Efficient electrochemical synthesis of a manganese-based metal-organic framework for H_2 and CO_2 uptake

Aisha Asghar[a], Naseem Iqbal[a*], Tayyaba Noor[b], Benson Kariuki[c], Luke Kidwell[c], Timothy L. Easun[c*]

[a] *U.S.-Pakistan Center for Advanced Studies in Energy (USPCAS-E), National University of Sciences & Technology (NUST), H-12, Islamabad, 44000, Pakistan*

[b] *School of Chemical & Materials Engineering (SCME), National University of Sciences & Technology (NUST), H-12, Islamabad, 44000, Pakistan*

[c] *School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK.*

The electrochemical synthesis parameters were simplistically optimised for maximum yield with minimum electrical, reagent and time costs in this study by varying first current density, then electrolyte amount and then reaction time (Figures S1, S2 and Table S1). This optimisation reveals a very prominent role of current density in the electrochemical synthesis of Mn-DABDC(EC). No yield was observed when current density was below 40 mA. Providing 40mA current density in the presence of 2 mmol (170 mg) of $NaNO_3$ electrolyte was sufficient to yield some Mn-DABDC (EC) crystals in a reaction time of 100 min, but under these conditions unreacted and crystalline DABDC linker was also observed in the PXRD pattern, characterised by a peak at 25 degrees 2θ (Figure S2, sample S1) and the solid yield was very low (18.9% by MOF mass). Linker diffraction peaks were not observed in the solid products when current density was increased beyond 40 mA. MOF yield increased with increasing current density until levelling off at ~85% yield for current densities of 70 mA and above (with this combination of electrolyte quantity and time). In order to determine the optimum electrolyte amount, tests were performed by varying electrolyte amount between 50-225 mg, while providing the optimised current density of 70 mA, for 100 min. Finally, the optimum reaction time was investigated by providing the optimised current density (70 mA) and optimised electrolyte amount (225 mg, 2.7 mmol), and found to be 120 minutes. While reaction time and electrolyte concentration impacted MOF yield, the variation in current density studied herein had the greatest effect in electrochemical Mn-DABDC MOF synthesis. Results for synthesis condition optimization are given in Figure S1 with example data provided in Table S1. In all reactions, with the exception of some crystalline unreacted DABDC linker precipitating at low current density, the powder diffraction patterns shown in Figure S2 confirm only a crystalline phase of Mn-DABDC was formed.

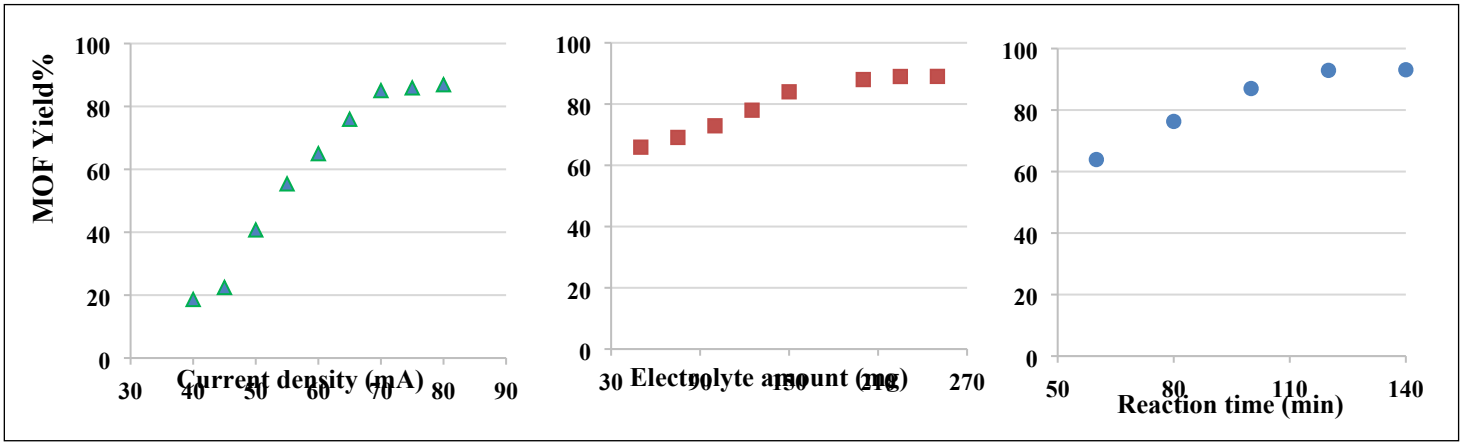

Figure S1. MOF yields of Mn-DABDC (EC) against the variables of current density (mA, *green*), electrolyte amount (mg, *orange*) and reaction time (minutes, *blue*). See text above for other parameters fixed for each case.

