Supporting Information

In-situ Formed Ag Nanoparticle Decorated $LiMn_2O_4$ Cathodes with Outstanding Electrochemical Performance

Wangqiong Xu,*[a] Qiling Li,[b] Shubiao Xia,[b] Zhe Li,[a] Feixiang Cheng,[b] Shimei Guo,[a]

[a]*College of Physics and Electronic Engineering, Qujing Normal University, Qujing, Yunnan 655011, China*

[b]*Yunnan Key Laboratory of Crystalline Porous Organic Functional Materials, College of Chemistry and Environmental Science, Qujing Normal University, Qujing, Yunnan 655011, China*

* Corresponding authors: xuwangqiong@mail.qjnu.edu.cn (W.Q. Xu)

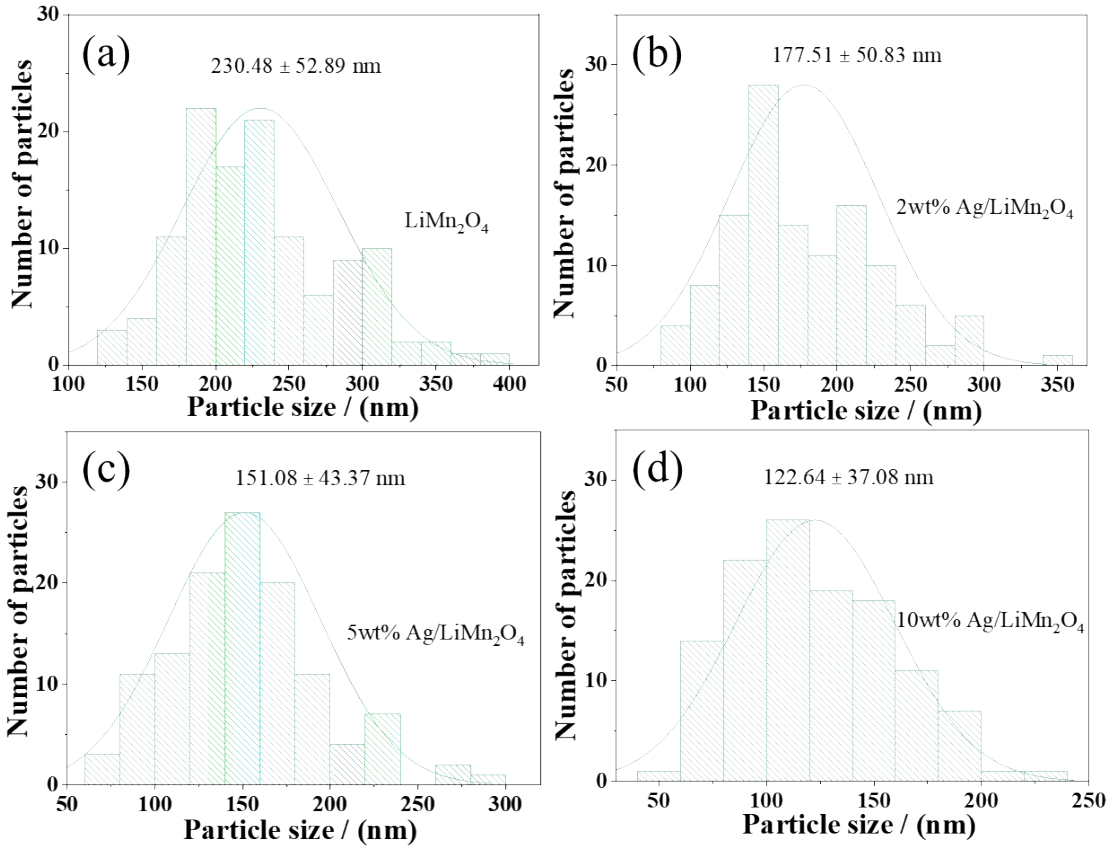

Fig. S1 (a-d) The particle size distribution of the $LiMn_2O_4$ and Ag-coated $LiMn_2O_4$ samples.

