

Controlling at elevated temperature the Na-intercalation capacity and rate capability of $P3\text{-Na}_{2/3}\text{Ni}_{1/2}\text{Mn}_{1/2}\text{O}_2$ via selective substitution of Ni by Mg

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Introduction

A key priority in the development and improving of the sodium-ion energy storage technology for large-scale applications is the need to design electrode materials whose electrochemical performance is less sensitive to ambient temperature. A valid approach for layered lithium transition metal oxides ($\text{Li}_{1-x}\text{TM}_{1-x}\text{O}_2$), allowing tailoring of the electrochemical properties by modeling electronic and crystal structures, is the replacement of transition metals (i.e. TM = Co, Ni and Mn) with electrochemically inactive ions (such as Mg^{2+} , B^{3+} , Al^{3+} , etc.).

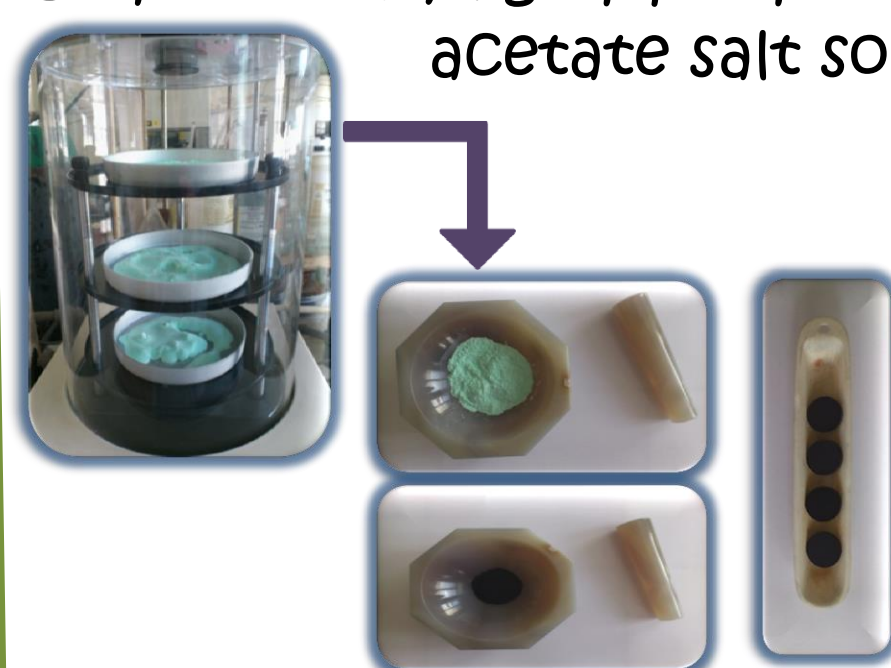
Aim

Developing of sodium transition metal oxide as a cathode material for sodium-ion battery that is designed to operate at elevated temperatures.

I. Synthesis

of $\text{Na}_{2/3}\text{Ni}_{1/2-x}\text{Mg}_x\text{Mn}_{1/2}\text{O}_2$ where $0 \leq x \leq 1/6$

- Freeze-drying of pre-frozen in liquid nitrogen acetate salt solutions of Na, Ni, Mg and Mn.



- Thermal decomposition at 400°C and heat treating at 700°C of the Na-Ni-Mg-Mn oxides.