Table S1. Summary of synthesis parameters employed for synthesis of electrochemical Mn-DABDC MOF samples.

Sample	Current density	Electrolyte amount	Reaction time	Yield %
S1	40 mA	170 mg	100 min	18.62
S2	45 mA	170 mg	100 min	22.43
S3	80 mA	170 mg	100 min	86.90
S4	70 mA	50 mg	100 min	65.92
S5	70 mg	150 mg	100 min	84.00
S6	70 mA	275 mg	100 min	89.00
S7	70 mA	225 mg	60 min	63.91
S8	70 mA	225 mg	100 min	87.00
S9	70 mA	225 mg	140 min	93.10

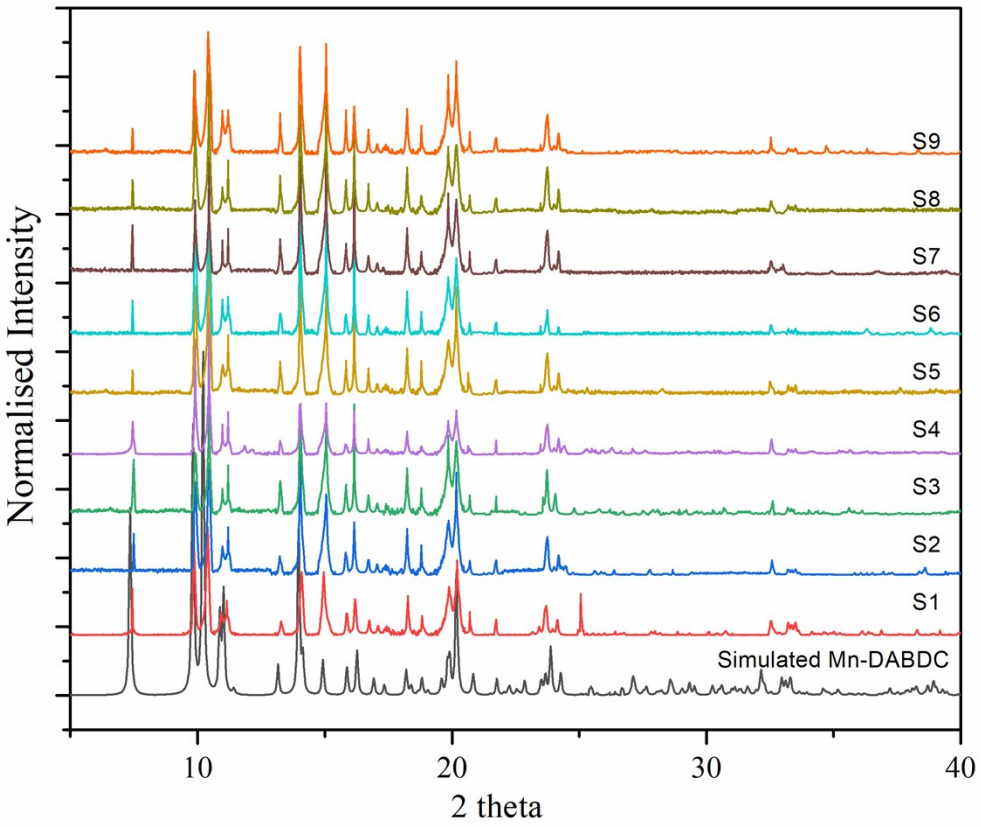

Figure S2. PXRD patterns of electrochemically synthesised Mn-DABDC(ES) samples compared with simulated PXRD pattern of Mn-DABDC. S1-S9 labelling corresponds to entries in Table S1.

Table S2. Single crystal XRD data for Mn-BDC and Mn-DABDC MOF samples.