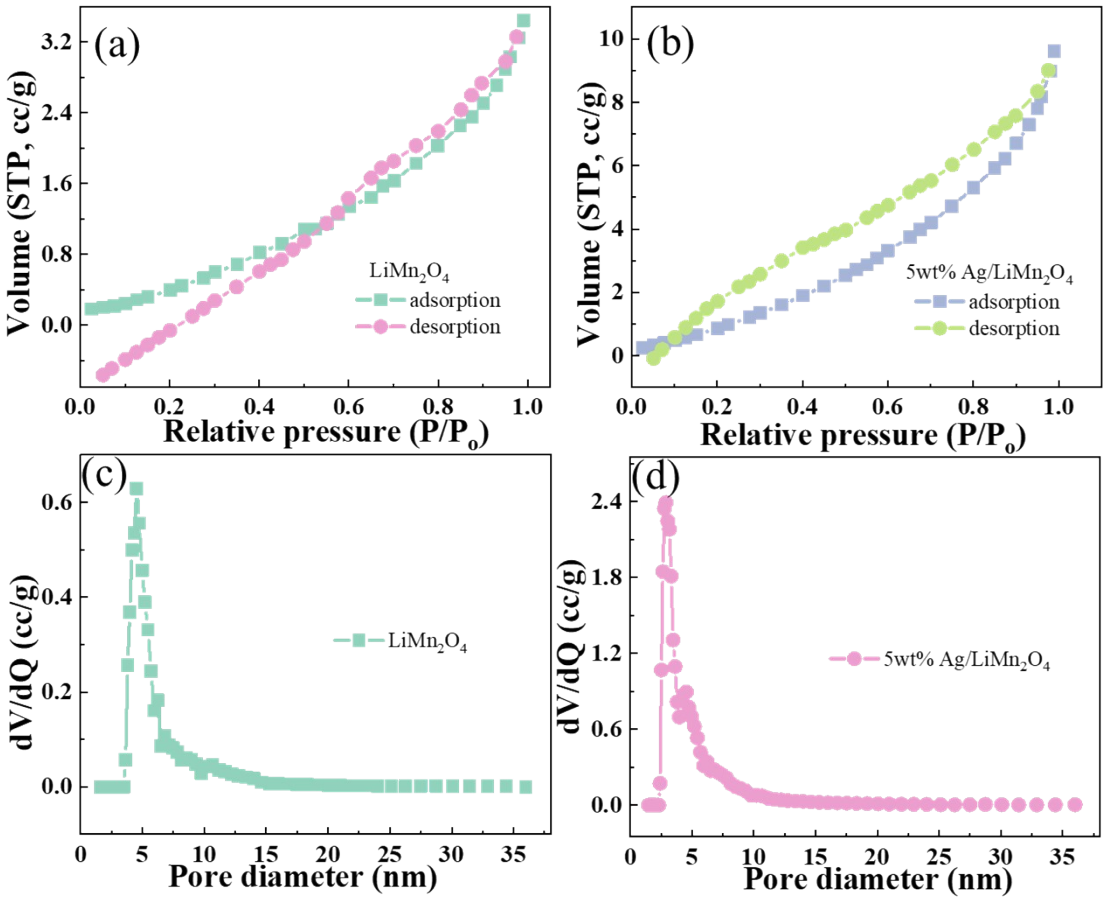

Fig. S2 Nitrogen adsorption/desorption isotherms of the (a) $LiMn_2O_4$ and (b) 5wt% $Ag/LiMn_2O_4$ samples. The pore size of (c) $LiMn_2O_4$ and (d) 5wt% $Ag/LiMn_2O_4$ calculated from adsorption/desorption experiments using the BJH model.

