Electronic Supporting Information

Ni_2Mn-layered double oxide electrodes in organic electrolyte based supercapacitors†

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Chemicals and Materials

Carbon black, (Super P® Conductive, 99+% metals basis, Alfa Aesar), Polyvinylidene fluoride (average molecular weight ~534,000 g mol^{-1}, powder, PVDF, Sigma-Aldrich), 1-Methyl-2-pyrrolidinone (NMP, Sigma-Aldrich), activated charcoal (AC, Sigma-Aldrich), tetraethylammonium tetrafluoroborate ($TEABF_4$, 99%, Sigma-Aldrich), acetonitrile (AN, anhydrous, 99.8%, Sigma-Aldrich), manganese(II) nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$, >97%, Honeywell), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, >98.5%, Sigma-Aldrich), sodium carbonate (Na_2CO_3, 99.6%, Acros Organics), nickel(II) hydroxide ($Ni(OH)_2$, Sigma-Aldrich), manganese dioxide (MnO_2, activated, ~85%, <10 μm, Sigma-Aldrich), nitric acid (70%, Fisher), sodium hydroxide (NaOH, Sigma-Aldrich) were received and used without further treatment. Nickel foam (purity > 99.99%, porosity >= 95%, thickness: 1.6 mm, MTI Corporation) were received, cut into 3 cm x 1 cm stripes and sonicated in hydrochloric acid (~37%, Fisher) for 5 minutes, followed sonication in deionised water for 5 minutes, sonication in acetone for another 5 minutes to remove surface nickel oxide layer, before drying overnight in an oven at 60 °C.

Materials characterisation

Powder X-ray diffraction (XRD) was conducted on a diffractometer (PAN-Analytical X'Pert Pro) at 40 kV and 40 mA using Cu K radiation (α1 = 1.54057 Å, α2 = 1.54433 Å, weighted average = 1.54178 Å) from 5 to 70°. The chemical state and chemical compositions of LDH and LDOs were studied using a Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS) System, with an ion pumped VG Microtech CLAM 4 MCD analyser system equipped with a 200 W unmonochromated Mg Kα X-ray radiation of 1253.6 eV, with detection limits of ~0.2 atomic %. Thermogravimetric analyses of LDH were carried out using a TGA/DSC1 STAR^e system (METTLER TOLEDO) from 30-900 °C at a ramp rate of 10 °C min^{-1} in constant air flow (50 mL min^{-1}). Differential thermogravimetric analysis (DTG) was obtained from the 1st derivative of TGA data. Morphology and elemental distribution of LDH and LDOs were observed using a Transmission Electron Microscopy (TEM, JEOL-2100, operated at 200 kV) with an energy-dispersive X-ray Inca spectrometer (EDS, Oxford Instruments). Nitrogen sorption analysis was performed using a porosity analyser (Micrometric TriStar) at -196 °C.

