Mixed Proton–electron–oxide Ion Triple Conducting Manganite as Efficient Cobalt-free Cathode for Protonic Ceramic Fuel Cells

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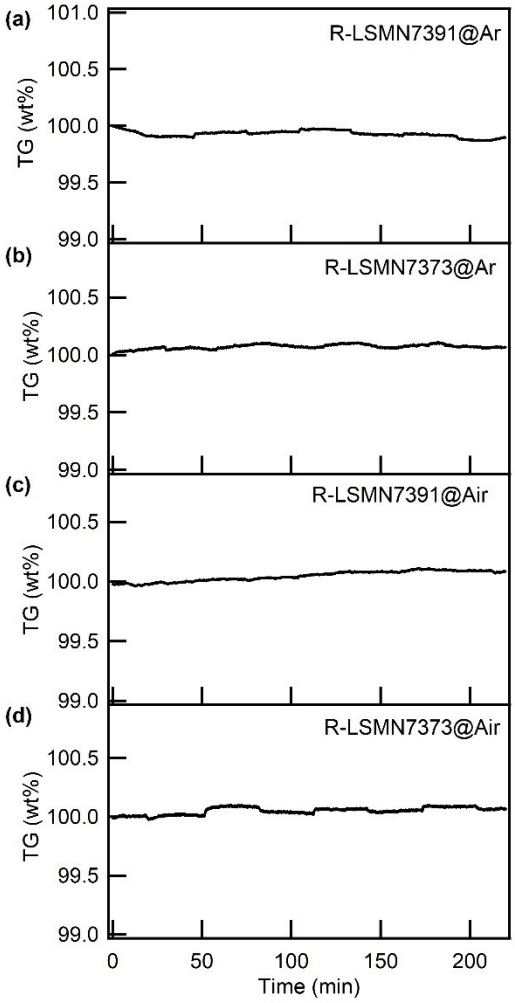

Figure S1. Weight gain/loss in response to atmospheres by repeatedly switching wet and dry Ar (a, b) / air (c, d) every 30 mins for *R*-LSMN7391 and *R*-LSMN7373 at 415 °C, p_{H2O}=0.023 p_0.

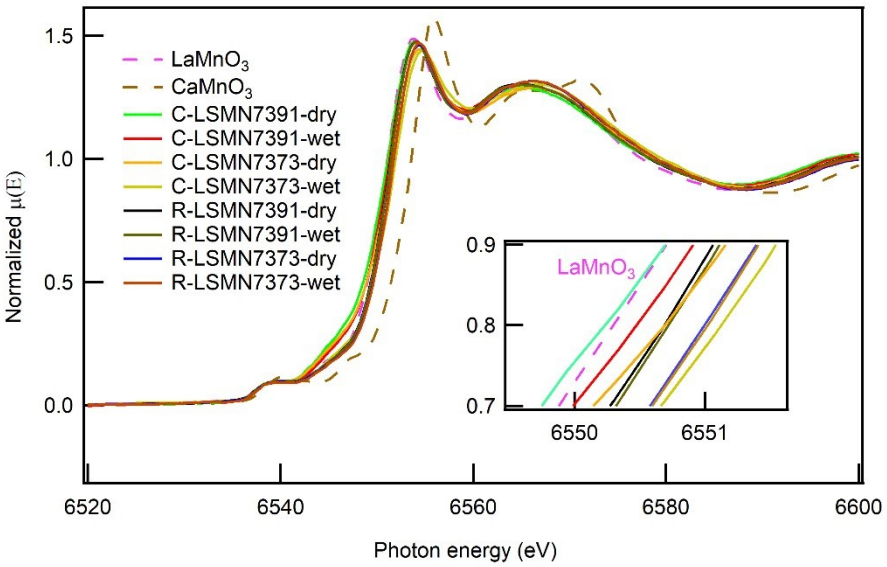

Figure S2. Mn K-edge XANES spectra of $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_{3-\delta}$ and reference samples $LaMnO_3$ and $CaMnO_3$ taking +3.20 and +3.99 valence states, determined by iodometry, respectively, at 415 ℃ under dry and wet air. The inset shows expansion of adsorption edge region.