	Mn-BDC	**Mn-DABDC**
Empirical formula	$C_{11}H_{11}MnNO_5$	$C_{36}H_{46}Mn_3N_{10}O_{16}$
Formula weight	292.15	1039.65
Temperature	150(2) K	293(2) K
Wavelength	0.71073 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 2_1/c	P 2_1/n
Unit cell dimensions	a = 13.4484(4) Å	a = 13.2958(7) Å
	b = 10.1799(3) Å	b = 10.0194(7) Å
	c = 17.6560(5) Å	c = 16.6456(7) Å
	α= 90°	α= 90°
	β= 90.271(3)°	β= 106.404(5)°
	γ = 90°	γ = 90°
Volume	2417.14(12) Å3	2127.2(2) Å3
Z	8	2
Density (calculated)	1.606 Mg/m3	1.623 Mg/m3
Absorption coefficient	1.104 mm-1	7.866 mm-1
F(000)	1192	1070
Crystal size	0.229 x 0.138 x 0.036 mm3	0.181 x 0.103 x 0.036 mm3
Theta range for data collection	3.405 to 29.829°.	3.776 to 73.945°.
Index ranges	-18<=h<=16, -13<=k<=13, -24<=l<=17	-8<=h<=16, -11<=k<=12, -20<=l<=19
Reflections collected	22087	8494
Independent reflections	6151 [R(int) = 0.0298]	4165 [R(int) = 0.0636]
Completeness to theta = 25.242°	99.80%	99.90%
Absorption correction	Gaussian	Gaussian
Max. and min. transmission	1.000 and 0.872	1.000 and 0.822
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	6151 / 0 / 329	4165 / 603 / 436
Goodness-of-fit on F2	1.056	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0711	R1 = 0.0772, wR2 = 0.2024
R indices (all data)	R1 = 0.0401, wR2 = 0.0772	R1 = 0.1136, wR2 = 0.2381
Largest diff. peak and hole	0.357 and -0.360 e.Å-3	0.576 and -0.586 e.Å-3

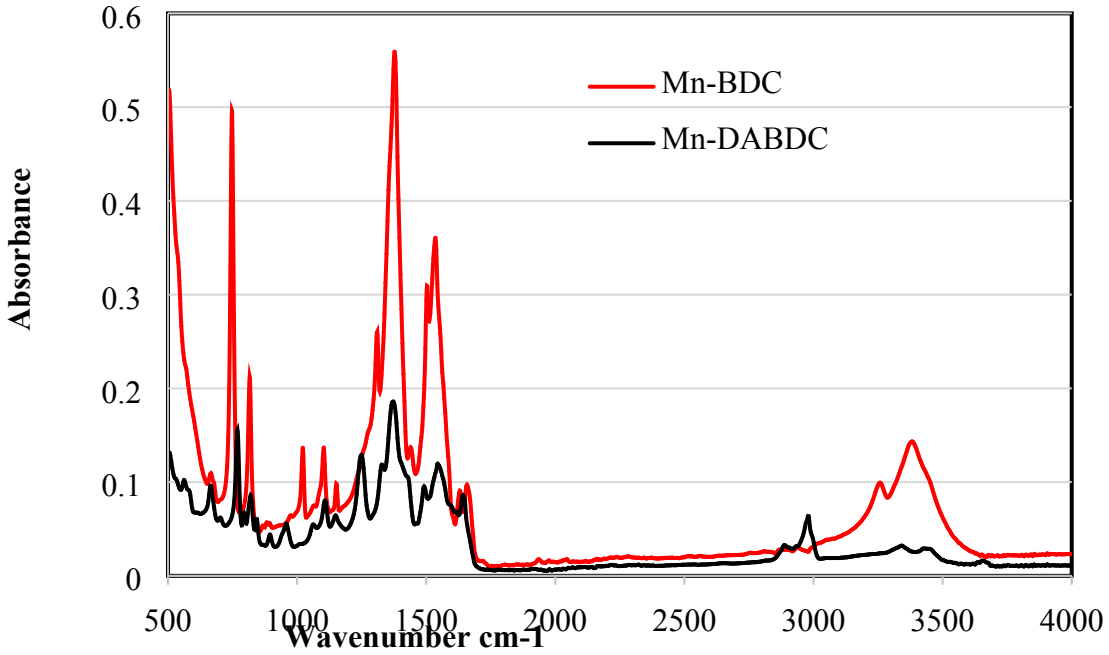

Figure S3. ATR-FTIR spectra for Mn-BDC (*red*) and Mn-DABDC (*black*).