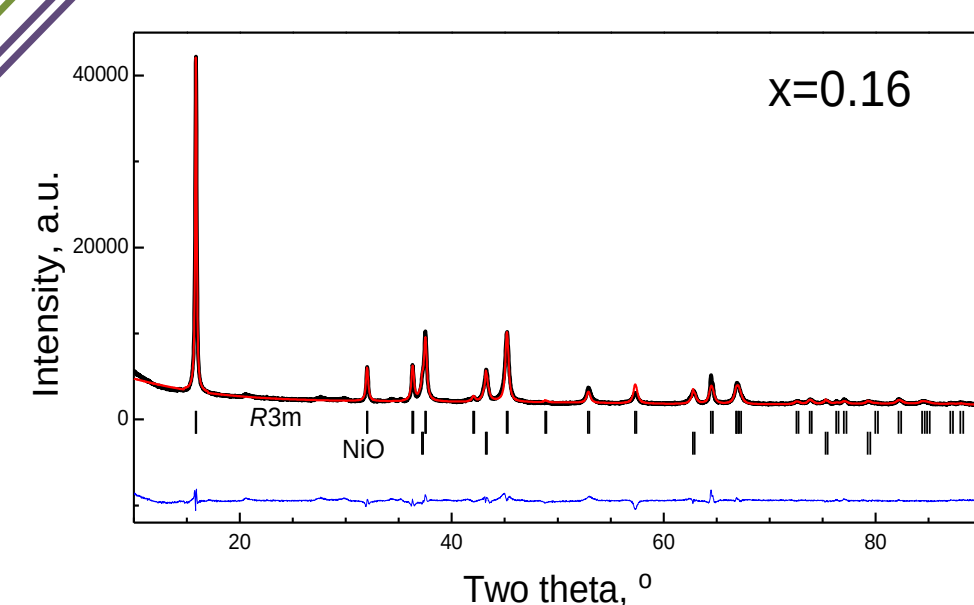


Figure 1. XRD patterns of $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mg}_{1/6}\text{Mn}_{1/2}\text{O}_2$ and Rietveld refinement.

II. Structure

Table 1. Chemical composition of $\text{Na}_{2/3}\text{Ni}_{1/2-x}\text{Mg}_x\text{Mn}_{1/2}\text{O}_2$ determined from ICP-OES

x	Ni		Mg		Mn	
	nominal	measured	nominal	measured	nominal	measured
0.0	0.50	0.49	0	0	0.50	0.51
0.04	0.46	0.46	0.04	0.03	0.50	0.51
0.08	0.42	0.42	0.08	0.07	0.50	0.51
0.16	0.33	0.32	0.16	0.17	0.50	0.51

*For all samples, the sodium content is 0.67 ± 0.04 .

Table 2. Lattice parameters of $\text{Na}_{2/3}\text{Ni}_{1-x}\text{Mg}_x\text{Mn}_{1/2}\text{O}_2$, $0 \leq x \leq 1/6$.

