A lithium ion battery exploiting a composite Fe_2O_3 anode and a high voltage $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ cathode

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SUPPLEMENTARY INFORMATION

A comparison of the structural and electrochemical properties of the $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ and the bare $LiNi_{0.5}Mn_{1.5}O_4$ [1], used as the reference cathode, is here reported in order to shed light on the effects of Fe-doping on the performances of the spinel electrode.

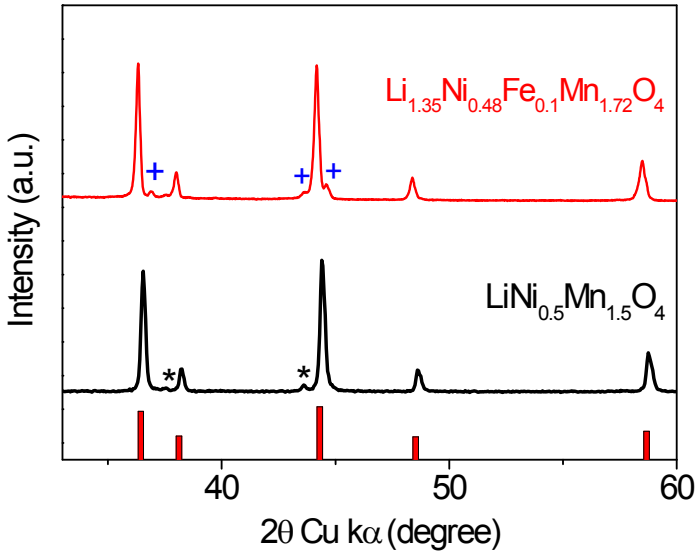


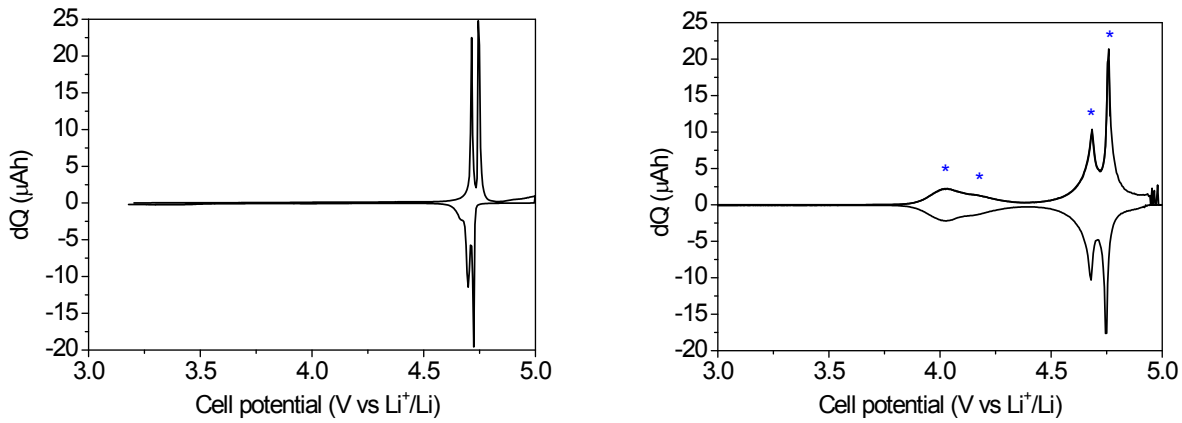
Figure S1

Figures S1 displays the XRD patterns of the undoped $LiNi_{0.5}Mn_{1.5}O_4$ and the Fe-substituted $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ powders.

The XRD patterns show the characteristic signals of the spinel, Fd-3m phase (JCPDS n. 802162). The peaks at about 37.6° and 43.5°, marked with asterisks in the $LiNi_{0.5}Mn_{1.5}O_4$ diffractogram, may be attributed to the presence of a $Li_xNi_{1-x}O$ impurity phase, as reported in literature papers [2-4].

As expected, the $Li_xNi_{1-x}O$ impurity phase can be barely detected in the $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$. pattern. According to literature data [4,5], partial substitution of Mn and Ni with other cations can reduce the amount of impurities formed during the synthesis of the spinel electrode.