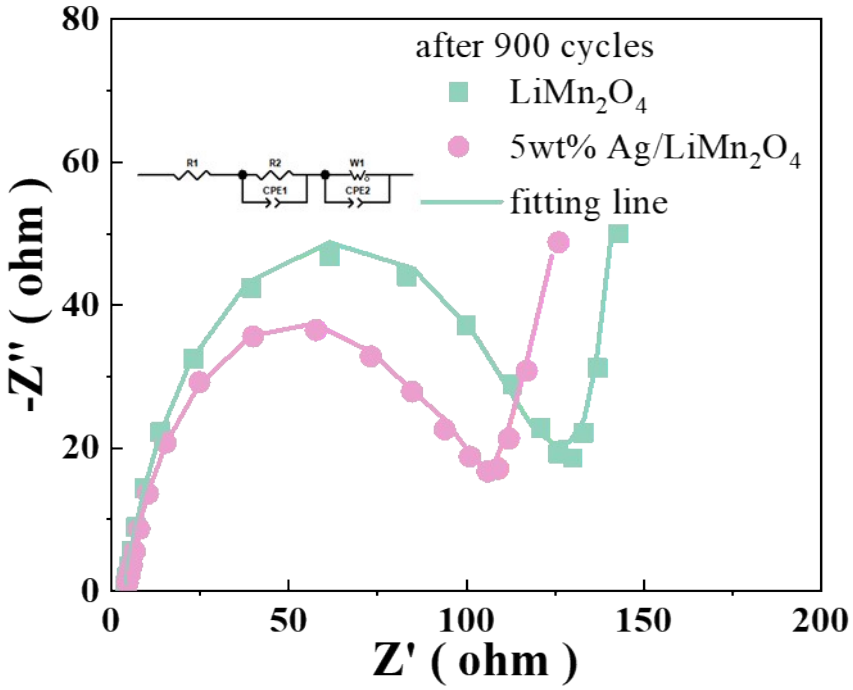

Fig. S3 Electrochemical impedance spectroscopy plots of $LiMn_2O_4$ and 5wt% $Ag/LiMn_2O_4$ after 900 cycles at 5 C, the inset in S2 is the equivalent circuit.

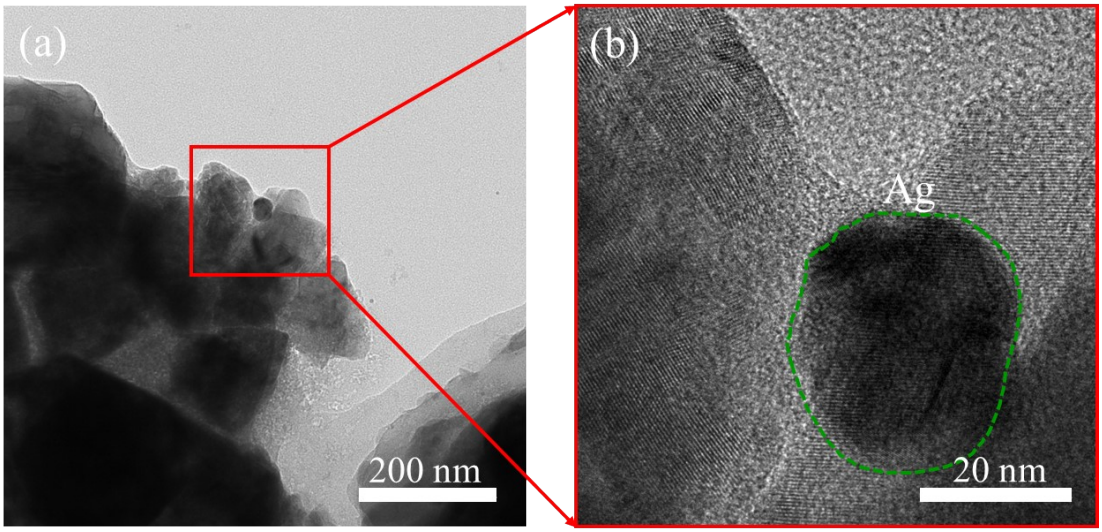

Fig. S4 (a) TEM and (b) HR-TEM images of 5wt% Ag/$LiMn_2O_4$ at 5 C after 900 cycles.

Table S1 Rietveld refinement results of the $LiMn_2O_4$ and Ag-coated $LiMn_2O_4$ samples.