x	a, Å	c, Å	V, Å ³
NNM	0.0	2.8867	16.7692
NM-4	0.04	2.8865	16.7723
NM-8	0.08	2.8871	16.7753
NM-16	0.16	2.8889	16.7789

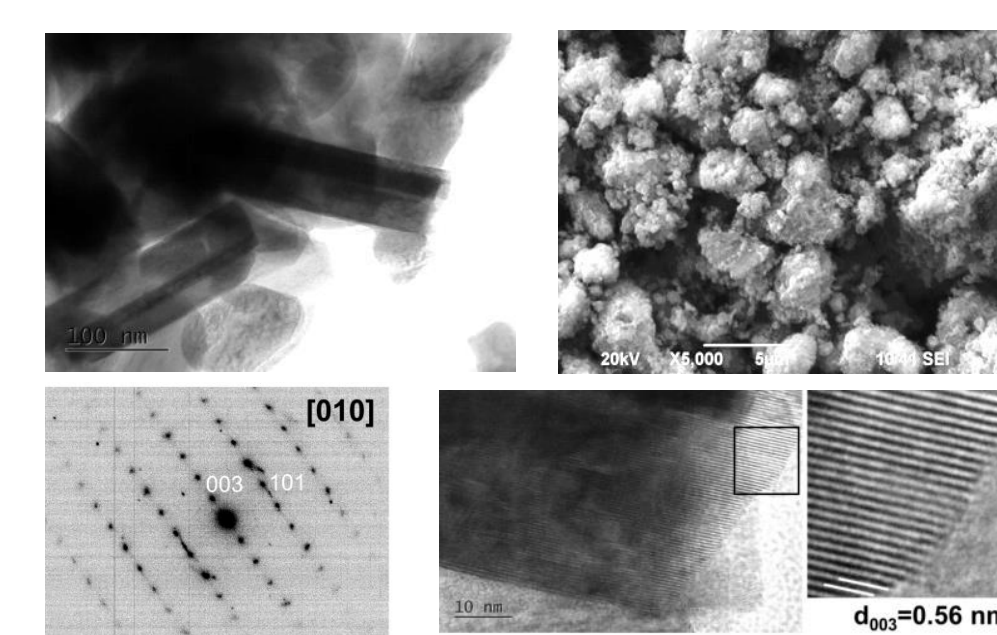
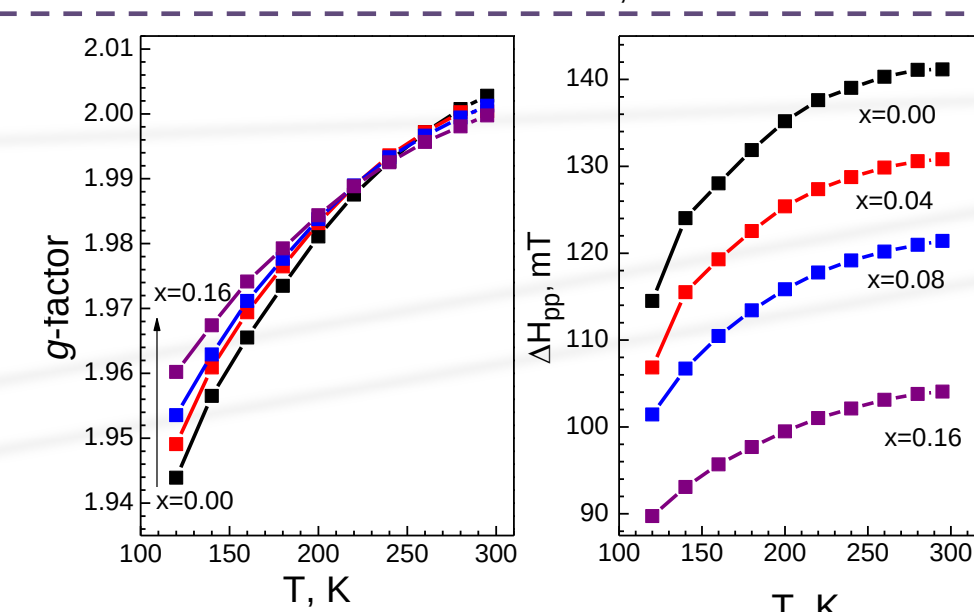


Figure 2.

TEM bright field micrograph (top, left), SEM image (top, right), SAED of NM-16 (bottom, left) and their HRTEM images corresponding to interlayer space of $d_{003}=0.56\text{ nm}$ (bottom, right).

Figure 3. Temperature evolution of the g-factor and the line width of the EPR signal for pristine $P3\text{-Na}_{2/3}\text{Ni}_{1/2-x}\text{Mg}_x\text{Mn}_{1/2}\text{O}_2$.



- The $\text{Na}_{2/3}\text{Ni}_{1-x}\text{Mg}_x\text{Mn}_{1/2}\text{O}_2$ oxides acquired a structure with three layered stacking sequence, i.e. $P3$ -type.
- The $P3$ -structure is preserved with increasing the degree of substitution of Ni^{2+} ions by Mg^{2+} ions. The unit cell volume shows a tendency to enlarge, which is consistent with a preferential substitution of Ni^{2+} by Mg^{2+} ions, having a slightly higher ionic radius (0.70 Å versus 0.72 Å).
- The preferential replacement of nickel by magnesium is also supported by the EPR study.
- The SAED and HR-TEM of NM-16 indicates that there is no lattice super-structure, which is typical of the unsubstituted $\text{Na}_{2/3}\text{Ni}_{1/2}\text{Mn}_{1/2}\text{O}_2$ oxide. This fact reveals that the Mg^{2+} doping disrupts the Ni and Mn ordering inside in the TM layer of parent $\text{Na}_{2/3}\text{Ni}_{1/2}\text{Mn}_{1/2}\text{O}_2$.

