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Charge storage mechanism of activated manganese oxide composites for pseudocapacitors

Supporting Information

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Table S1. Reported material characterisation analyses on electrochemical activation from Mn_3O_4 to MnO_2.

Synthesis method	Post treatment	Total time	Analyses during activation[a]	Identified activated MnO_x	references
Pyrolysis (ramping to 300 ^oC) from $Mn(CH_3COO)_2$ precursor	N/A	~6 hr	XRD, TEM, XPS, *in situ* Raman, *ex situ* Raman	Amorphous MnO_2 and hausmannite-Mn_3O_4 composite	This work
Electrostatic spray deposition from $Mn(CH_3COO)_2$ precursor at 260 ^oC by 10 kV	Annealing at 900 ^oC for 10 hr	>10 hr	XRD, XPS, SEM	Birnessite-MnO_2	22
Electrostatic spray deposition from $MnCl_2$ precursor by 12 kV	Annealing at 200-400 ^oC for 3 hr	>3 hr	XRD, XANES (Mn-K edge), Raman	Amorphous MnO_2	23
Chemical bath deposition from $MnSO_4$ and urea precursor for 12 hr	N/A	~12 hr	XRD, SEM, Raman, contact angle	Birnessite-MnO_2	24
Thermal reduction of electrolytic manganese dioxide at 1050 ^oC for 72 hr	Ball-milled at 1000 rpm for 10 hr with acetone	~82 hr	SEM, XRD, XPS	Birnessite-MnO_2	25

[a] Except for the electrochemical analyses, the methods used for identifying as-prepared Mn_3O_4 and activated MnO_2.

Table S2. Peak position (cm^{-1}) and Full Width at Half Maximum (FWHM, cm^{-1} in parenthesis) of the Mn_3O_4 and MnO_2 peaks by Lorentz fitting of *ex situ* Raman spectra.

	Mn_3O_4	MnO_2	MnO_2	MnO_2	MnO_2	Mn_3O_4	MnO_2	Mn_3O_4	$I_{MnO_2}/I_{Mn_3O_4}$	Specific Capacitance (F/g)
as-prepared	658 (36)	648 (42)	618 (51)	575 (70)	506 (55)	477 (50)	408 (55)	289 (65)	0.42	N/a
5th cycle	658 (36)	648 (45)	618 (45)	575 (61)	506 (55)	477 (55)	408 (55)	284 (65)	0.63	132
10th cycle	658 (36)	648 (52)	618 (52)	575 (70)	506 (60)	477 (55)	408 (45)	285 (65)	0.89	144
50th cycle	658 (35)	648 (46)	618 (48)	575 (55)	506 (55)	477 (40)	408 (56)	285 (65)	1.62	166
100th cycle	658 (37)	648 (49)	618 (64)	575 (45)	506 (50)	477 (45)	408 (56)	285 (45)	2.53	169
150th cycle	658 (33)	648 (55)	618 (50)	575 (70)	506 (55)	477 (65)	408 (55)	280 (65)	2.51	170
200th cycle	658 (30)	648 (55)	618 (50)	575 (70)	506 (50)	477 (55)	408 (55)	284 (61)	2.45	171
500th cycle	658 (30)	648 (53)	618 (42)	575 (53)	506 (56)	477 (55)	408 (50)	281 (60)	2.44	174

Table S3. Normalised area (by atomic sensitivity factor) and area ratio calculated from XPS spectra

MnO_x composite electrode	C 1s normalised area	Mn 3s normalised area	C1s/Mn3s area ratio
As-prepared MnO_x	5792	3722.6	2.59
Activated MnO_x (at region 1)	35096	34120	1.03
Activated MnO_x (at region 2)	45909	43889	1.05

Table S4. Capacitive performance of electrochemically activated birnessite-MnO_2.

Specific capacitance ($F\ g^{-1}$)	Potential window (V)	Electrolyte	Mass loading ($mg\ cm^{-2}$)	references
174 at 25 mV s^{-1}	1.2	0.5 M Na_2SO_4	0.71	This work
133 at 50 mV s^{-1}	0.9	0.2 M Na_2SO_4	0.15[a]	22
150 at 50 mV s^{-1}	1.0	0.1 M Na_2SO_4	0.116[a]	23
~160 at 20 mV s^{-1}	1.0	1.0 M Na_2SO_4	0.72[b]	24
~160 at 10 mV s^{-1}	1.0	0.5 M Na_2SO_4	1.33[c]	25

[a] The electrode is prepared by MnO_x without mixing with conductive agent and binder.

[b] The specific capacitance is estimated from CV profile.