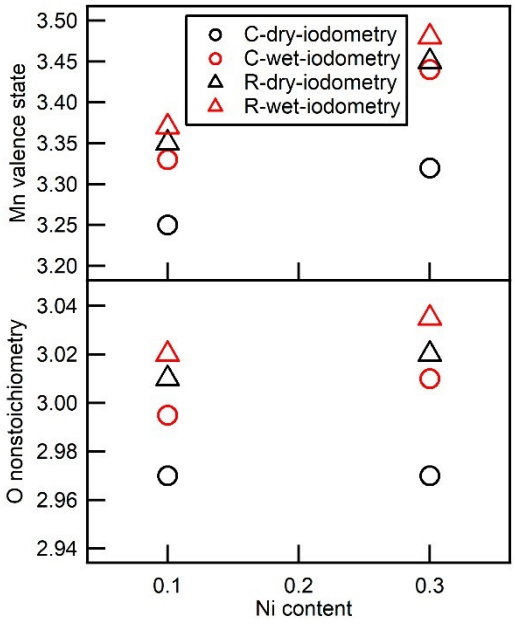

Figure S3. Mn valence state and oxygen nonstoichiometry determined by iodometry for C- and R-LSMN oxides annealed in dry and wet air at 415 °C for 6 h.

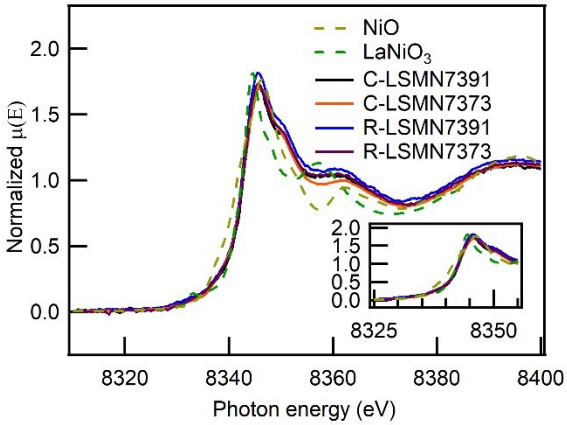

Figure S4. Ni K-edge XANES spectra of $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_{3-\delta}$ and reference samples NiO and $LaNiO_3$ taking +2 and +3 valence states, respectively, at 415 ℃ under dry air. The inset shows expansion of adsorption edge region.