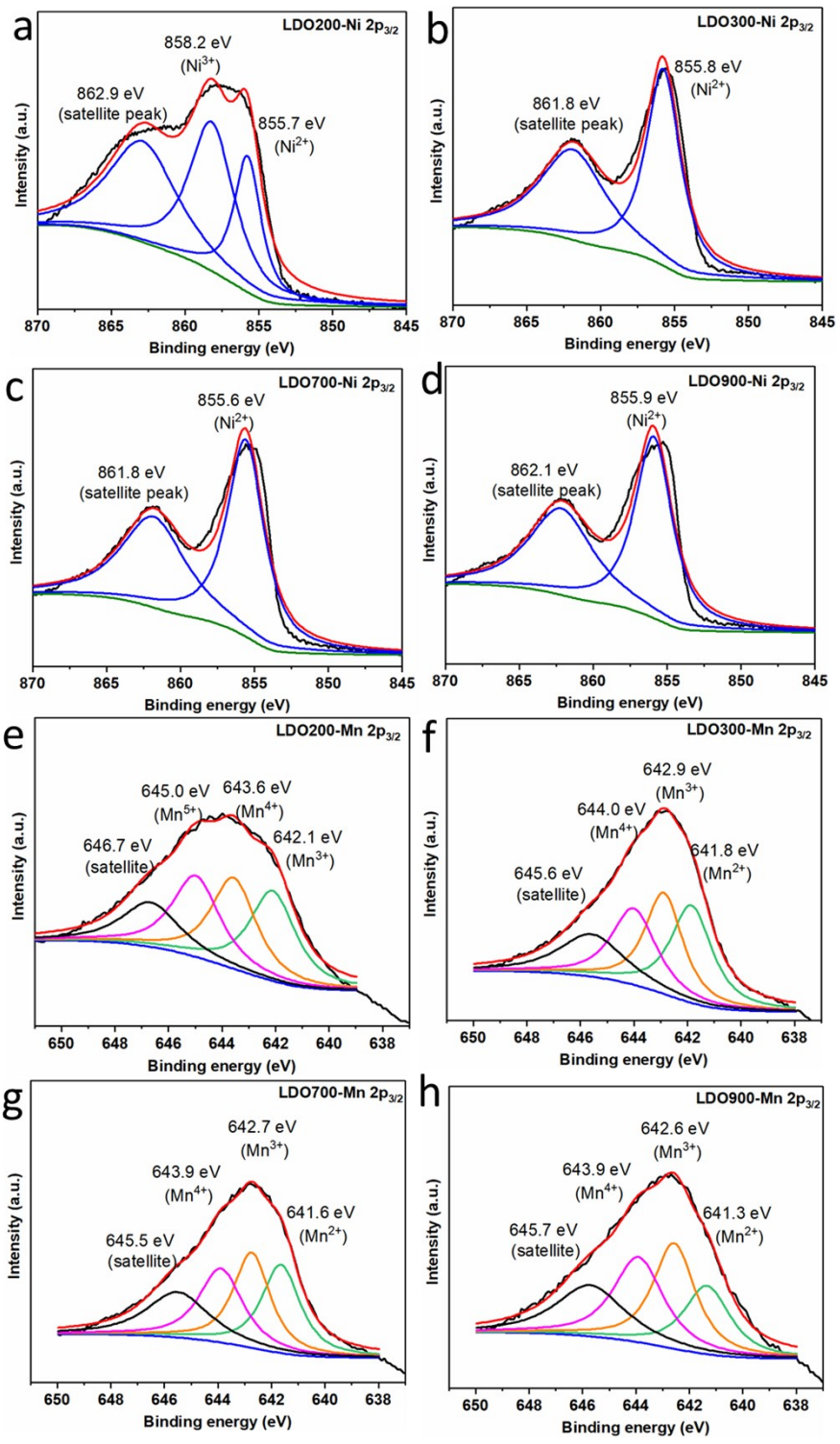
a
LDO200-Ni 2p3/2
858.2 eV
(Ni3+)
862.9 eV
(satellite peak)
855.7 eV
(Ni2+)
b
LDO300-Ni 2p3/2
855.8 eV
(Ni2+)
861.8 eV
(satellite peak)
c
LDO700-Ni 2p3/2
855.6 eV
(Ni2+)
861.8 eV
(satellite peak)
d
LDO900-Ni 2p3/2
855.9 eV
(Ni2+)
862.1 eV
(satellite peak)
e
LDO200-Mn 2p3/2
645.0 eV
(Mn5+)
643.6 eV
(Mn4+)
646.7 eV
(satellite)
642.1 eV
(Mn3+)
f
LDO300-Mn 2p3/2
642.9 eV
(Mn3+)
644.0 eV
(Mn4+)
641.8 eV
(Mn2+)
645.6 eV
(satellite)
g
LDO700-Mn 2p3/2
642.7 eV
(Mn3+)
643.9 eV
(Mn4+)
641.6 eV
(Mn2+)
645.5 eV
(satellite)
h
LDO900-Mn 2p3/2
642.6 eV
(Mn3+)
643.9 eV
(Mn4+)
641.3 eV
(Mn2+)
645.7 eV
(satellite)
Intensity (a.u.)
Binding energy (eV)