Moreover an additional phase in the $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ pattern, with signals at about 36.9°, 43.6° and 44.6° (blue crosses in Fig.S1) can be detected. These signals may be most reasonably assigned to a mixed $Li_xNi_yFe_wO_z$ phase.



a **b**

Figure S2

The results of Potentiodinamic Cycling with Galvanostatic Acceleration (PCGA) tests on a Li / $LiPF_6$ 1M, EC:DMC 1:1/ $LiNi_{0.5}Mn_{1.5}O_4$ and a Li/$LiPF_6$ 1M, EC:DMC 1:1/$Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ cell are shown in Figure S2 a and S2 b, respectively.

Both the $LiNi_{0.5}Mn_{1.5}O_4$ and the $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ profiles show the signals associated to the Ni^{2+}/Ni^{3+} and the Ni^{3+}/Ni^{4+} redox couples, respectively at 4.71 and 4.75 V vs Li^+/Li and at 4.68 and 4.76 V vs Li^+/Li (The corresponding reduction processes can be noticed at 4.69 and 4.73 V vs Li^+/Li and at 4.68 and 4.75 V vs Li^+/Li, respectively).

The $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ electrode shows two additional redox processes at about 4 and 4.17 V vs Li^+/Li. As already discussed in the manuscript (see Fig. 4a discussion), iron-doping may alter

the Mn^{3+} ions concentration, thus inducing the appearance of a redox process at about 4V vs Li^{+}/Li, attributed to the Mn^{3+}/Mn^{4+} redox couple.

Moreover oxygen deficiencies in the cathode structure, possibly formed during the synthetic annealing step, can account for the increase of Mn^{3+}concentration for ensuring charge neutrality.

The signal at about 4.17 V and 4.16 V vs Li^{+}/Li in the anodic and cathodic scan, respectively, can be attributed to the $Fe^{2+/}Fe^{3+}$ redox couple and, partially, to a possible shift of the 4 V oxidation peak of Mn^{3+} to higher potentials induced by Fe-doping [6].

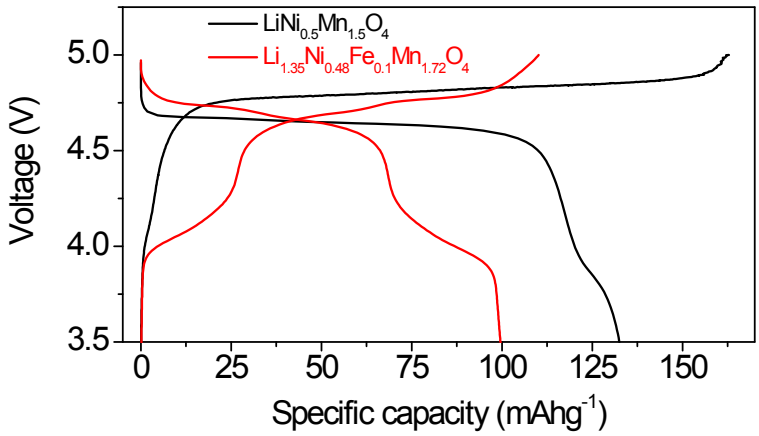
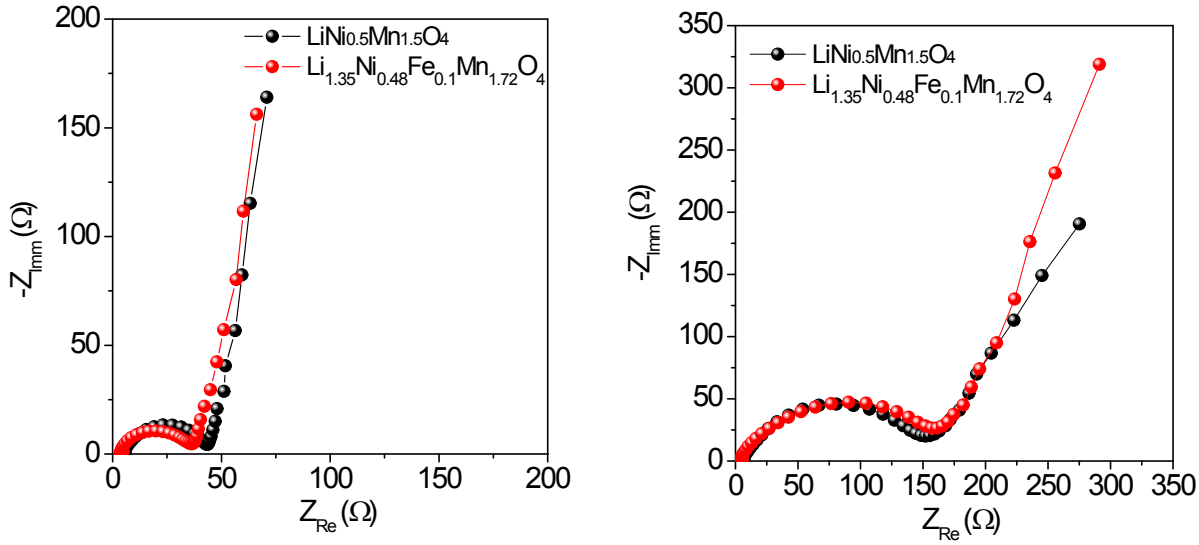


