Lithium storage in metal organic framework with diamondoid topology – A case study on metal formates

Kuppan Saravanan, Mangayarkarasi Nagarathinam, Palani Balaya* and Jagadese J. Vittal*

Supporting Information

Gibb's free energy calculations:

$Zn_3(HCOO)_6 + 6\ Li^+ + 6\ e^- \leftrightarrow 3Zn + 6HCOOLi$ (reaction spontaneous)----------(1)

Zinc formate (KJ/mol)	Lithium formate (KJ/mol)	$\Delta G = \Delta Gp - \Delta G_R$ (KJ/mol)
-864.8	-612	-360 KJ/mol

$Zn(HCOO)_2 \leftrightarrow ZnO + CO + CO_2 + H_2$ (Reaction not spontaneous)----------(2)

Zinc formate (KJ/mol)	ZnO (KJ/mol)	CO_2 (KJ/mol)	CO (KJ/mol)	H_2 (KJ/mol)	$\Delta G = \Delta G_p - \Delta G_r$ (KJ/mol)
-864.8	-307	-394	-137	0	+26 KJ/mol

$Zn(HCOO)_2 + Li \leftrightarrow ZnO + Li_2O + 2CO + H_2$ (Reaction spontaneous)----------(3)

Zinc formate (KJ/mol)	Li_2O (KJ/mol)	ZnO (KJ/mol)	CO (KJ/mol)	H_2 (KJ/mol)	$\Delta G = \Delta G_p - \Delta G_r$ (KJ/mol)
-864.8	-367	-307	-137	0	-84 KJ/mol

From this calculation it is clear that formation of lithium formate (eqn-1) is more favourable than ZnO/Li_2O formation (eqn-3).

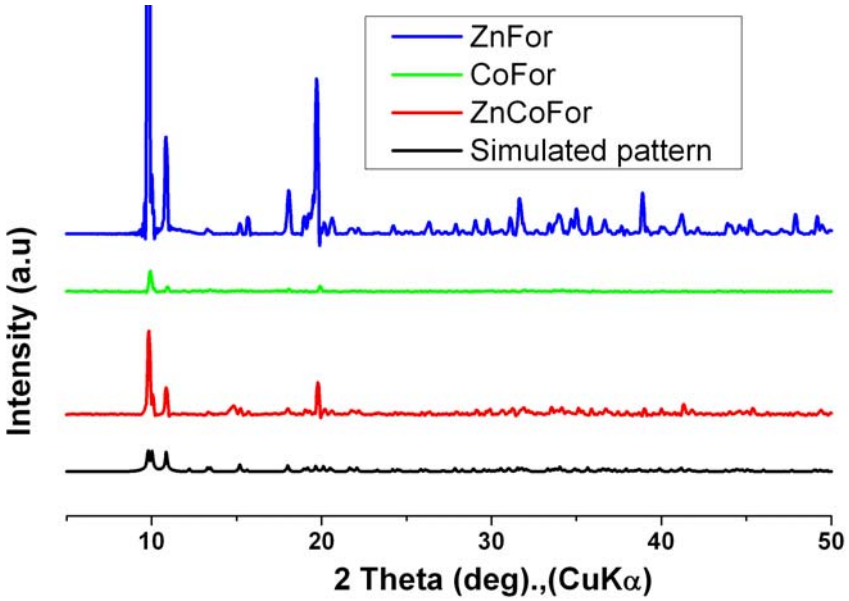


Fig. S1 PXRD patterns of MFor [M = Zn (FOR1), Co (FOR3) and ZnCo (FOR4)] with their simulated PXRD pattern.

