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$LiMn_2O_4/LiMn_{1.5}Ni_{0.5}O_4$ composite to boost the electrochemical cyclic stability of $LiMn_2O_4$

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Outline of my talk

- Introduction & applications of LIB
- $LiMn_2O_4$ (LMO), $LiMn_{1.5}Ni_{0.5}O_4$(LMNO) cathodes and their challenges
- LMO nanorods
- Microwave irradiated LMNO, LMNOmic
- LMO/LMNO composite cathode
- Conclusion

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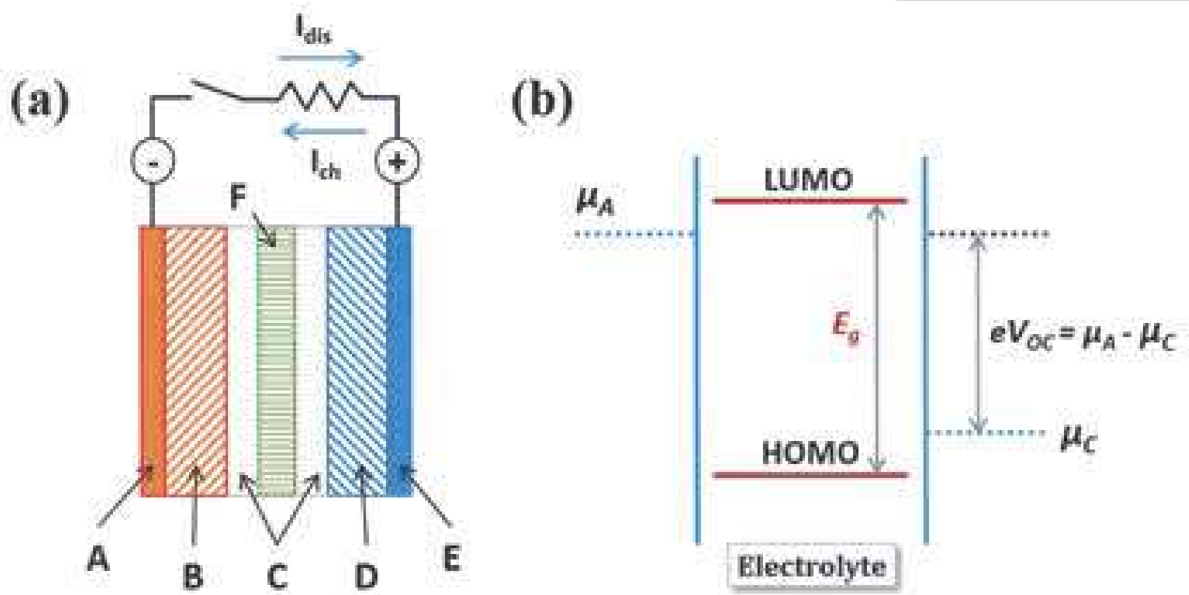
Components of a Battery Cell



- The difference in chemical potential between the anode (μ_A) and the cathode (μ_C) is the working voltage (open circuit voltage), V_{OC} :

$$V_{oc} = \frac{\mu_A - \mu_c}{e}$$

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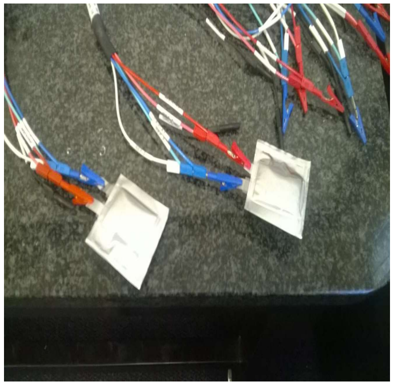
Electrochemical Energy Technologies (EET)

- Lithium & Sodium ion batteries
- Electrochemical capacitors

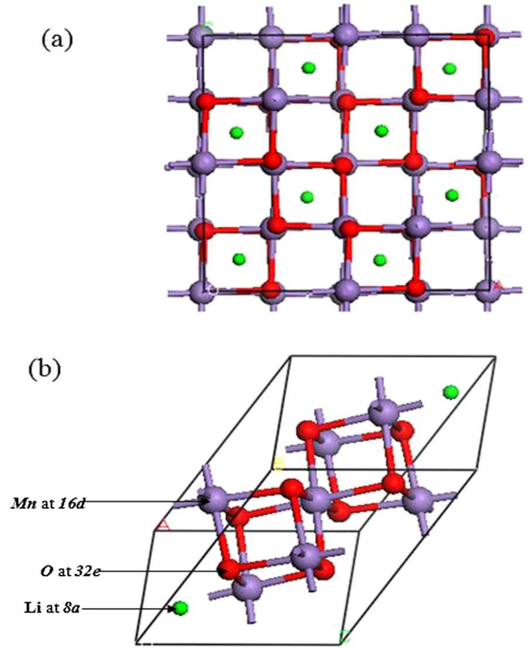
<u>Targets</u>

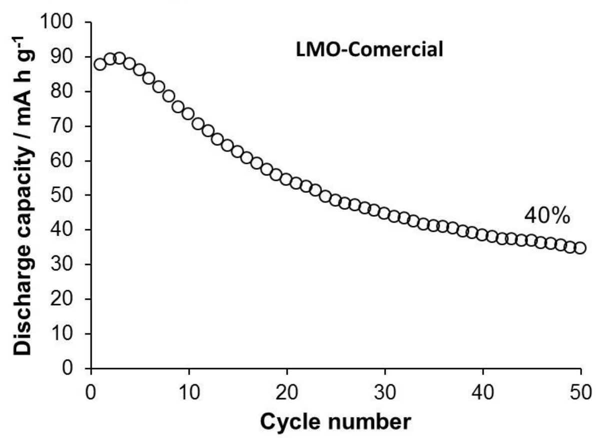
- Electric vehicles
- Stationary / utility