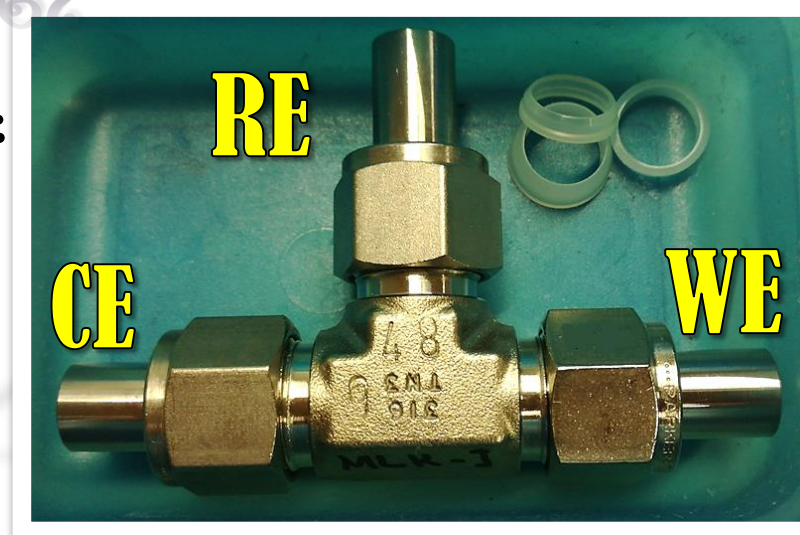
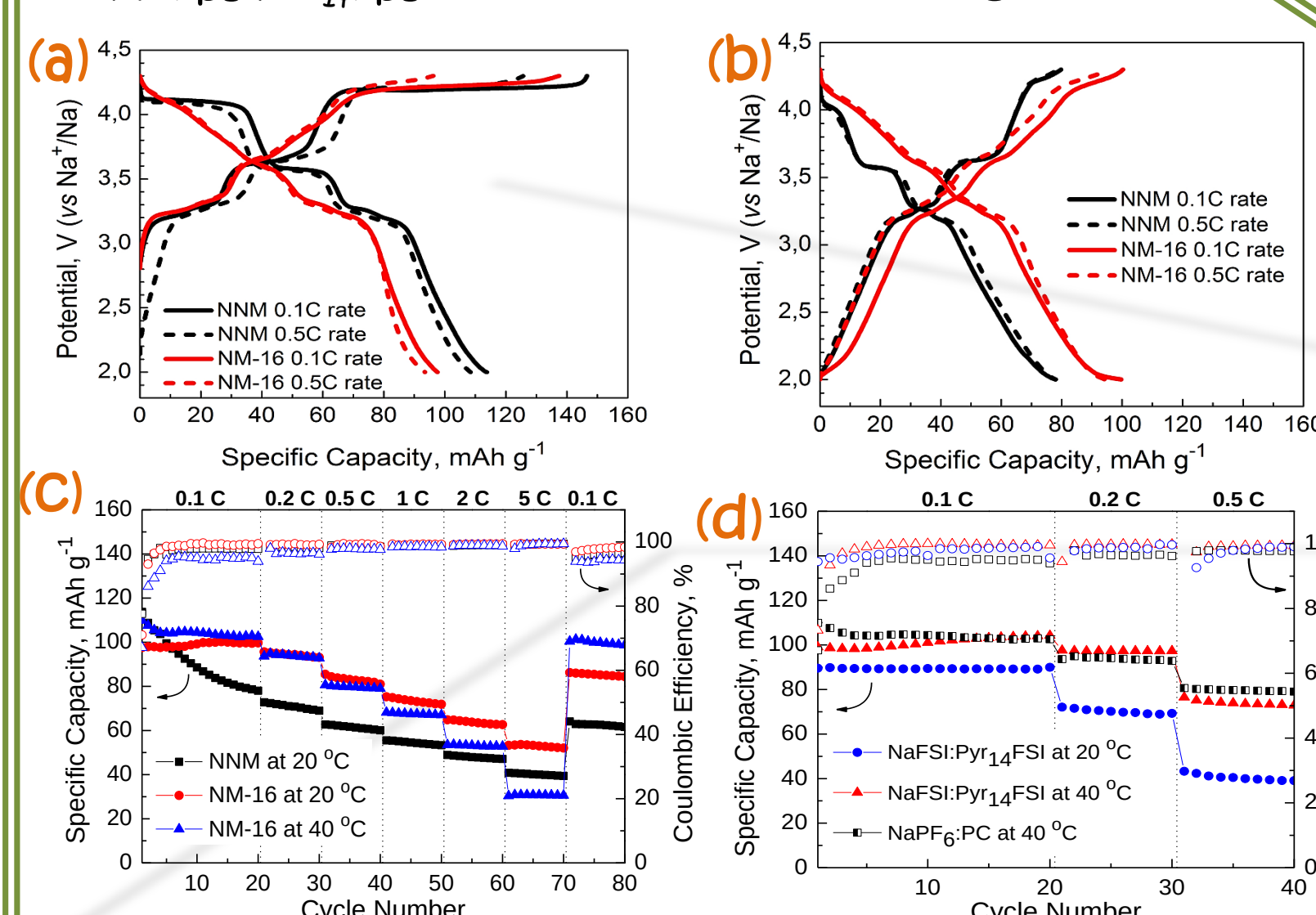
III. Electrochemical properties