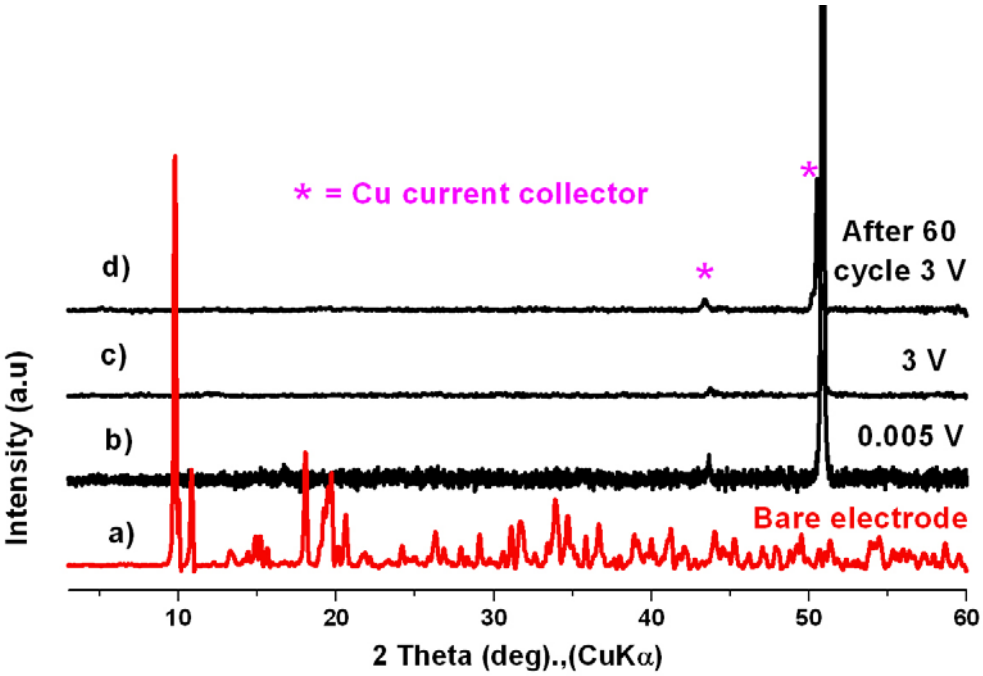


Fig S2 Ex-situ PXRD patterns of the electrodes of bare FOR1, and those b) discharged to 0.005 V, c) charged to 3.0 V and d) after 60 cycles. Lines due to Cu-current collector are marked with *.

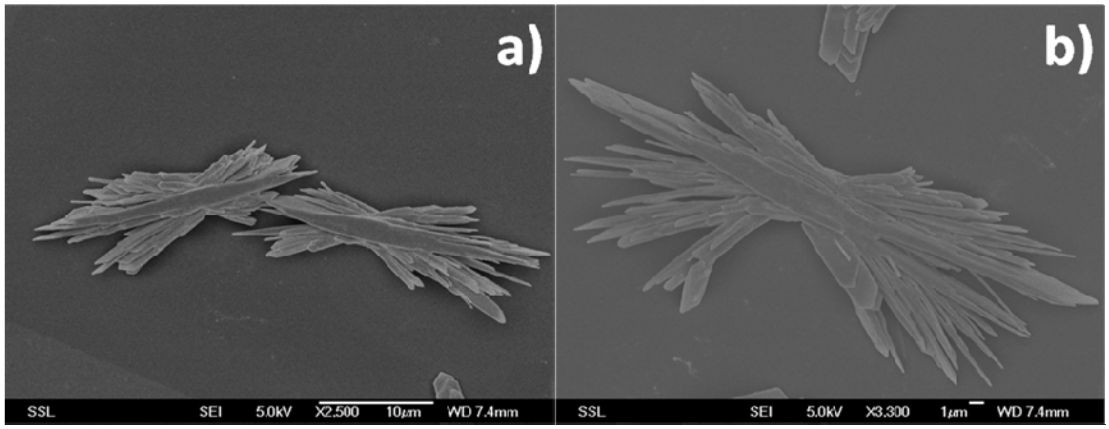


Fig.S3 FESEM images of the FOR1 $[Zn_3(HCOO)_6]$ plates at two different magnifications