$LiMn_2O_4$	Phase	Atoms	Sites	*x*	*y*	*z*
	$LiMn_2O_4$	Li	8a	0.12500(0)	0.12500(0)	0.12500(0)
		Mn	16d	0.50000(0)	0.50000(0)	0.50000(0)
		O	32e	0.26122(0)	0.26122(0)	0.26122(0)
		Space group	R_p	R_{wp}		CHI^2
		$Fd\bar{3}m$	2.37%	3.10%		3.61
2wt% $Ag/LiMn_2O_4$	Phase	Atoms	Sites	*x*	*y*	*z*
	$LiMn_2O_4$	Li	8a	0.12500(0)	0.12500(0)	0.12500(0)
		Mn	16d	0.50000(0)	0.50000(0)	0.50000(0)
		O	32e	0.26122(0)	0.26122(0)	0.26122(0)
		Space group	R_p	R_{wp}		CHI^2
		$Fd\bar{3}m$	2.01%	2.59%		3.33
5wt% $Ag/LiMn_2O_4$	Phase	Atoms	Sites	*x*	*y*	*z*
	$LiMn_2O_4$	Li	8a	0.12500(0)	0.12500(0)	0.12500(0)
		Mn	16d	0.50000(0)	0.50000(0)	0.50000(0)
		O	32e	0.26122(0)	0.26122(0)	0.26122(0)
		Space group	R_p	R_{wp}		CHI^2
		$Fd\bar{3}m$	2.52%	3.23%		3.74
10wt% $Ag/LiMn_2O_4$	Phase	Atoms	Sites	*x*	*y*	*z*
	$LiMn_2O_4$	Li	8a	0.12500(0)	0.12500(0)	0.12500(0)
		Mn	16d	0.50000(0)	0.50000(0)	0.50000(0)
		O	32e	0.26294(49)	0.26294(49)	0.26294(49)
		Space group	R_p	R_{wp}		CHI^2
		$Fd\bar{3}m$	2.65%	3.48%		3.93

Table S2 Mn $2p_{3/2}$ peak parameters for Mn in $LiMn_2O_4$ sample.

Peak	B.E. (eV)	FWHM (eV)	Percent (%)
Mn^{4+} (total)=48.30			
Mn^{4+}	642.16	0.97	21.93
Mn^{4+}	642.82	0.92	15.29
Mn^{4+}	644.17	0.99	8.51
Mn^{4+}	645.30	0.95	0.46
Mn^{4+}	645.98	1.00	2.11
Mn^{3+} (total)=51.70			
Mn^{3+}	640.43	1.00	11.31
Mn^{3+}	641.30	1.00	20.18
Mn^{3+}	642.48	0.98	3.08
Mn^{3+}	643.47	0.90	12.83
Mn^{3+}	644.98	1.00	4.30

Table S3 Mn $2p_{3/2}$ peak parameters for Mn in 5wt% Ag coated $LiMn_2O_4$ sample.

Peak	B.E. (eV)	FWHM (eV)	Percent (%)
Mn^{4+} (total)=49.10			
Mn^{4+}	641.99	0.90	16.14
Mn^{4+}	642.68	0.98	13.37
Mn^{4+}	643.79	1.00	11.78
Mn^{4+}	644.50	0.96	4.96
Mn^{4+}	645.98	1.00	2.85
Mn^{3+} (total)=50.90			
Mn^{3+}	640.55	1.00	11.06
Mn^{3+}	641.30	0.95	16.18
Mn^{3+}	642.45	1.00	8.64
Mn^{3+}	643.18	1.00	11.48
Mn^{3+}	645.11	0.97	3.54

Table S4 Cycling performance comparison of the 5wt% Ag/$LiMn_2O_4$ (in this work) and other Ag nanoparticle or metal surface-coating spinel Li-Mn-O (from previous literatures).

Samples	C-Rate/testing temperature/cycle number	First discharge capacity (mAh g^{-1})	Capacity retention (%)	Ref.
5wt% Ag/$LiMn_2O_4$	**5 C/25°C/900 cycles**	**100**	**80**	**This work**
0.1 mol% Ag coated $LiMn_2O_4$	1 C/25°C/30 cycles	105.4	90.7	1
3 wt.% Ag coated $LiMn_2O_4$	0.1 C/25°C/60 cycles	115	81.9	2
6.3 wt % Ag coated $LiMn_2O_4$	1 C/25°C/50 cycles	125	96	3
5wt% Ag coated $LiNi_{0.5}Mn_{1.5}O_4$	4 C/25°C/100 cycles	96	72.9	4
5wt% Ag coated $LiMn_2O_4$	0.5 C/25°C/50 cycles	120	98.8	5
5wt% Ag coated $LiMn_2O_4$	2 C/25°C/20 cycles	100	95	6
Ag coated $LiMn_2O_4$	1 C/25°C/50 cycles	122	81	7
Au coated $LiMn_2O_4$	1 C/25°C/400 cycles	140	78	8

Table S5 The fitting results of EIS plots.