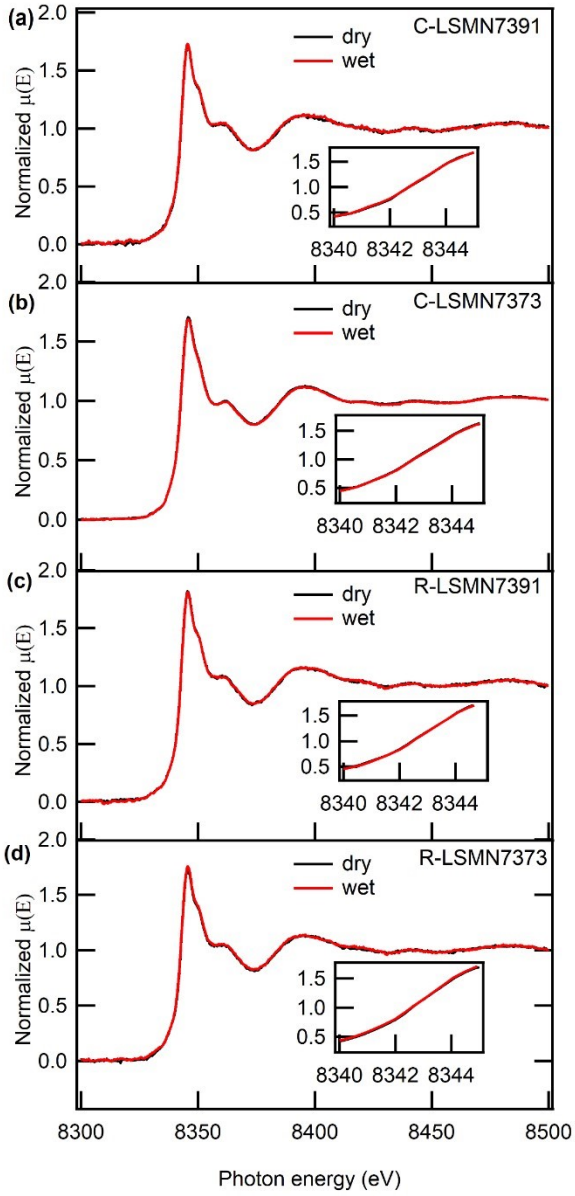

Figure S5. *In-situ* Ni *K*-edge XANES spectra of *C*-LSMN7391 (a), *C*-LSMN7373 (b), *R*LSMN7391 (c) and *R*-LSMN7373 (d) in a cycle of dry and wet air supply at 415 ℃. Insets of (a)-(c) show the enlarged absorption edge regions.

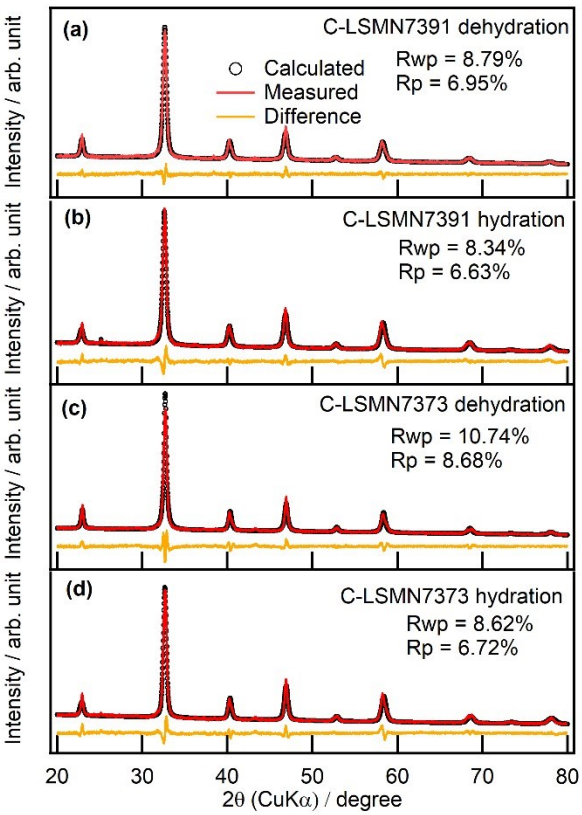

Figure S6. Rietveld refinement profiles for hydrated and dehydrated *C*-LSMN7391 and *C*LSMN7373 assuming models of (a) cubic (*Pm-3m*, #221). Here, the *C*-LSMN was annealing under dry and wet air at 415 ºC to obtain dehydrated and hydrated samples.

Table S1. Lattice constants and *R* factors refined by Rietveld analysis for hydrated and dehydrated *C*-LSMN.

Samples	Space group	a=b=c (Å)	α=β=γ	R_{wp}	R_p
C-LSMN7391 (dehydrated)	Pm-3m	3.878	90°	8.79%	6.95%
C-LSMN7391 (hydrated)	Pm-3m	3.867	90°	8.34%	6.63%
C-LSMN7373 (dehydrated)	Pm-3m	3.872	90°	10.74%	8.67%
C-LSMN7373 (hydrated)	Pm-3m	3.866	90°	8.62%	6.72%

Table S2. Atomic coordinates and site occupanciesrefined by Rietveld analysis for hydrated and dehydrated *C*-LSMN.