Pouches lighting LED

LMO structure, challenges & strategies





Research Challenges for $LiMn_2O_4$ spinel

- ✓ Jahn-Teller distortion in the 3V region, which is due to the generation of new phases during cycling
- ✓ Disproportion reaction in the 4 V.

$$2Mn^{3+}\,(S) \rightarrow Mn^{4+}\,(S) + Mn^{2+}\,(solution)$$

- ❑ ***Doping***
  - ✓*Structural stabilisation, enhanced electrochemistry*
- ❑ ***Nano-sizing***
  - ✓*Enhanced mass transport properties*
- ❑ ***Surface-coating***
  - ✓*Structural stabilisation, enhanced electrochemistry*
- ❑ ***Microwave irradiation***
  - ✓ *Control manganese valence state*
  - ✓*Structural stabilization*

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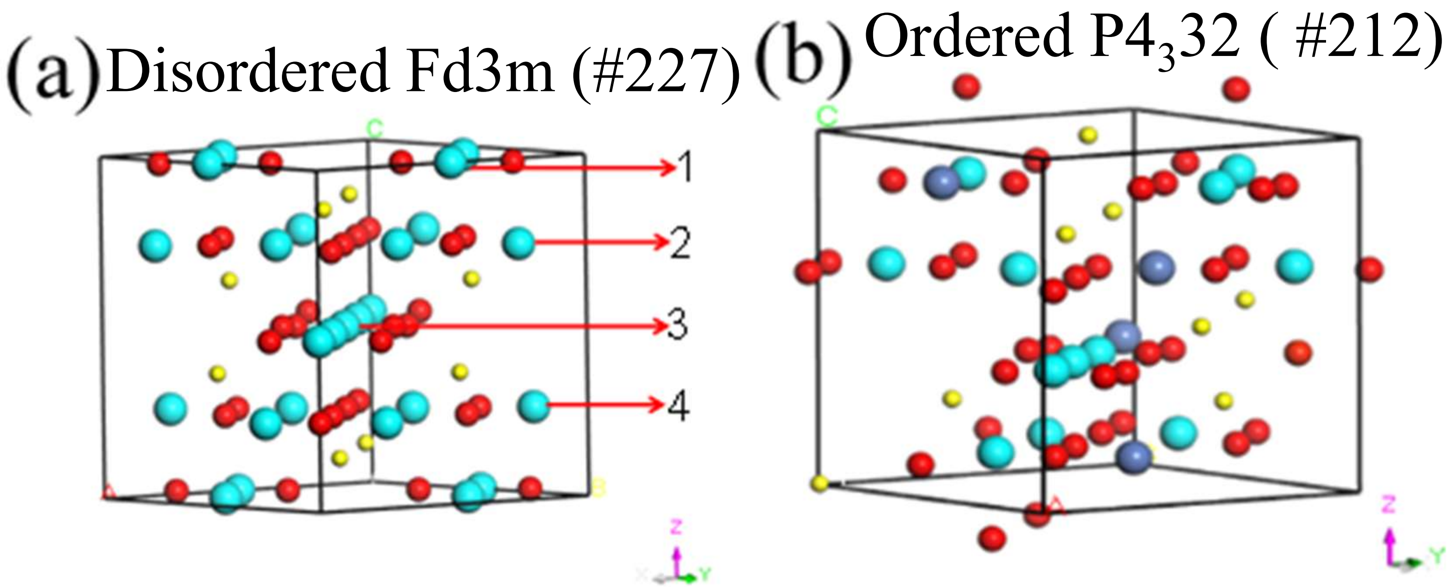
LMNO structure, challenges & strategies



Research Challenges for LMNO spinel

✓ Capacity fading at high C-rate.

Strategy

✓ Co-doping (i.e. Co, Cr, Fe, etc.)