Sample	R_s (Ω)	R_{ct} (Ω)
$LiMn_2O_4$ before cycle	2.19	388.48
5wt% Ag/$LiMn_2O_4$ before cycle	2.21	250.77
$LiMn_2O_4$ after 900 cycles	4.16	129.07
5wt% Ag/$LiMn_2O_4$ after 900 cycles	4.45	107.16

Table S6 Mn $2p_{3/2}$ peak parameters for Mn in $LiMn_2O_4$ after 900 cycles.

Peak	B.E. (eV)	FWHM (eV)	Percent (%)
Mn^{4+} (total)=61.13			
Mn^{4+}	641.65	0.97	17.57
Mn^{4+}	642.31	0.97	19.74
Mn^{4+}	643.87	1.00	13.76
Mn^{4+}	644.89	1.00	6.23
Mn^{4+}	646.20	1.00	3.83
Mn^{3+} (total)=38.87			
Mn^{3+}	640.38	0.98	9.87
Mn^{3+}	641.10	0.92	11.16
Mn^{3+}	642.78	0.93	5.59
Mn^{3+}	643.13	0.91	12.08
Mn^{3+}	644.32	1.00	0.17

Table S7 Mn $2p_{3/2}$ peak parameters for Mn in 5wt% Ag coated $LiMn_2O_4$ after 900 cycles.

Peak	B.E. (eV)	FWHM (eV)	Percent (%)
Mn^{4+} (total)=57.05			
Mn^{4+}	641.22	1.00	19.46
Mn^{4+}	642.00	1.00	23.09
Mn^{4+}	643.81	1.00	7.25
Mn^{4+}	645.00	1.00	3.76
Mn^{4+}	646.20	1.00	3.49
Mn^{3+} (total)=42.95			
Mn^{3+}	640.23	1.00	15.44
Mn^{3+}	641.00	1.00	8.47
Mn^{3+}	642.68	0.90	9.28
Mn^{3+}	643.12	0.90	8.54
Mn^{3+}	644.33	0.90	1.22

The Li^+ diffusion coefficient (D_{Li^+}) can be calculated by the following equation [9]:

$$D_{Li^+} = R^2T^2/2A^2n^4F^4C^2\sigma^2$$

Where D_{Li^+} is the diffusion coefficient of Li^+ ($cm^2\ s^{-1}$), R is the gas constant (8.314 J $mol^{-1}K^{-1}$), T is the absolute temperature (298.15 K), A is the surface area of electrode (1.26 cm^2), n refers to the number of electrons involved in redox reaction, F is the Faraday constant (9.65×10^4 C mol^{-1}), C is the concentration of Li^+ in active material (0.0238 mol cm^{-3}), and σ is the Warburg coefficient obtained from the slope. By linear fitting of the relationship plot Z' and the square root of the angular frequency ω (Fig. 6e), the Warburg coefficient σ was obtained.

References

1 W.-J. Zhou, B.-L. He and H.-L. Li, *Mater. Res. Bull.*, 2008, **43**, 2285-2294.

2 S. M. Abbas, A. M. Hashem, A. E. Abdel-Ghany, E. H. Ismail, M. Kotlar, M. Winter, J. Li and C. M. Julien, *Energies*, 2020, **13**, 5194.

3 S. Huang, Z. Wen, X. Yang, X. Zhu and B. Lin, *Electrochemical and Solid State Letters*, 2006, **9**, A443-A447.

4 J. Arrebola, A. Caballero, L. Hernán, J. Morales and E. R. Castellón, *Electrochemical and Solid State Letters*, 2005, **8**, A303-A307.

5 R. Jiang, C. Cui, H. Ma, H. Ma and T. Chen, *J. Electroanal. Chem.*, 2015, **744**, 69-76.

6 J. T. Son, K. S. Park, H. G. Kim and H. T. Chung, *J. Power Sources*, 2004, **126**, 182-185.

7 M. O. Guler, A. Akbulut, T. Cetinkaya, M. Uysal and H. Akbulut, *Int. J. Hydrogen Energy*, 2014, **39**, 21447-21460.

8 J. L. Esbenshade, M. D. Fox and A. A. Gewirth, *J. Electrochem. Soc.*, 2015, **162**, A26-A29.

9 B. Li, M. Wang, Y. Zhang, Q. Guo, R.-N. Tian, J. Chen, D. Wang, C. Dong and Z. Mao, *Electrochim. Acta*, 2023, **464**, 142898.