	Atomic %
O K	52.06	58.44	57.89
Ca K	8.25	9.97	13.63
La L	17.02	11.76	5.86
Mn K	22.66	19.84	22.62

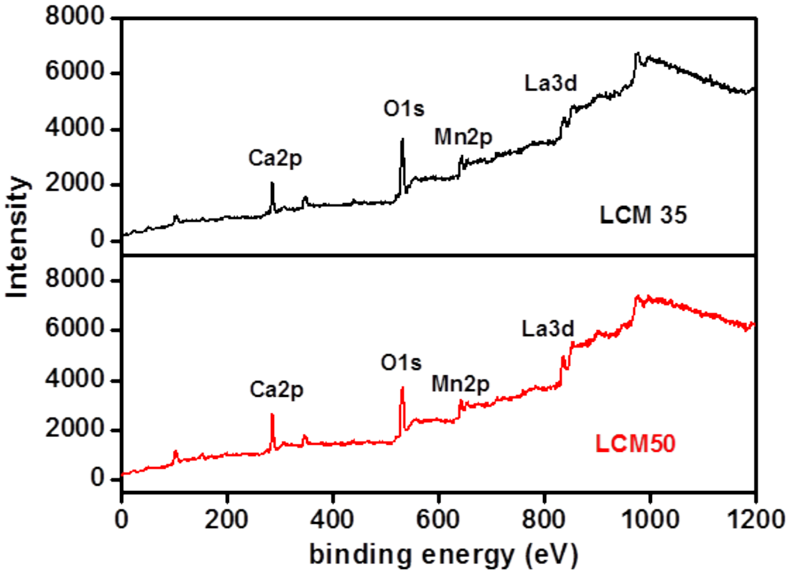

Fig. S4 X- Ray photoelectron survey spectra of LCMs

The intensity ratio of La, Ca and Mn was calculated as,

$$R1,2 = \frac{I1/A1}{I2/A2} \quad \text{..........................} \quad (3)$$

Where I is the intensity obtained from the XPS spectrum after background correction and A is the atomic sensitivity factors.

Table S2. The cation ratio of La, Ca and Mn in LCMs as calculated from XPS survey scan.

	I_{La}/A_{La}	I_{Ca}/A_{Ca}	I_{Mn}/A_{Mn}	$R_{La/Ca/Mn}$
LCM 35	448	255	680	0.66/0.37/1
LCM 50	407	409	815	0.5/0.5/1

Table S3 Quantity of O_2 released and CO produced during three consecutive thermochemical cycles of LCM 50.

Cycle No.	Reduction temperature (°C)	O_2 produced (μmol/g)	CO_2 splitting temperature (°C)	CO produced (μmol/g)
Cycle 1	1400	309	1100	631
Cycle 2	1400	300	1100	600
Cycle 3	**1350**	**237**	**1000**	**481**