Samples	Elements	*x*	*y*	*z*	Occupancy	U_{iso} / Å$_2$
C-LSMN7391 (dehydrated)	La	0	0	0	0.711	0.084
	Sr	0	0	0	0.302	0.052
	Mn	0.5	0.5	0.5	0.904	0.08
	Ni	0.5	0.5	0.5	0.099	0.129
	O	0	0.5	0.5	0.956	0.040
C-LSMN7391 (hydrated)	La	0	0	0	0.714	0.030
	Sr	0	0	0	0.294	0.003
	Mn	0.5	0.5	0.5	0.916	0.026
	Ni	0.5	0.5	0.5	0.099	0.003
	O	0	0.5	0.5	1.013	0.001
C-LSMN7373 (dehydrated)	La	0	0	0	0.701	0.008
	Sr	0	0	0	0.302	0.005
	Mn	0.5	0.5	0.5	0.695	0.013
	Ni	0.5	0.5	0.5	0.295	0.020
	O	0	0.5	0.5	0.965	0.013
C-LSMN7373 (hydrated)	La	0	0	0	0.705	0.014
	Sr	0	0	0	0.302	0.076
	Mn	0.5	0.5	0.5	0.716	0.027
	Ni	0.5	0.5	0.5	0.296	0.076
	O	0	0.5	0.5	1.042	0.025

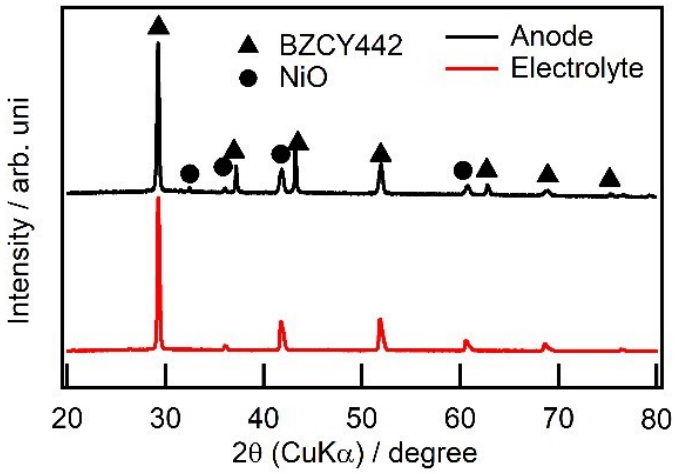

Figure S7. XRD patterns of anode and electrolyte for pulverized anode supported half cells based on BZCY442 electrolyte.