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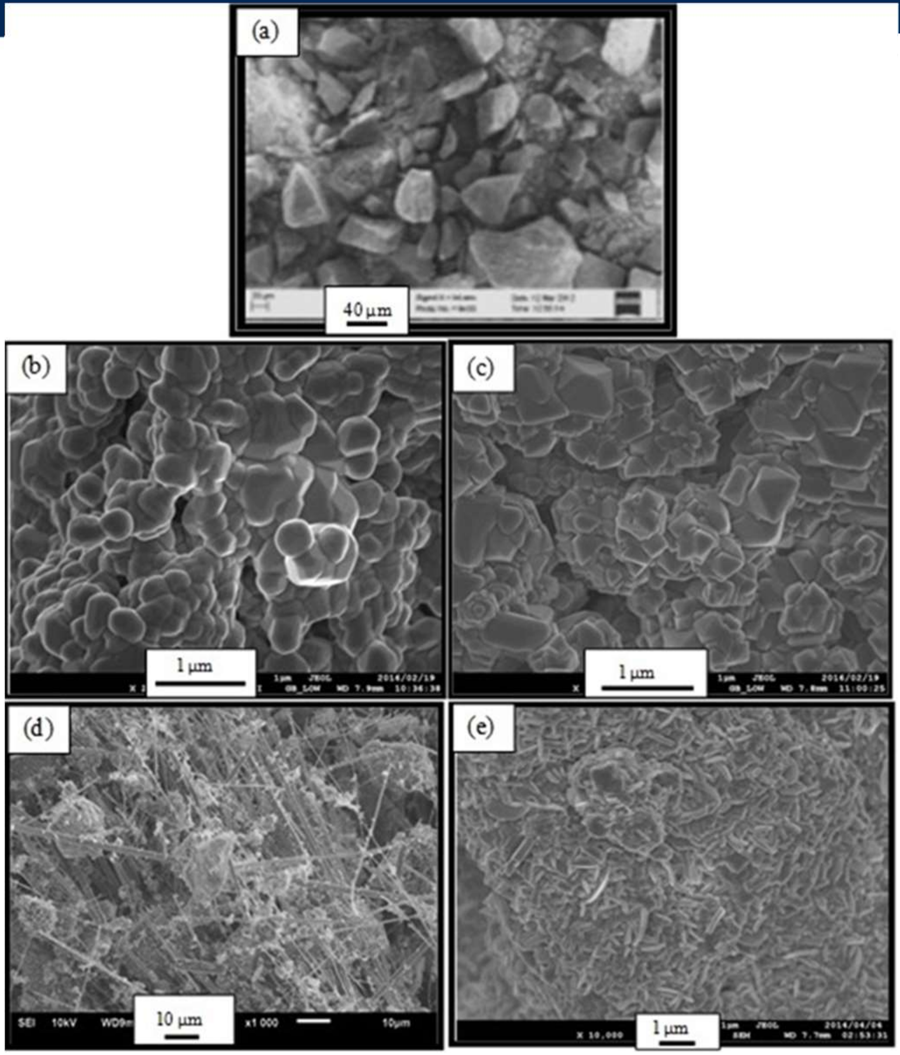
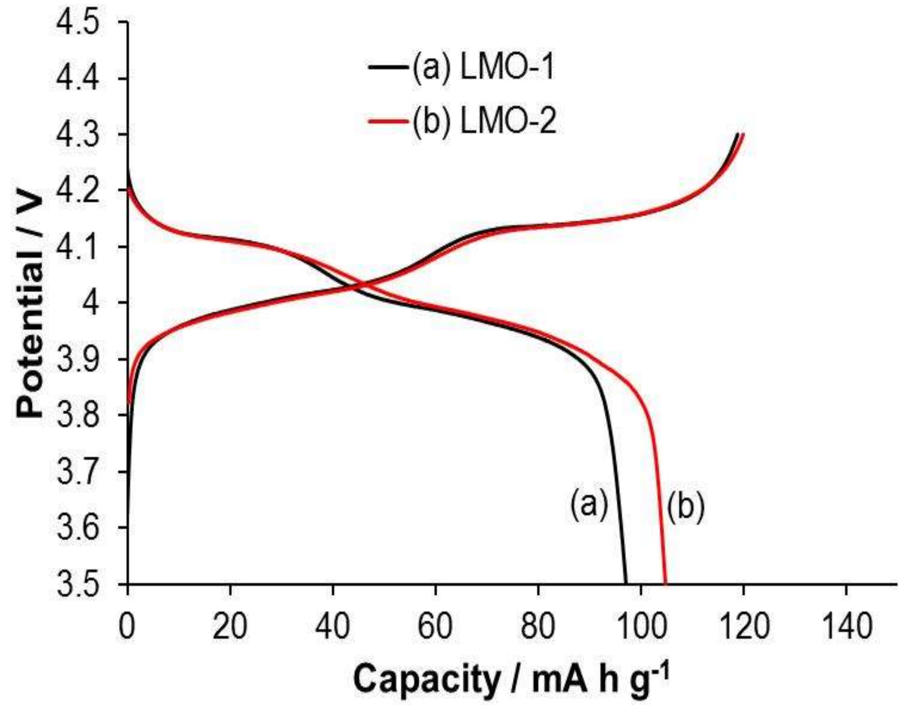
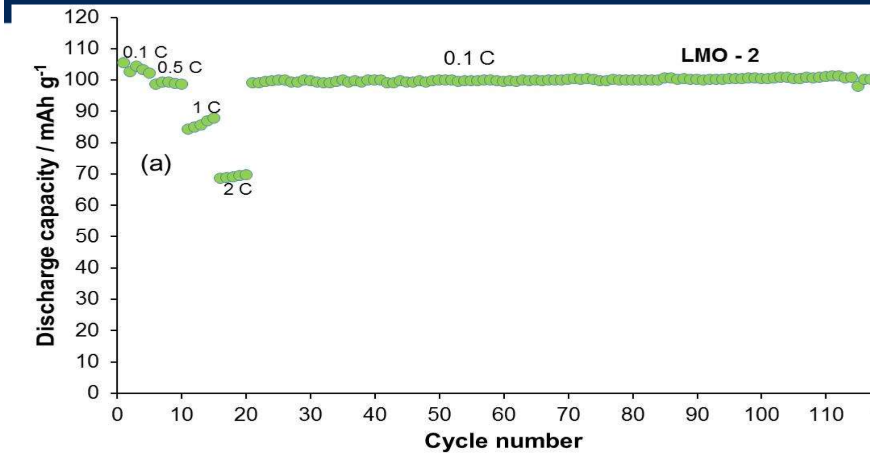
(i) - LMO nanorods





Cyclic performance



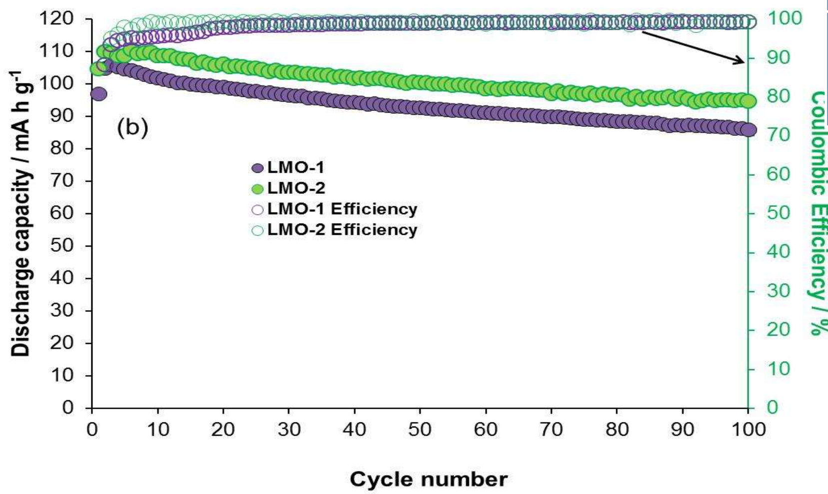


Table 1 Comparison results of discharge capacity and capacity retention with previously reported results