[c] The electrode consists of 80% MnO_x, 10% conductive agent (carbon), and 10% poly(vinylidenefluoride) binder.

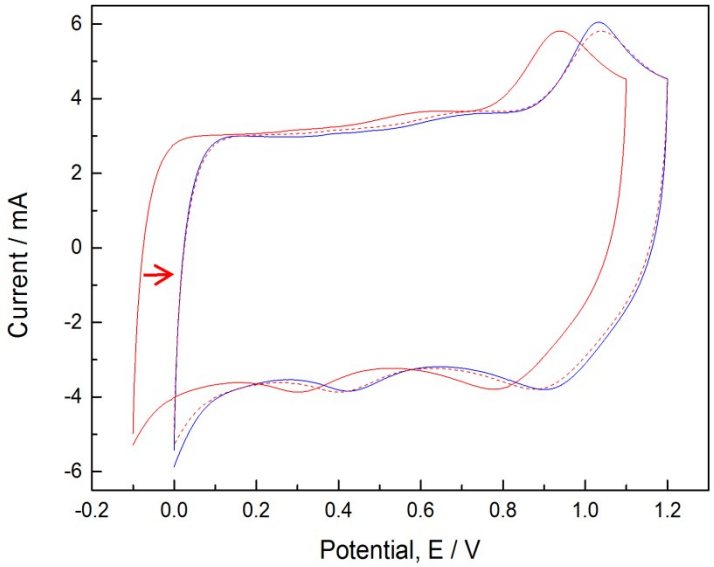

Figure S1. CV of MnO_x measured at a sweep rate of 25 mV s^{-1} in 0.5M Na_2SO_4 against Ag/AgCl (blue) and quasi-reference electrode (red). The dash curve is measured against quasi-reference electrode after shifting by +0.1 V.