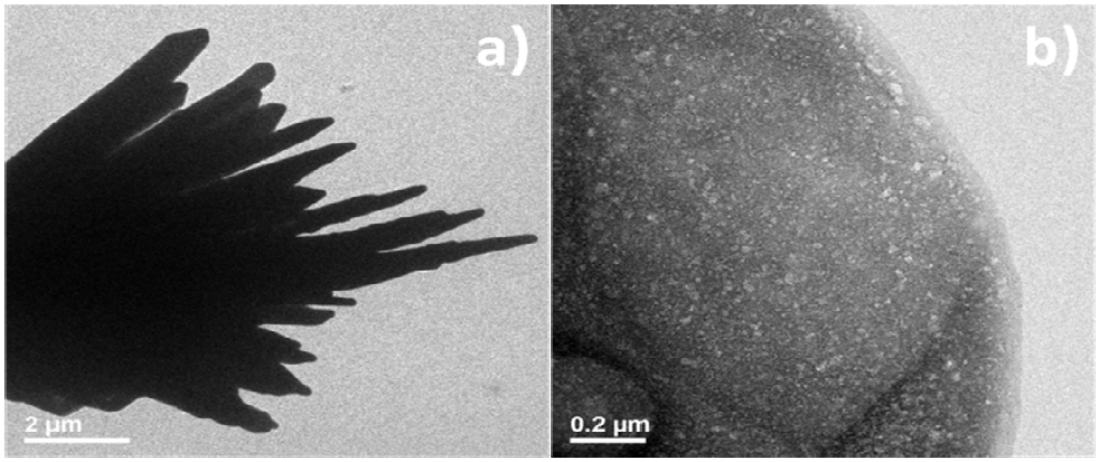


Fig. S4 TEM images of the diamondoid FOR1 $[Zn_3(HCOO)_6]$ at two different magnifications

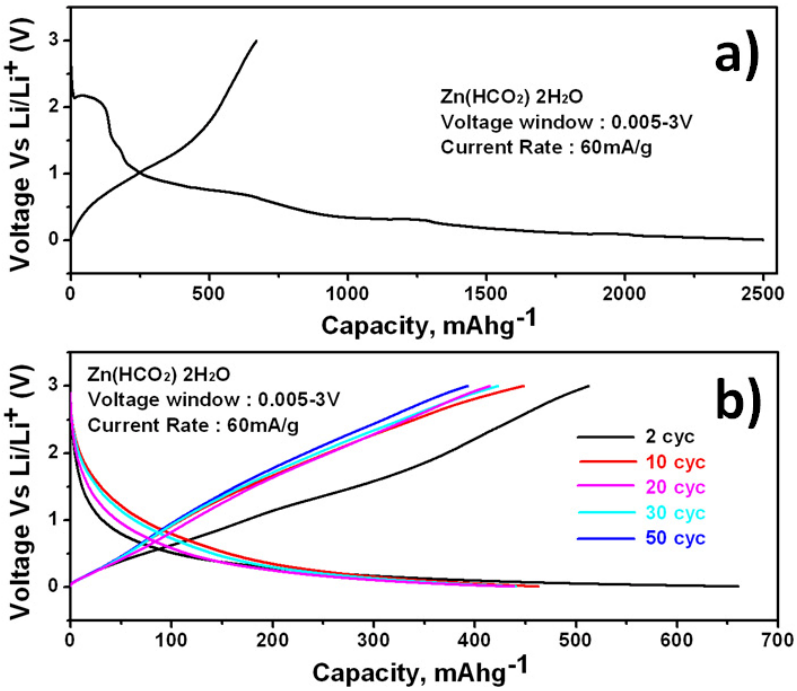


Fig. S5 Galvanostatic charge–discharge cycle curves for FOR2 (a) 1st cycle and (b) selected cycles. (Current density of 60 mA/g (0.11C) plot. Potential window 0.005 – 3 V, recorded at room temperature)