Material name	Capacity 1st (cycle)	Capacity 100th (cycle)	Retention 100th (%)	Current density (C)
$LiMn_2O_4$ [18] (nanorod)	100	92	92	0.1
$LiMn_2O_4$ [7] (nanorod)	110	105 (5th cycle)	95	0.1
$LiMn_2O_4$ [11] nanorod	120	109	91	0.1
Present work $LiMn_2O_4$ nanorod	107	95	96	0.1

- LMO-1 and LMO-2 retain 88% and 95% of their 1st discharge capacity after 100 cycles.

Mater. Res. Express 4 (**2017**) 025030

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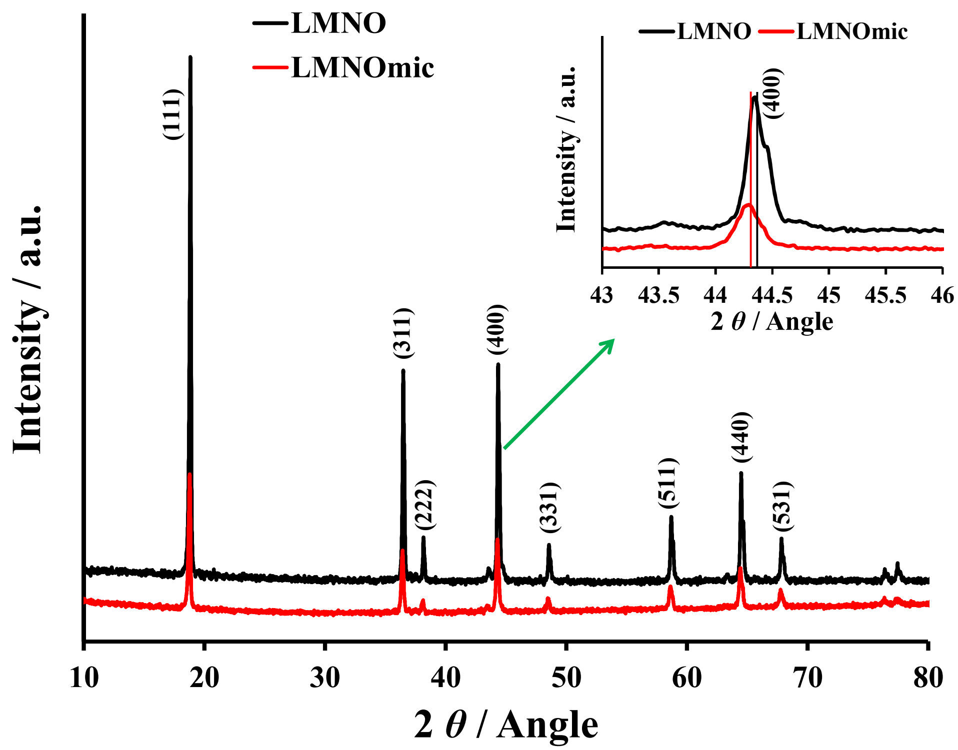
(ii)- High-Voltage $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ Spinel Material Synthesized by Microwave-Assisted Thermo-Polymerization



- Oxygen-deficient pristine (LMNO) and microwave-treated (LMNOmic) cathode materials have been synthesized with modified thermo-polymerization synthesis technique.
- Lattice parameters of LMNO and LMNOmic are **8.167 and 8.182 Å**, respectively.