Figure S3

A comparison of the $LiNi_{0.5}Mn_{1.5}O_4$ and $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ galvanostatic cycling responses in terms of voltage versus specific capacity profiles is shown in Figure S3. As already pointed out in the discussion of the PCGA profiles (Figure S2), the doped $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ electrode shows a multi-step voltage profile, characterized by two main working regions, i.e. one between 4 and 4.25 V and the other between 4.6 and 4.8 V. The spinel cation substitution with iron ions induces a remarkable increase of the capacity delivered at the low voltage working region, due to the Mn^{3+}/Mn^{4+} and $Fe^{2+/}Fe^{3+}$ redox couples. The capacity delivered by the $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ and the $LiNi_{0.5}Mn_{1.5}O_4$ cathodes in the 4 - 4.25 V region is about 25 mAh g^{-1} and 5 mAh g^{-1}, respectively.

Moreover the $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ galvanostatic cycling profile in the high voltage working region evolves with a multi-step, sloppy trend while the undoped $LiNi_{0.5}Mn_{1.5}O_4$ shows a plateau-like curve, that is characteristic of solid solution Lithium intercalation processes.

Although decreasing the energy density, the reduction of the electrode operating voltage to lower values improves the cell stability and safety level upon cycling by avoiding electrolyte decomposition.



a **b**

Figure S4

The electrode-electrolyte interface of the $LiNi_{0.5}Mn_{1.5}O_4$ and $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ cathodes is investigated by Electrochemical Impedance Spectroscopy (EIS). Figures S4 a and S4 b display the Nyquist plots of the Li/$LiPF_6$ 1M, EC:DMC 1:1/$LiNi_{0.5}Mn_{1.5}O_4$ and Li/$LiPF_6$ 1M, EC:DMC 1:1/$Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ half-cells before and after a galvanostatic cycle, respectively. The equivalent circuit adopted for fitting the Nyquist plots is $R_{el}(R_{int}Q_{int})Q$, where R_{el} indicates the electrolyte resistance, R_{int} and Q_{int} correspond to the resistance and constant phase element (CPE) associated to the electrode/electrolyte interface and Q accounts for the diffusion of Li-ions in the low frequency range and the cell geometric capacity. The $(R_{int}Q_{int})$ element includes the

contribution of the resistance and capacitance associated both with the formation of a passivation film at the electrode surface and the charge transfer process.

Figures S4 a and b reveal only minor charge of the cell impedance before and after cycling using both $LiNi_{0.5}Mn_{1.5}O_4$ and $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ electrodes. These results evidence that the presence of the iron doping in the spinel-structure doesn't affect remarkably the electrode/electrolyte interface properties.

The resistance values determined by fitting the EIS data are about 40 Ω and 32 Ω for the pristine $LiNi_{0.5}Mn_{1.5}O_4$ and $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ electrodes, respectively. After the charge-discharge cycle the cathodes show interface resistance of about 148 Ω and 157 Ω, respectively. Further studies are required in order to investigate the effects of cation substitution on the properties of the solid electrode-electrolyte interface (SEI).

Experimental: Table S1

Table S1 lists the results of the ICP analysis on the $Li_{1.35}Ni_{0.48}Fe_{0.1}Mn_{1.72}O_4$ material .

Element	Wavelenght	SD	%RSD	Int(c/s)	Calc. Conc.
Li	670.78	0.0125	1.2	45948.0	1.0283 ppm
Fe	238.204	0.0012	0.2	3857.8	0.6138 ppm
Mn	257.610	0.2507	2.4	401111.0	10.413 ppm
Ni	231.604	0.0198	0.6	3331.4	3.0636 ppm

References

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