- Three-electrode Swagelok-type cell
- Two types of electrolyte solutions:
 - carbonate-based electrolyte consisting of 1M NaPF_6 in PC
 - the IL-based electrolyte comprising 1M NaFSI in Pyr₁₄FSI (1:9)

Figure 4. Charge/discharge curves of NNM and NM-16 of the 1st cycle (a) and the 20th cycle (b) at 0.1 and 0.5 rate in $\text{NaPF}_6\text{:PC}$ electrolyte.

Rate capability tests for NNM (at 20°C) and NM-16 (at 20 and 40°C) electrodes in $\text{NaPF}_6\text{:PC}$ electrolyte (c).

Rate capability tests for NM-16 electrodes employing the $\text{NaFSI}\text{:Pyr}_{14}\text{FSI}$ electrolyte (at 20 and 40°C) (d).



WE: NNM and NM-16

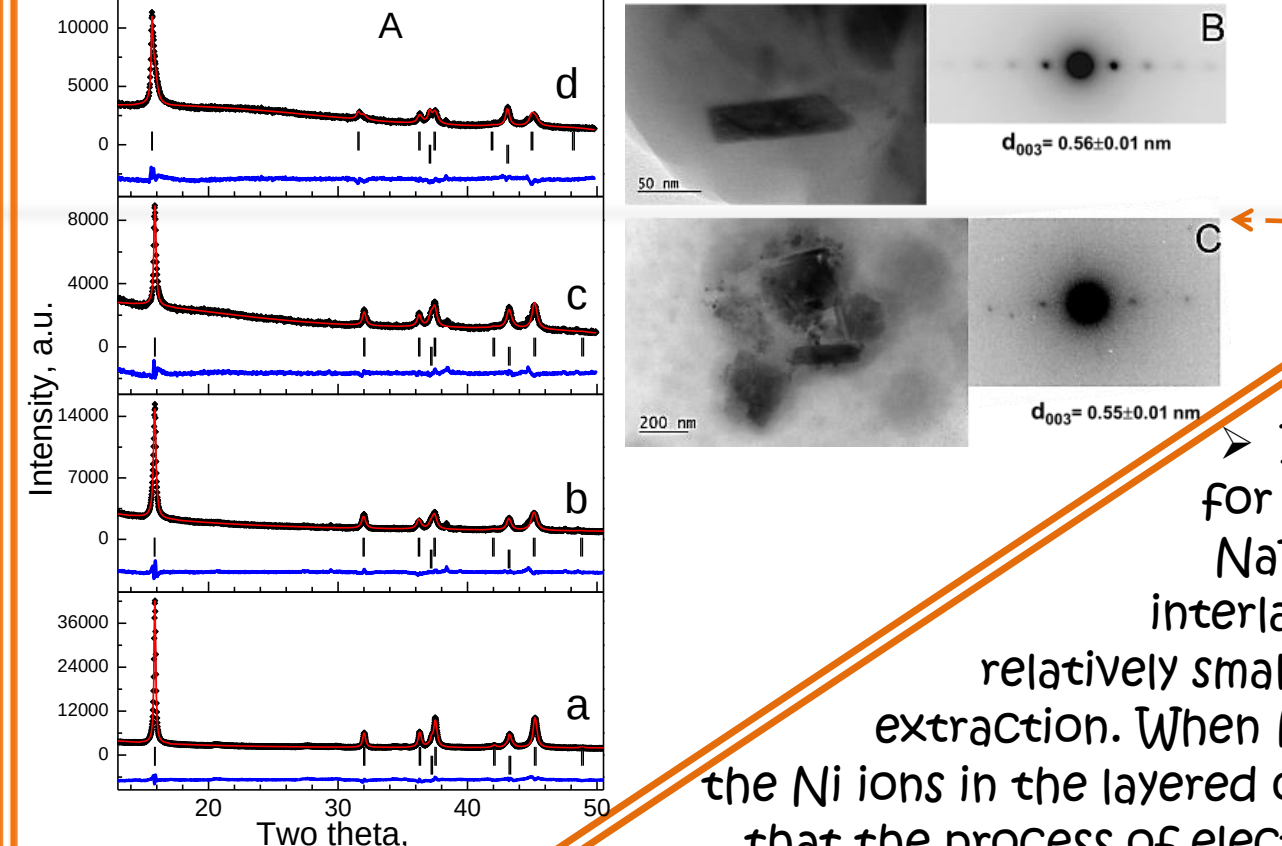