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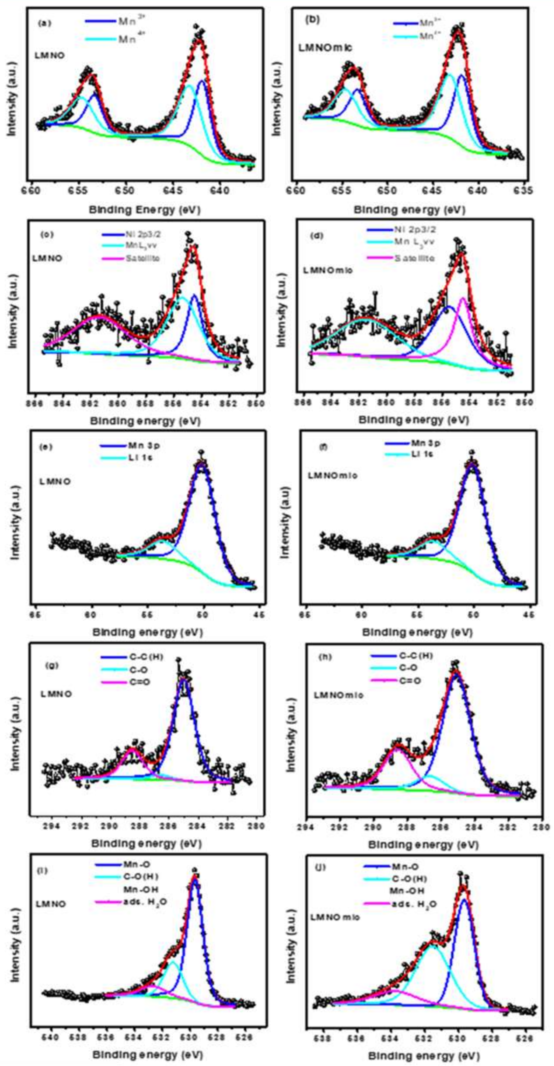
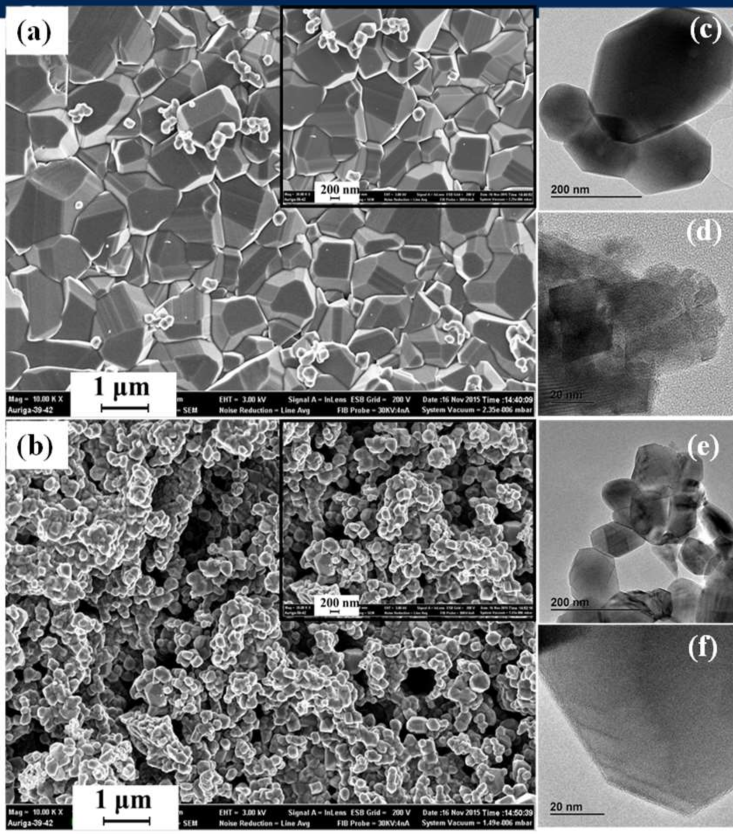
XPS result



Sample	Atomic concentration Li:Mn:Ni:O	% at. ratio Mn^{3+}	% at. ratio Mn^{4+}	Mn valance
LMNO	1:1.17:**0.29**:2.85	46	54	3.54
LMNOmic	1:1.17:**0.23**:2.90	**47**	53	3.53

Particle size of pristine & microwave-treated samples



SEM images of (a) LMNO and (b) LMNOmic; TEM and HR-TEM images of (c, d) LMNO and (e, f) LMNOmic.

This study confirms **microwave treatment reduces the particle size** of the powders which is in consistence with previously reported results[1,2].

- The particle size of microwave-treated samples is reduced to nanoscale **(90 – 210 nm)** as compared to the micron-sized pristine LMNO **(200 nm–1.5 µm).**

1. *ACS applied materials & interfaces., 5, 15 (2013).*
2. *RSC Advances, 5, 41 (2015).*

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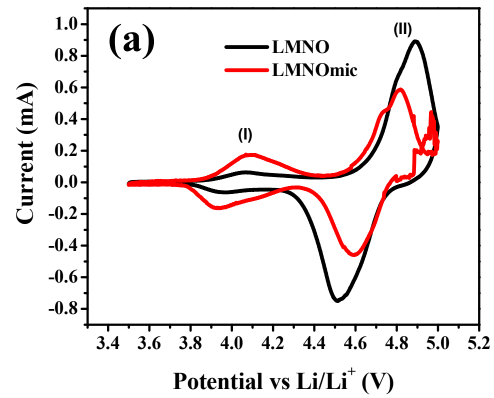
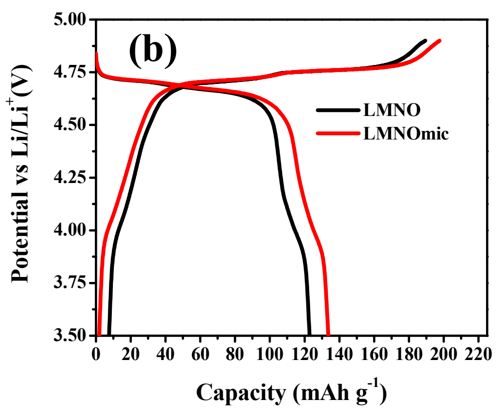
Electrochemical Properties: Cyclic Voltammetry and 1st Cycle Charge-Discharge:





- The initial discharge capacities are **122** and **133 mA h g^{-1}** for the LMNO and LMNOmic, respectively. This result indicates that the microwave irradiation increased the oxygen-defect degree of the LMNO sample, thus improving the capacity.

(a) cyclic voltammogramms of the LMNO and LMNOmic; (b) The first cycle voltage profiles of pristine LMNO and microwave-treated LMNO, between 3.5 and 4.9 V at 0.1 C rate.