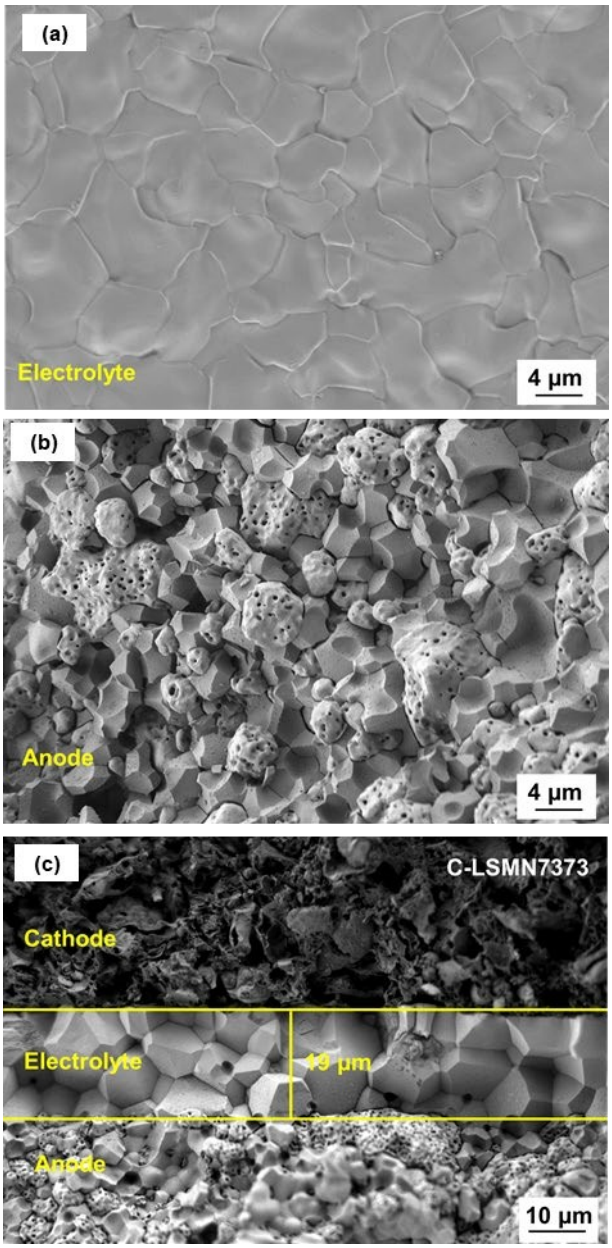

Figure S8. SEM images for the surface of electrolyte (a), cross section of anode (b), and cross section of anode-supported cells with *C*-LSMN7373 cathode (c).

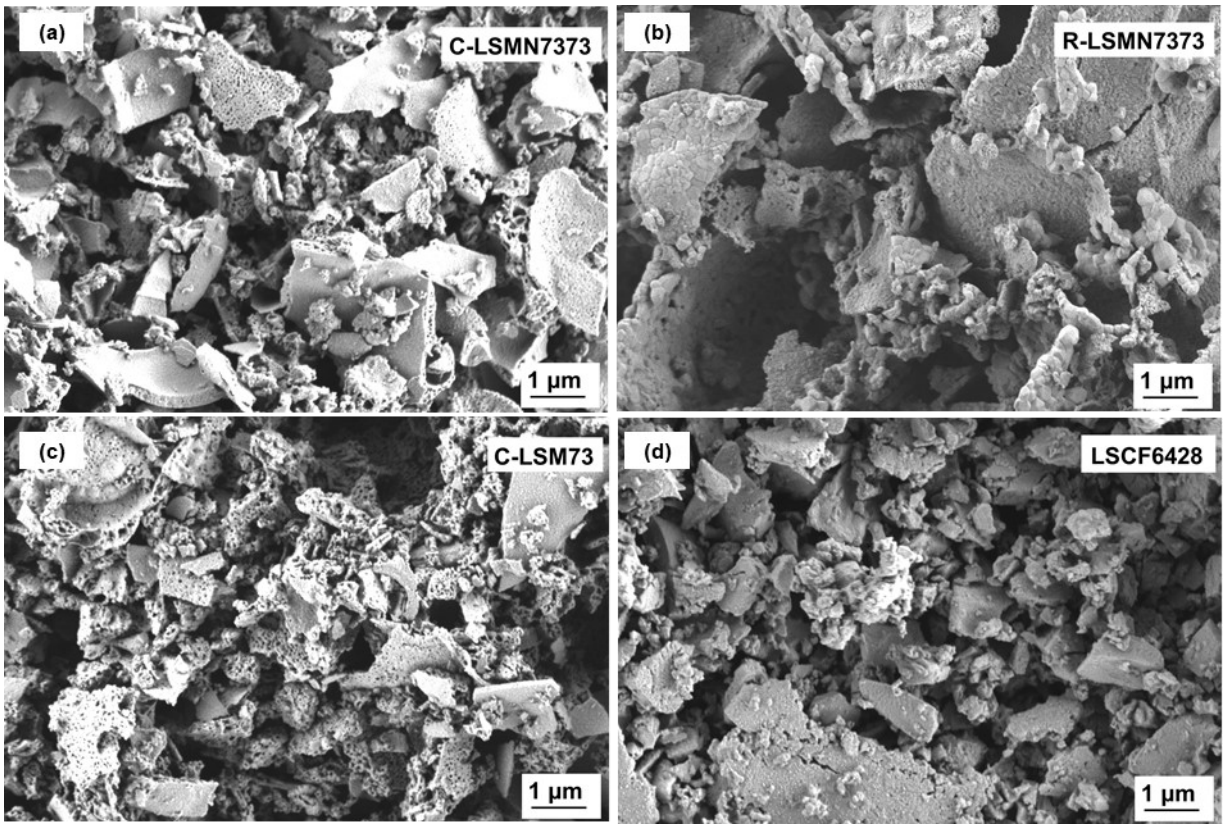

Figure S9. SEM images of *C*-LSMN7373 (a), *R*-LSMN7373 (b), *C*-LSM73 (c), and LSCF6428 (d) cathodes after annealed at 700 ℃ for 2 hours.