Fig. S1. XPS spectra of Ni 2p3/2 for (a) LDO200, (b) LDO300, (c) LDO700, (d) LDO900, XPS spectra of Mn 2p2/3 for (e) LDO200, (f) LDO300, (g) LDO700 and (h) LDO900 indicated that there are Ni2+ and mixing of Mn2+/Mn3+/Mn4+ in LDO300, LDO700 and LDO900 while mixing of Ni2/Ni3+ and mixing of Mn3+/Mn4+/Mn5+ for LDO200.

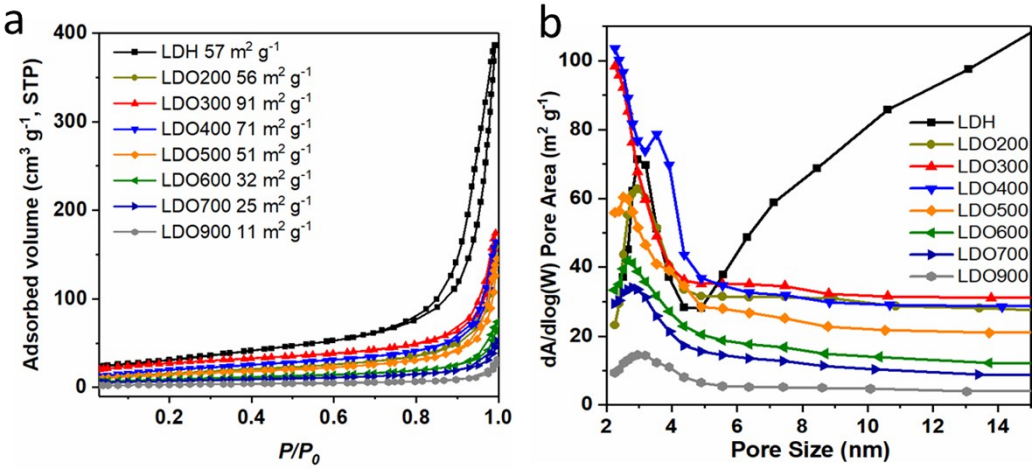

Fig. S2. (a) N_2 adsorption isotherms of LDH and LDOs and (b) BJH pore size distribution of LDH and LDOs.