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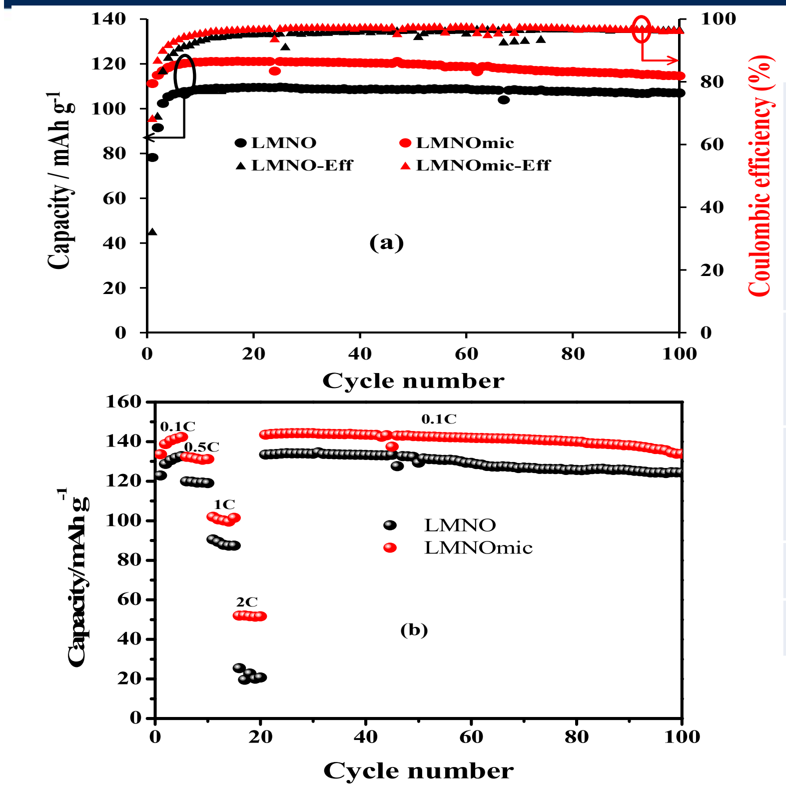
Galvanostatic Charge-Discharge:



Sample	1^{st} cycle capacity	100^{th} cycle capacity	Current rate (C=14.7 mA/g)	Capacity retention (%)	References
LMNO	**121.2** (25^{th})	118.24	0.1	97	This work
LMNO mic	**133.3** (17^{th})	126.3	0.1	95	This work
LMNO	121.4	84.1	0.1	69.3	Ref. 26
LMNO	133	129	1.0	97	Ref. 27

- Different C-rates, at 0.1 C the LMNO and LMNOmic materials delivered initial capacity **of 123 and 134 mAh g-1**, respectively.
- At **2 C**, LMNO and LMNOmic materials delivered initial capacity of **25 and 52 mA h g^{-1}**.
- The LMNOmic showed superior capacity compared to the LMNO at all C-rates. Our result is comparable to reported LMNO samples.26,27

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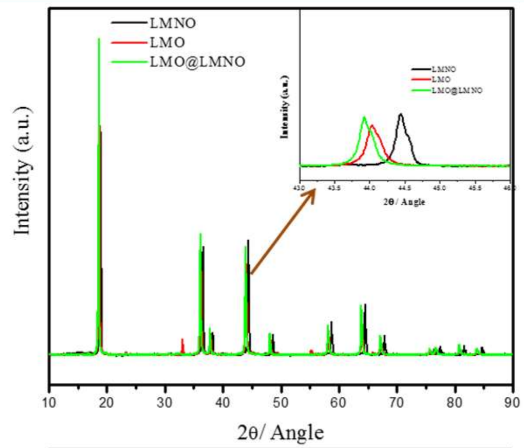
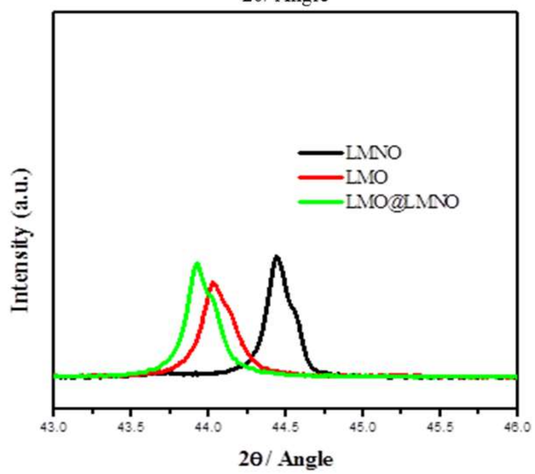
(iii)-XRD of LMO, LMNO, and LMO/LMNO