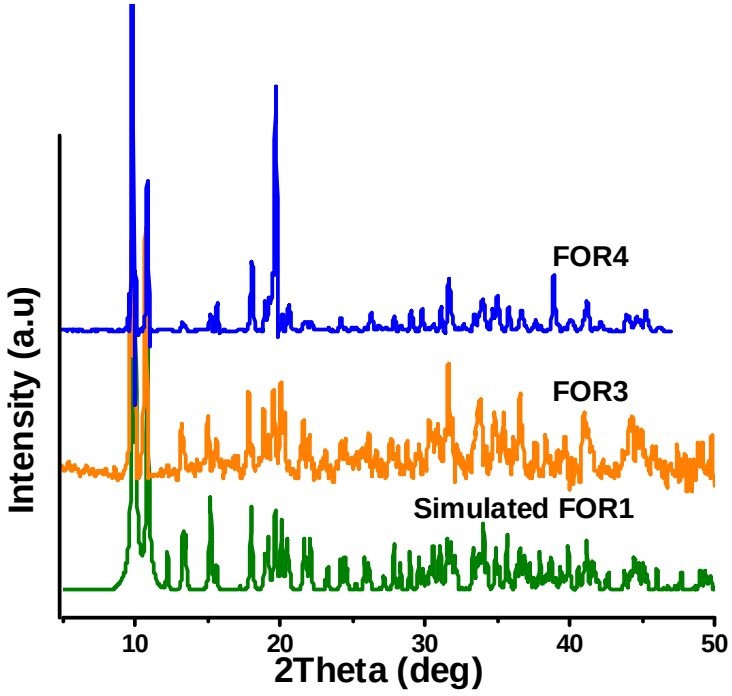
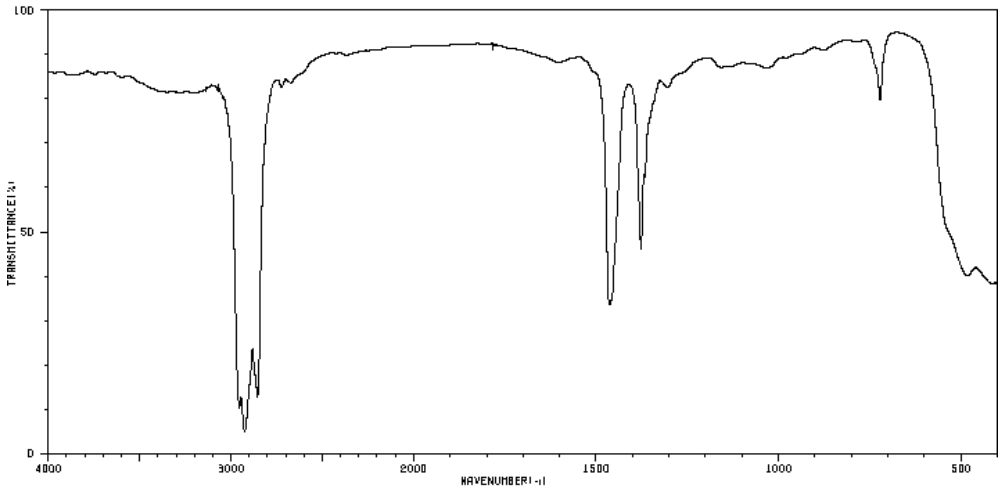


Figure S6 PXRD patterns of FOR1, FOR3 and FOR4

FTIR of ZnO



CAS Registry Number:1314-13-2

Formula: Zn O

CA Index Name: Zinc oxide (ZnO)

SpectrumID: NIDA69905

Spectrometer: Nicolet 170SX or JASCO FT/IR-410

Source: Integrated Spectral Database System of Organic Compounds. (Data were obtained from the National Institute of Advanced Industrial Science and Technology (Japan))