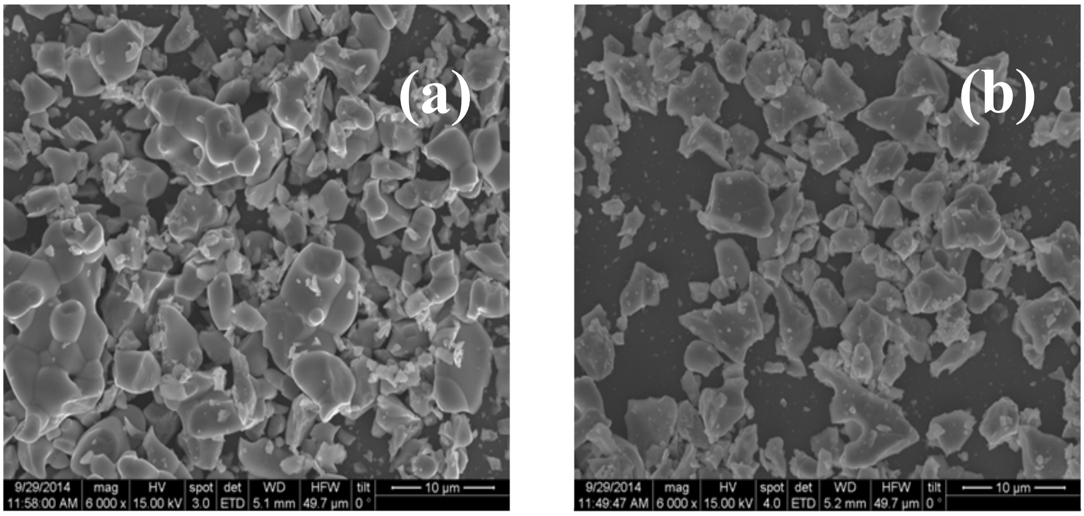

Fig. S5 FESEM images of LCM 50 (a) before and (b) after TG analysis.

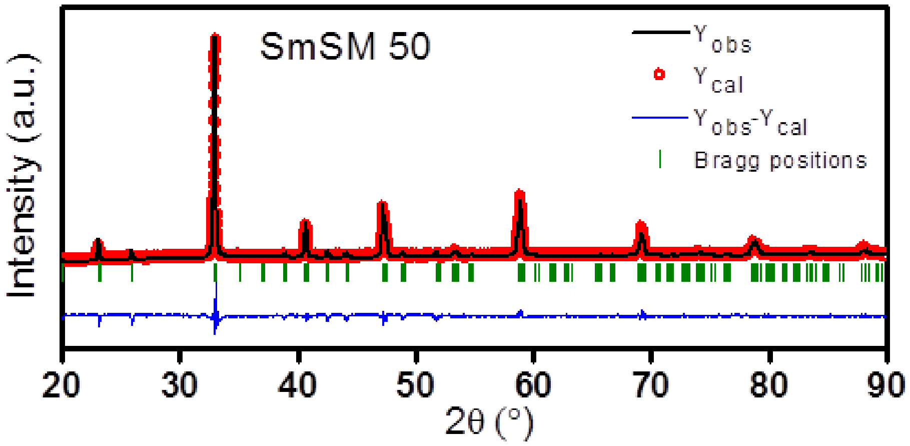

Fig. S6 XRD patterns of $Sm_{0.5}Sr_{0.5}MnO_3$ (SmSM 50). The cell parameters obtained by fitting the Powder XRD patterns of SmSM50 (space group Pnma) is a= 5.4273 (3) Å, b= 7.6562(4) Å, c= 5.4494 (2) Å.

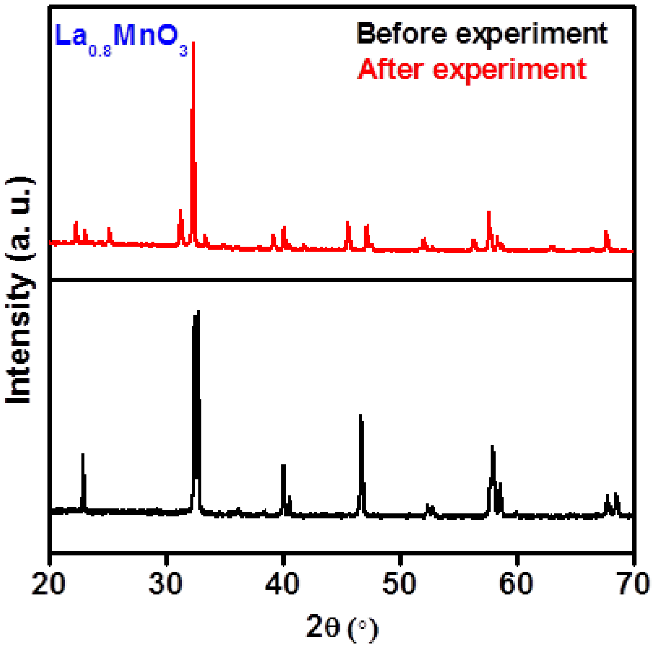

Fig. S7 Powder XRD pattern of $La_{0.8}MnO_3$ before and after TGA experiment.