Table S3. Theoretical and observed open circuit voltages (OCVs) of PCFCs with LSMN and LSCF cathodes at 700, 600 and 500 ℃

	Theoretical	C-LSMN7391	C-LSMN7373	R-LSMN7391	R-LSMN7373	LSCF6428
700℃	1.140	0.99	1.02	0.97	0.98	0.99
600℃	1.152	1.03	1.08	1.00	1.05	1.04
500℃	1.164	1.08	1.12	1.06	1.08	0.98

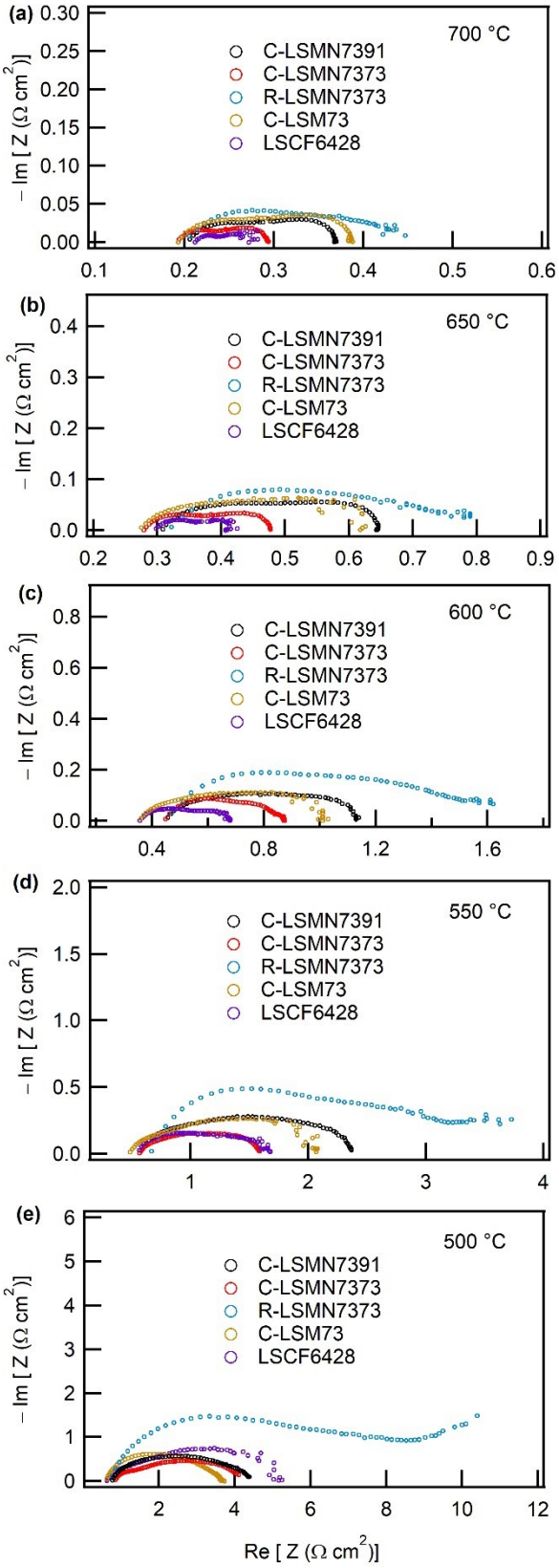

Figure S10. Electrochemical impedance spectroscopy of the anode-supported cells with various cathodes, measured at 700, 650, 600, 550 and 500 ℃ under OCV condition.