CE, RE: Na metal

WE – working electrode
CE – counter electrode
RE – reference electrode

- The best cycling stability and rate capability at elevated temperatures is observed for NM-16 cycled in IL-based electrolyte.

IV. Ex-situ Structural Characterization

Figure 5. (a) XRD patterns of pristine NM-16 electrodes (a) and after charge to 4.3 V in IL-based electrolyte at 20°C (b), discharging at 2.0 V cycled in the IL-based electrolyte at 20°C (c) and 40°C (d).

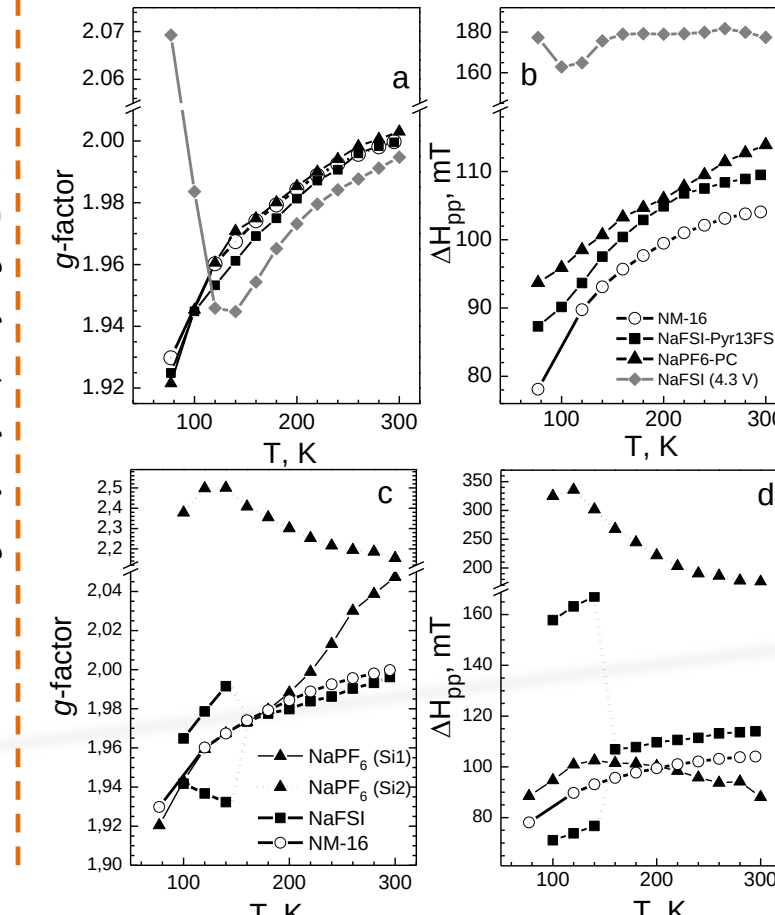


(right) Bright field micrographs and SAED of a discharged at 40°C (b) and a charged at 20°C (c) NM-16 electrode cycled in the IL-based electrolyte.