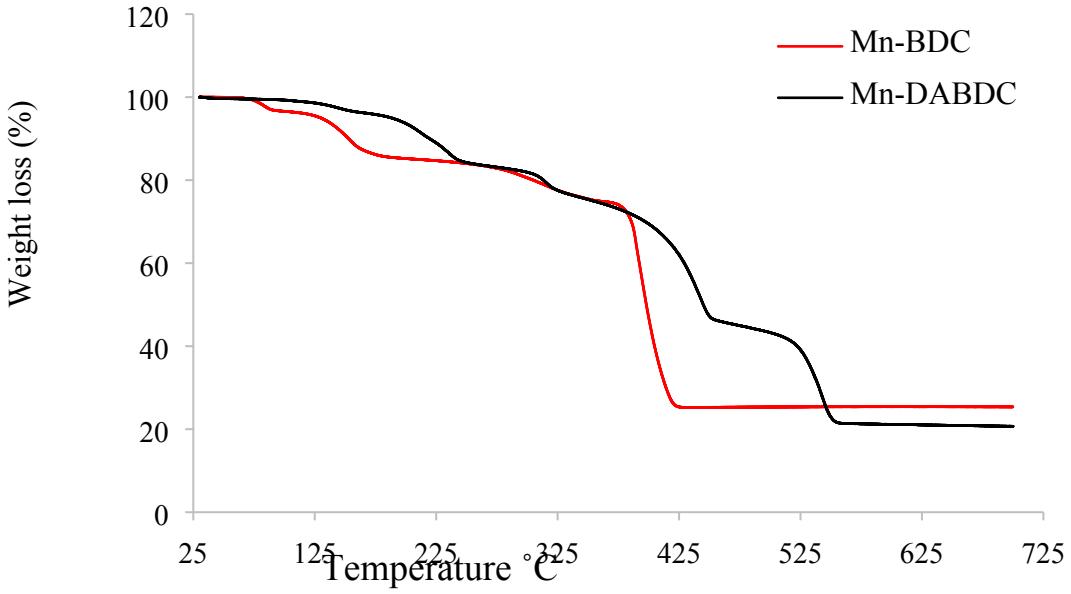

Figure S4. TGA traces of Mn-BDC (*red*) and Mn-DABDC (*black*) heated from 27 °C to 700 °C at a heating rate of 5 °C min under air.