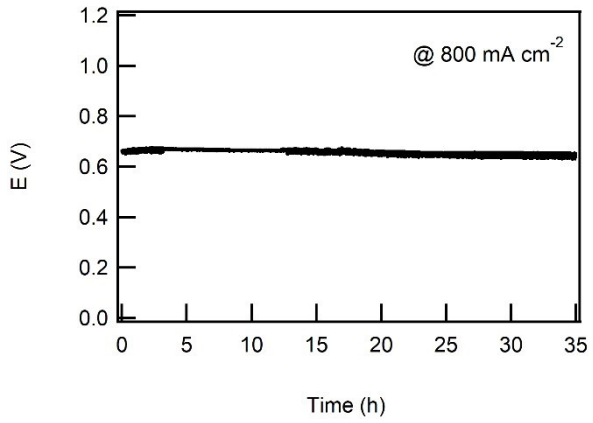

Figure S11. Durability test of C-LSMN7373 cell in a galvanostatic operation under 800 mA cm^{-2} at 700 °C.

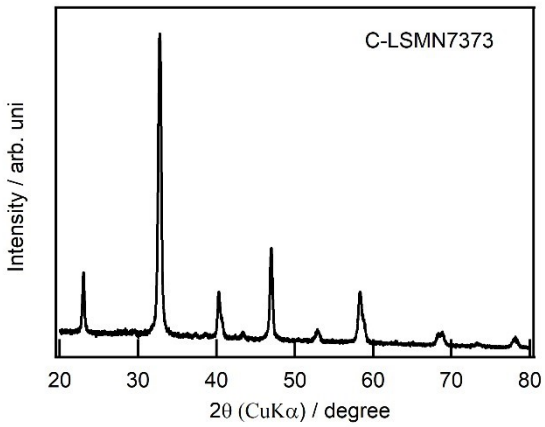

Figure S12. XRD pattern of C-LSMN7373 after the durability test shown in Figure S11.

Table S4. Performances of PCFCs comprising BZCY442 electrolyte with various cathodes at 600 ℃, and ones using $La_{1-x}Sr_xMnO_3$ cathodes at 600 ℃.

Cathode	Electrolyte	Ea (kJ mol^{-1})	PPD (mW cm^{-2})	R_p (Ω cm^2)	Ref
C-LSMN7391	BZCY442	96.7	296	0.68	This work
C-LSMN7373	BZCY442	108.1	386	0.43	This work
R-LSMN7391	BZCY442	114.8	84	2.14	This work
R-LSMN7373	BZCY442	123.1	100	1.14	This work
C-LSM73	BZCY442	88.1	291	0.69	This work
LSCF6428	BZCY442	134.5	273	0.29	This work
BSCF	BZCY442	79.5	276	0.74	33
Pr_2NiO_4	BZCY442	102.9	102	0.77	31
BZCY-BSCFT	BZCY442	100.2	194	0.91	32
BSCF	BZCY442	-	230	0.74	33
BSCF	BZCY442	-	161	0.18	30
LSM82	BZCYYb4411	-	350	-	25
LSM6530	BZCY622	-	17	0.52	27
LSM6530	BZYbCu	-	51	0.55	28
LSM82	BCY85	-	80	7.3	29

Abbreviations: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF6428), $Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_3$ (BSCF), $Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{0.9}Ti_{0.1}O_{3-\delta}$ (BZCY-BSCFT), $(La_{0.65}Sr_{0.3})MnO_{3-\delta}$ (LSM6530) , $La_{0.8}Sr_{0.2}MnO_3$ (LSM82), $BaZr_{0.4}Ce_{0.4}Y_{0.2}O_3$ (BZCY442), $BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_3$ (BZCYYb4411), $Ba(Zr_{0.84}Yb_{0.15}Cu_{0.01})O_{3-\delta}$ (BZYbCu), $BaCe_{0.85}Y_{0.15}O_3$ (BCY85).