- It is found that, for NM-16 cycled in $\text{NaFSI}\text{:Pyr}_{14}\text{FSI}$, the interlayer expansion is relatively small during the Na^+ extraction. When Mg^{2+} substitutes the Ni ions in the layered oxide, it appears that the process of electrolyte molecule insertion is restricted.
- Based on EPR spectroscopy, Ni^{2+} ions are detected in the interlayer space of cycled NM-16, as Mg^{2+} ions initiate the Ni^{2+} mobility too. The cationic redistribution during cycling can be considered as a factor giving rise to an oxygen redox activity.

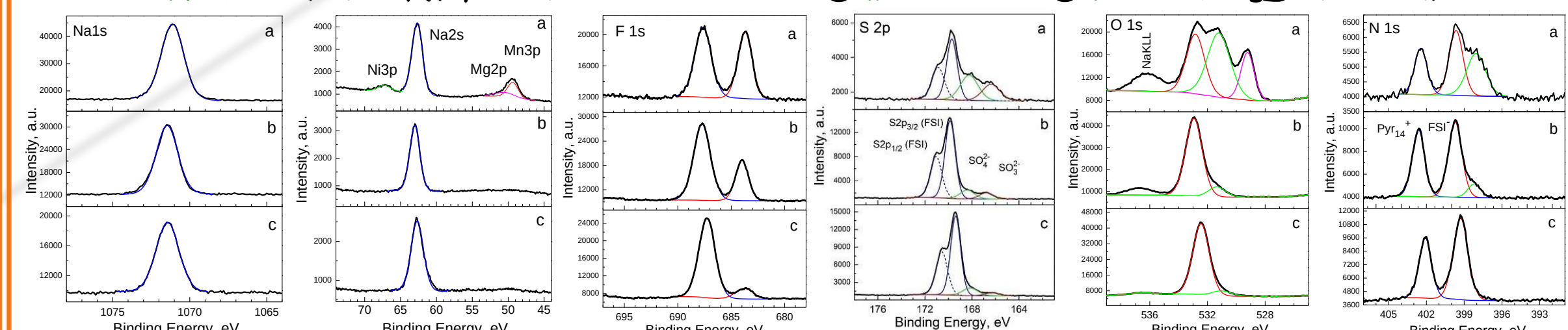
Figure 6.

Temperature evolution of the g-factor (a, c) and EPR line width (ΔH_{pp} , b, d) for NM-16 electrode cycled in $\text{NaFSI}\text{:Pyr}_{14}\text{FSI}$ and $\text{NaPF}_6\text{:PC}$ electrolytes at 20 (a, b) and 40°C (c, d).



V. Ex-situ Surface Characterization

Figure 7. XPS spectra in the energy region of Na 1s, Na 2s, F 1s, S 2p, O 1s and N 1s for soaked (a) and cycled NM-16 electrodes at 20°C (b) and 40°C (c) in the IL electrolyte.



- The composition of the surface film is dominated by the adsorption of the electrolyte ions. The electrolyte-electrode interaction leading to the deposition of sulfates, sulfites/sulfonyls, nitrates, NaF products, takes place in a low extent. This suggests a low reactivity of the IL electrolyte towards the layered oxide. In comparison with IL electrolyte, NaPF_6 -based electrolyte has been shown to be highly reactive, resulting in the formation of interface rich in inorganic and organic decomposition products.

Conclusion

Herein, we demonstrated firstly the elaboration of the oxide-based electrode material with optimized layered structure and composition that is designed to work at elevated temperatures. Through selective substitution of Mg^{2+} ions for Ni^{2+} in the three layered oxide, $P3\text{-Na}_{2/3}\text{Ni}_{1/2}\text{Mn}_{1/2}\text{O}_2$, the oxidation state of Ni ions, the cationic distribution in the layers, the sodium intercalation capacity and the rate capability is manipulated. The electrochemical behaviour of $P3\text{-Na}_{2/3}\text{Ni}_{1/2}\text{Mg}_{1/6}\text{Mn}_{1/2}\text{O}_2$ was discussed on the basis of *ex-situ* diffraction, microscopic and spectroscopic methods in terms of redox activity of the lattice oxygen, the reversible transfer of Mg^{2+} and Ni^{2+} ions between layers during Na^+ intercalation, thermal stability of cycled electrodes and surface reactivity of the layered oxide towards the IL electrolyte. At 40°C , the rate capability of the oxide is improved upon cycling using an IL electrolyte rather than the carbonate-based electrolyte.

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