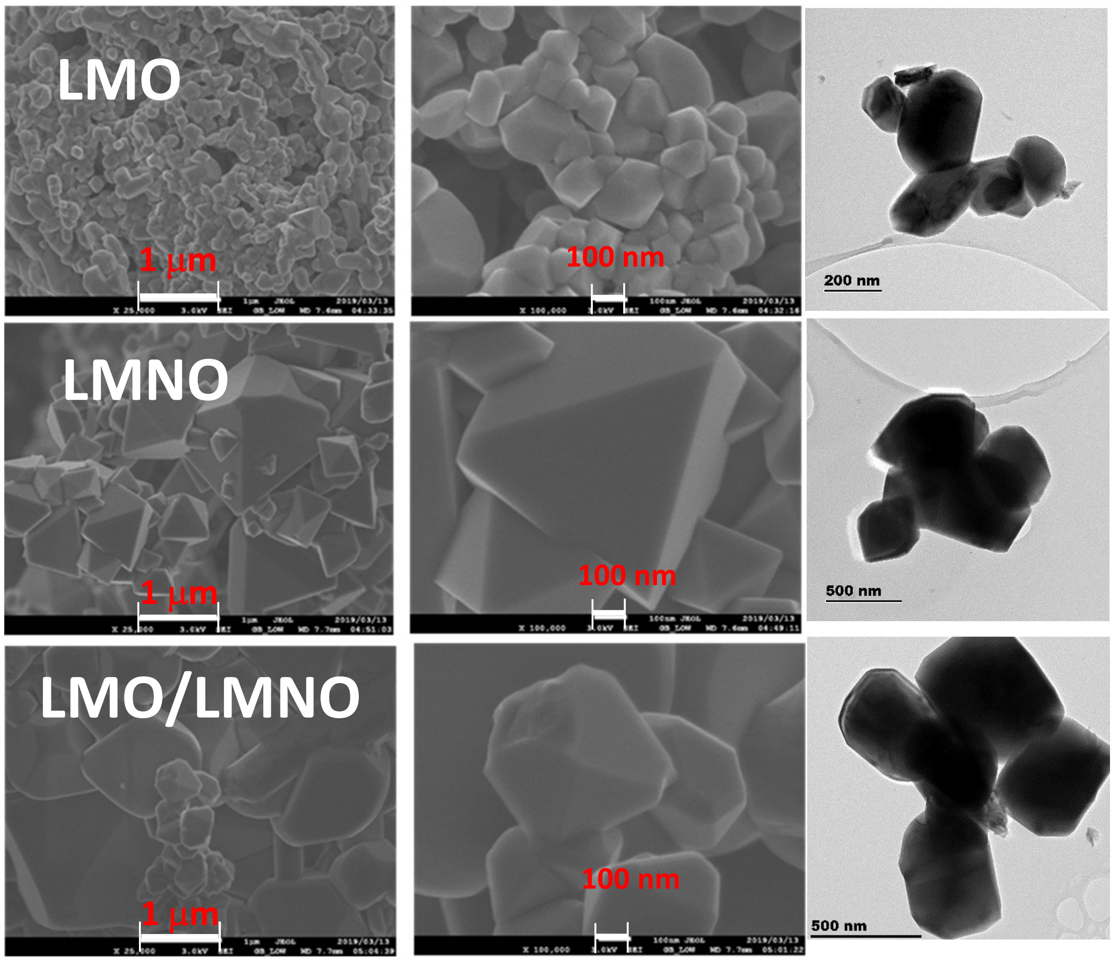




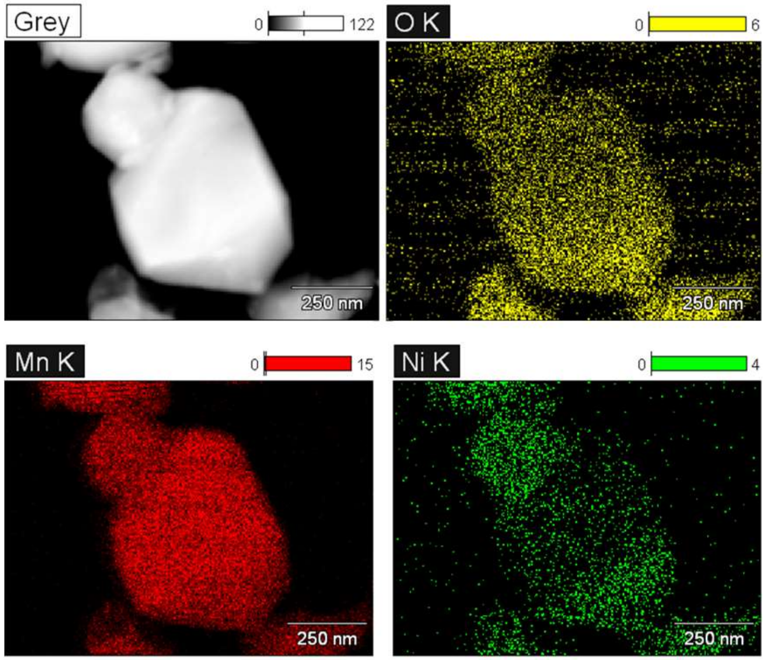
Materials Name	Lattice parameter (Å)	Crystalline size (nm)
LMO	8.234	70.9
LMNO	8.174	84.4
LMO/LMNO	8.233	71.0

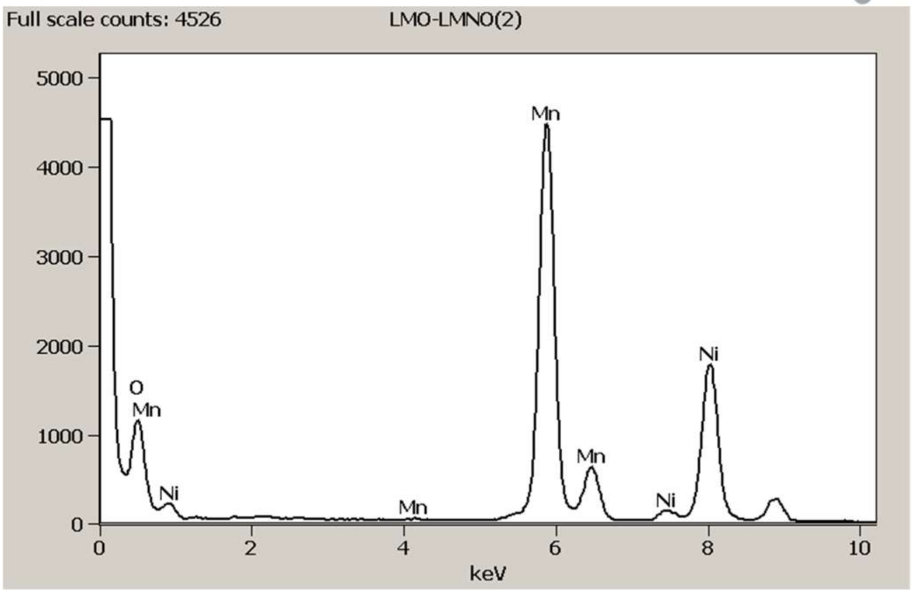
Fig. (a) XRD pattern, and (b) peak shift at (440) plane for LMO, LMNO, and LMO/LMNO.