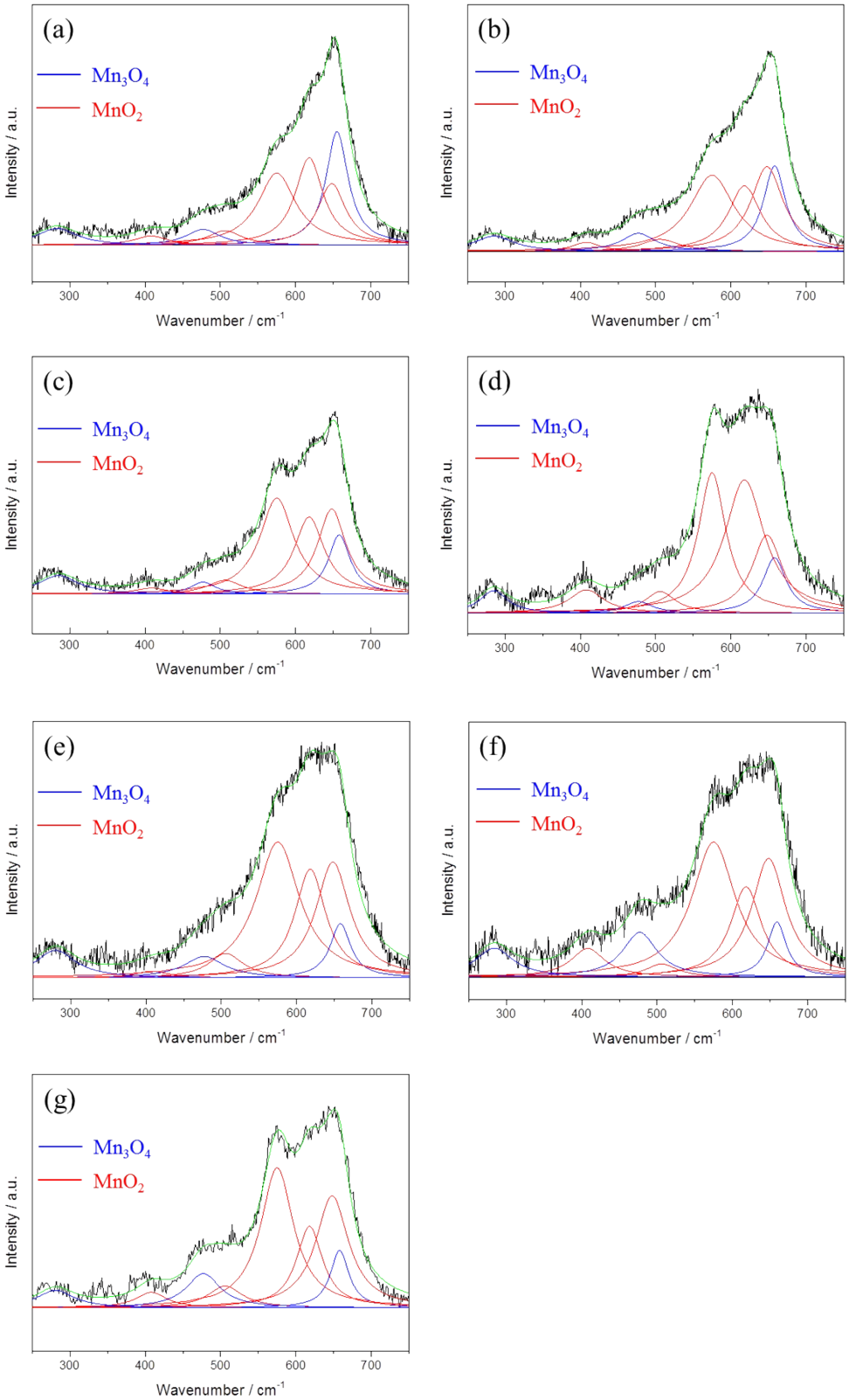

Figure S2. Lorentz fitting of *ex situ* Raman spectra recorded after (a) 5th, (b) 10th, (c) 50th, (d) 100th, (e) 150th, (f) 200th, and (g) 500th CV cycle. Green line = envelope of total of the fitted peaks.

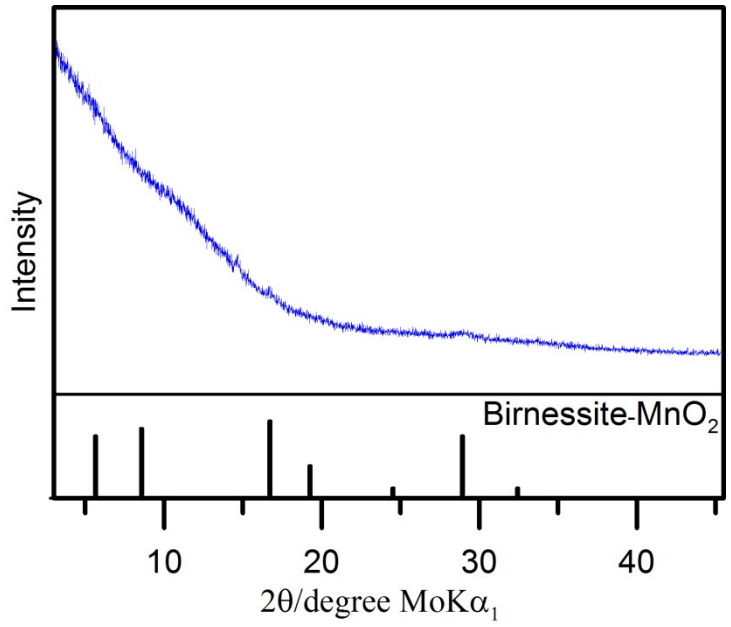

Figure S3. PXRD of activated MnO_x (MoKα1 source) JCPDS CARD 18-0802 is standard birnessite-MnO_2 from database.

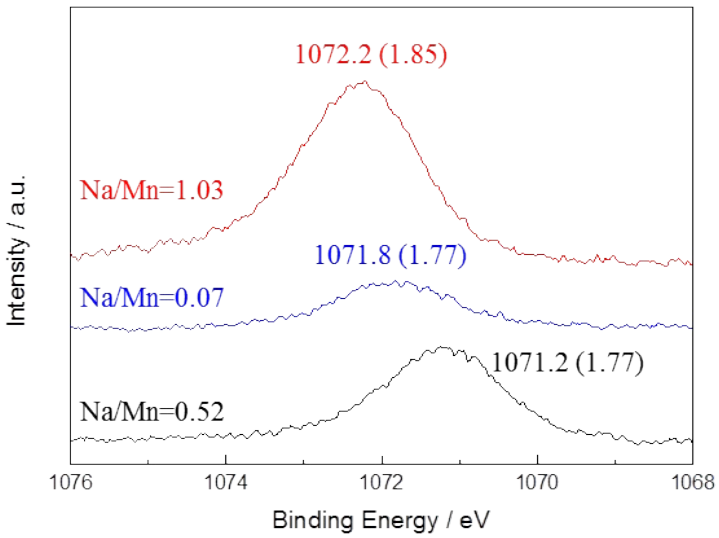

Figure S4. XPS Na 1s of (blue) as-prepared, (red) activated MnO_x, and (black) $Na_{0.33}MnO_2$ sample. The denoted values are the fitted peak position (eV) and Full Width at Half Maximum (FWHM, eV in parenthesis)