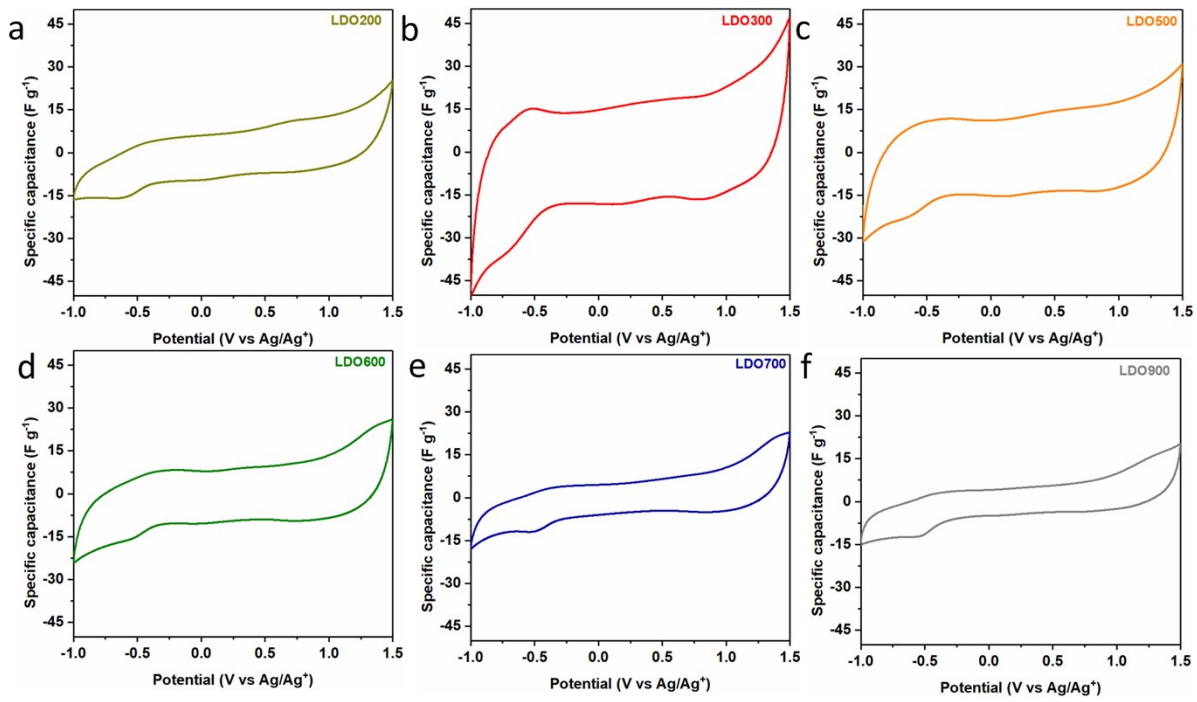

Fig. S3. CV curves of (a) LDO200, (b) LDO300, (c) LDO500, (d) LDO600, (e) LDO700 and (f) LDO900 at the scan rate of 50 mV S^{-1}. Electrolyte: 1 M tetraethylammonium tetrafluoroborate ($TEABF_4$) in acetonitrile.

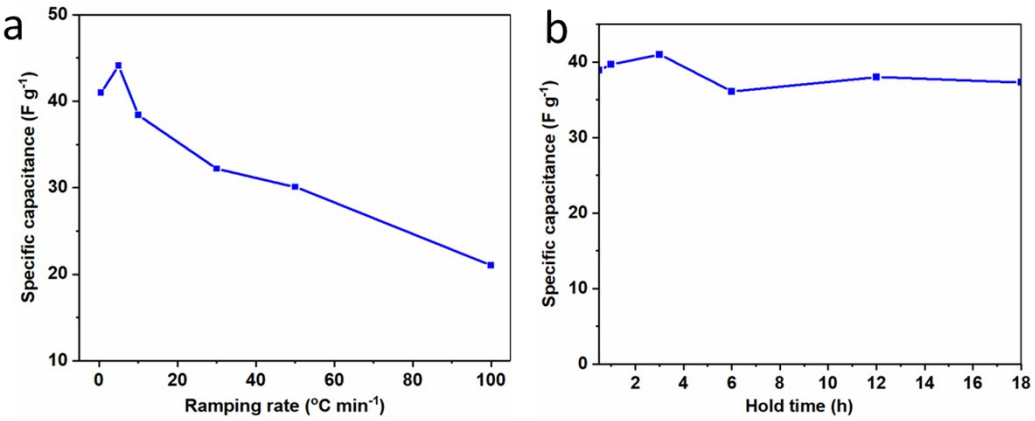

Fig. S4. (a) The effect of calcination ramping rate (calcination temperature and holding time fixed at 400 ˚C and 3 h, respectively) and (b) the effect of calcination holding time rate (calcination temperature and ramping rate fixed at 400 ˚C and 5 ˚C min^{-1}, respectively) on the specific capacitance of LDO400 showing that generally, lower ramping rate, higher specific capacitance and the effect of calcination hold time is negligible. Electrolyte: 1 M tetraethylammonium tetrafluoroborate ($TEABF_4$) in acetonitrile.