SEM, TEM and HR-TEM images

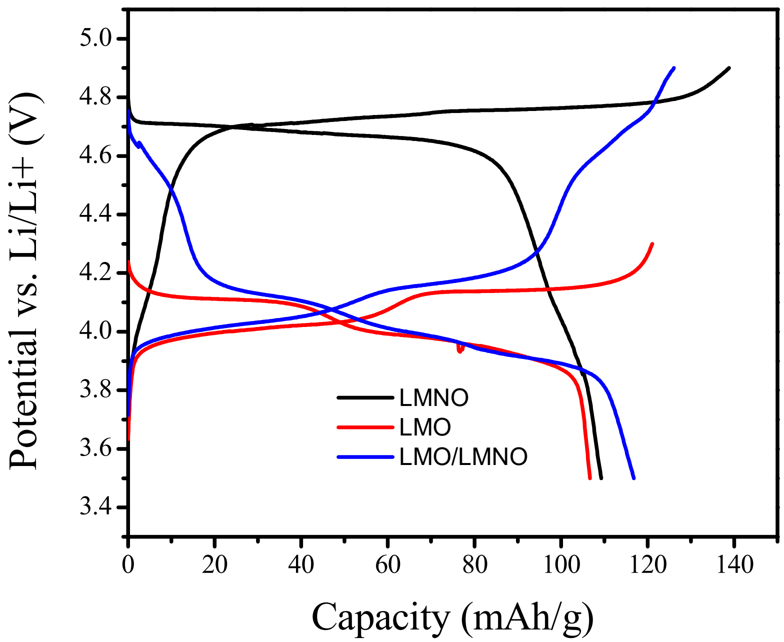


Mapping and EDS





Electrochemical performance



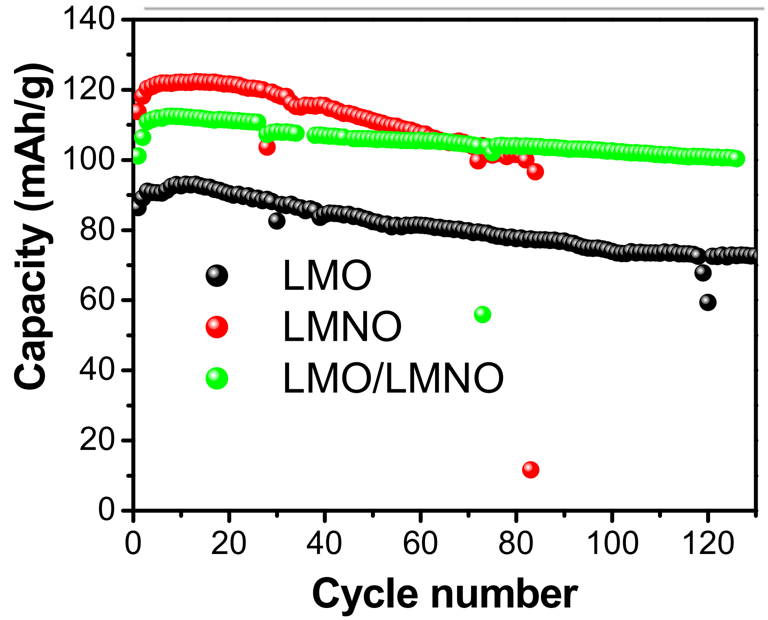
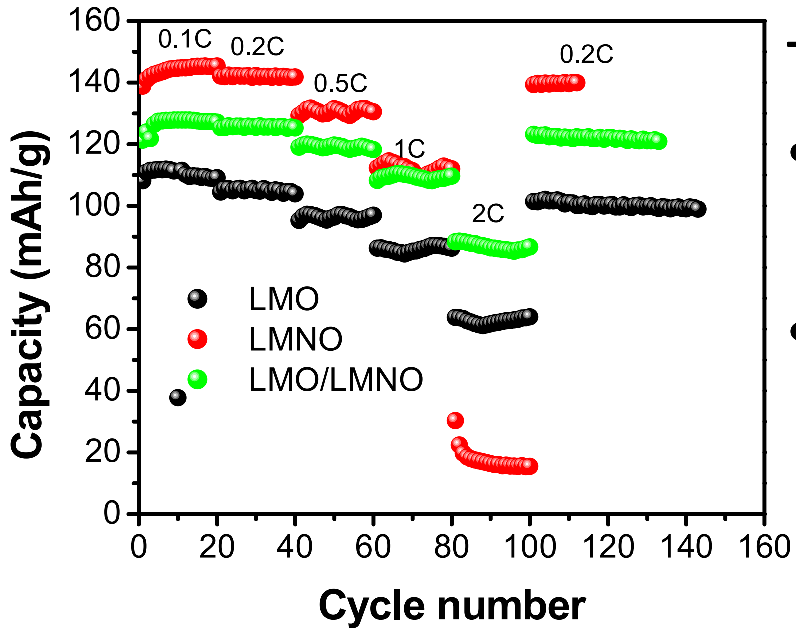


Fig. (a) 1st cycle of voltage vs. capacity, (b) cycling performance graphs for LMO, LMNO, and LMO/LMNO.

Rate capability



The rate capability result

- For 0, 1, 0,2, and 0,5C LMNO shows high capacity.
- From 1C and 2C rates the combined LMO/LMNO shows high capacity and stable.

Fig. Shows rate performance of LMO, LMNO, LMO/LMNO

CONCLUSIONS

- LMO-2 nanorods successfully synthesized
- LMO-2 nanorods have retained about 95% of 105 mA h g^{-1} whereas LMO-1 nanoparticles retained 88% of 97 mA h g^{-1}.
- High-voltage, oxygen-deficient $LiMn_{1.5}Ni_{0.5}O_{4-\delta}$ cathode materials were synthesized with microwave-assisted thermo-polymerisation synthesis method.
- The results confirmed that microwave radiation is inherently able to **nanostructure the spinel for improved physic-chemical properties and electrochemical performance**.
- For example, microwave **irradiation slightly decreased Ni-content** in the structure with enhanced capacity, without compromising on the high voltage.
- LMO/LMNO composite material showing a **better electrochemical performance** as compared to both LMO and LMNO.

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Acknowledgments

- CSIR, Electrochemical Energy Tech Group
- NRF

Thank you for your attention

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