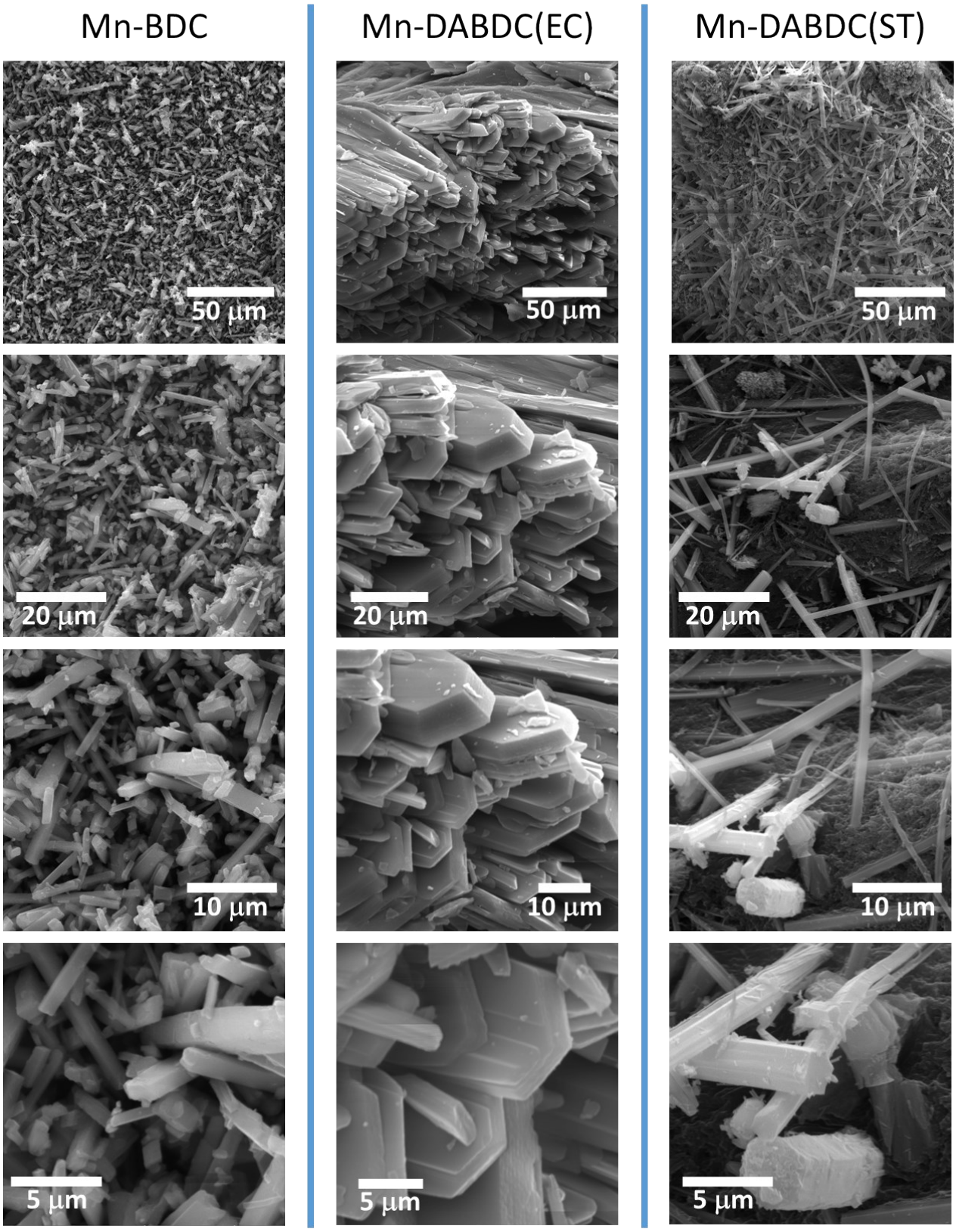

Figure S5. SEM images at increasing magnification for Mn-BDC (*left column*), Mn-DABDC(ES) (*centre column*), Mn-DABDC(ST) (*right column*).

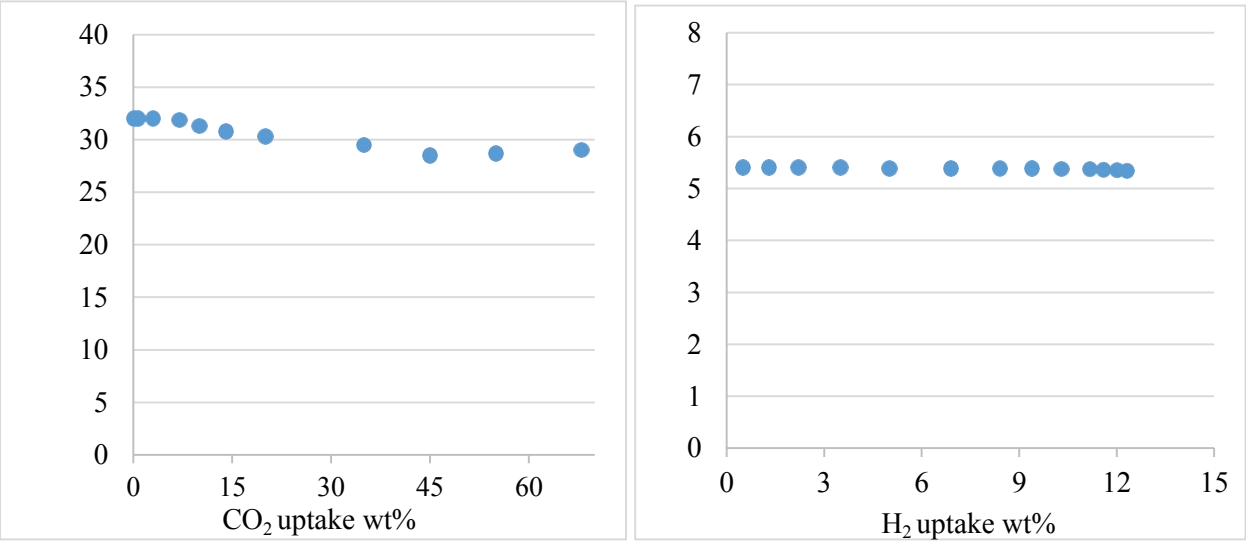

Figure 6. Isosteric heats of adsorption for CO_2 and H_2 for Mn-DABDC(ES) calculated using Clausius-Clapeyron equation.

	Surface area (m^2/g)	**Pore size (nm)**	**Temperature (K)**	**Pressure (bar)**	**H_2 adsorption (wt %)**	**Qst ($kJmol^{-1}$)**
Mn-DABDC (EC)	BET =1453 Langmuir = 1780	3.53	77 77 273 273	1 80 1 80	2.2 12.3 0.02 1.9	5.4

Table S3. Surface area, pore size, H_2 uptake and Qst for Mn-DABDC(ES).