


CHEMICAL SYNTHESIS OF Al AND Co DOPED $\text{LiNi}_6\text{Mn}_2\text{Fe}_2\text{O}_2$ (NMF) CATHODE MATERIAL

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Abstract

Al and Co doped $\text{LiNi}_x\text{Mn}_y\text{Fe}_z\text{O}_2$ (NMF) was synthesized using sol-gel method. The effect of dopants on the structural stability of $\text{LiNi}_x\text{Mn}_y\text{Fe}_z\text{O}_2$ (NMF) cathode material was investigated. For this purpose, the powder preparation was carried out using an aqueous solution of the nitrate precursors followed by calcination at 850 °C 5h. The chemical composition of $\text{LiNi}_x\text{Mn}_y\text{Fe}_z\text{O}_2$ base material was selected as 622 (Ni/Mn/Fe atomic ratio) and were successfully synthesized in layered form. Chemical composition of the obtained powders was determined by Energy dispersive spectroscopy. Scanning electron microscopy was applied to investigate the morphology of the powders. The crystal structure of the samples was analyzed using X-ray diffraction and Rietveld analysis. Average crystallite size from Rietveld refinement was calculated to be between 60-70 nm. Co-doped and Al-doped 622 cathode materials showed [006]/[102] and [108]/[110] doublets, which is the sign of layered structure with hexagonal ordering.

Keywords: Al and Co doped cathode materials, chemical synthesis of layered material

Al ve Co İLAVELİ $\text{LiNi}_6\text{Mn}_2\text{Fe}_2\text{O}_2$ (NMF) KATOT MALZEMESİNİN KİMYASAL YOLLA SENTEZLENMESİ

Özet

Al ve Co katkılı $\text{LiNi}_x\text{Mn}_y\text{Fe}_z\text{O}_2$ (NMF) sol-gel yöntemi kullanılarak sentezlenmiştir. Katkılarının $\text{LiNi}_x\text{Mn}_y\text{Fe}_z\text{O}_2$ (NMF) katot malzemelerinin yapısal stabilitesi üzerindeki etkisi araştırılmıştır. Bu amaçla, tozlar, nitrat öncüllerinin sulu bir çözeltisi kullanılarak hazırlanmış ve 850 °C'de 5 saatte kalsine edilmiştir. $\text{LiNi}_x\text{Mn}_y\text{Fe}_z\text{O}_2$ sisteminin kimyasal bileşimi 622 (Ni / Mn / Fe atomik oran) olarak seçilmiş başarıyla sentezlenmiştir. Elde edilen tozların kimyasal bileşimi enerji saçılım spektroskopisi ile kontrol edilmiştir. Tozların morfolojisi taramalı elektron mikroskopu kullanılarak incelenmiştir. Numunelerin kristal yapısı, X ışını kırınımı ve Rietveld analizi kullanılarak analiz edilmiş ve ortalama kristal büyüklüğü 60-70 nm arasında hesaplanmıştır. Co katkılı ve Al katkılı 622 katot malzemelerin tabakalı yapıya sahip olduğu [006] / [102] ve [108] / [110] difraksiyon çiftleri ile görülmüştür.

Anahtar Kelimeler: Al ve Co ilaveli katot malzemeler, tabakalı yapıların kimyasal sentezi

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1. Introduction

Rechargeable lithium-ion batteries are the key parts of a mobile application device, especially as an energy source[1-3]. New technologies that are dependent on energy storage can be extended by decreasing the cost of batteries and increasing their performance, because Li-ion batteries are the first choice for portable electrochemical energy storage. So far, extensive research on electrode materials for Li-ion batteries has been made[4]. The critical requirements for these applications are energy density and life cycle. To improve these properties, main components of the battery, anode and cathode materials, are the issue of

the researchers[5]. Main challenge to achieve better performance is the limited discharge capacity obtained for commercial cathode materials[6]. Electrode materials have a significant effect on these properties. The success of electrode material depends on its structure as well as its morphology[7]. Microstructurally, nanomaterials have been shown to provide higher reactivity and shorter diffusion lengths for Li ions, allowing scientists to adjust existing electrodes to develop new concept[3,8].

Among cathode materials, layered systems, which are the oldest form of intercalating cathodes, are used in various applications[9,10]. The composition, structure,

and cation ordering of these compounds have significant effect on the theoretical charge capacity and intercalation voltage. Extrinsic features such as microstructure and particle size control the features such as power capability and cycle life[11,12].

Within these layered cathode materials based on LiCoO_2 is the commercialized in Li-ion battery applications[13].

However, studies on finding alternative candidates have been continuing due to high cost, toxicity and limited cathode performance (50 % of their theoretical value) of cobalt[14]. The layered LiNiO_2 and LiMnO_2 have been proposed for being alternative to LiCoO_2 however they have some difficulties during synthesizing as pure material together with thermal degradation during cycling. Another candidate LiFePO_4 have also been widely investigated but inherent conductivity of the material restricts the performance of the cell[15,16]. One of the most common alternative has been $\text{Li}(\text{NiMnCo})\text{O}_2$ (NMC) are well experimented and find use in commercial lithium-ion batteries as cathode material[17]. In this system, although it was proposed as next-generation cathode material, cation mixing between Ni and Li and capacity loss in the first discharge cycles are the main complications[16,18,19].

Development of low-cost, less toxic and high capacity cathode materials are needed[20]. The studies dedicated to the development of cobalt-free layered cathodes based on solid solutions of the transition metals of Mn, Ni. The addition of Fe as third element into Mn, Ni transition metals, due to its great theoretical capacity, its low cost and it's environmental friendly properties may have additional improvements. The replacement of Fe into the crystal structure may help decrease the cost of cathode materials and lithium ion batteries[21]. In addition, the use of Fe can be considered the best choice to reduce the number of toxic elements in layered systems[22]. Recent study of Tabuchi et al.[23] described development of iron-containing cathode material in Mn containing layered system. They found that the iron including system exhibit good structural properties. However, complex production steps, co-precipitation followed by hydrothermal reaction production process results in some complications in the resulted electrode material in this study[22,24].

Another approach can be doping with certain elements to improve the structural stability of cathode materials[25,26]. Various additions i.e. Al[25], Cr[27], Fe[23], Mo[27], Si[28], to the Li based layered cathode material have been studied with respect to their effect on the structural stability and electrochemical performance. The effect of doping is usually described as reducing the phase transition during Li-ion insertion and extraction. Al is one of the common dopant in this context[29]. For instance, Wang et al. [30] found that Al substitution improves the cyclability of NMC. Ngalam et al.[31] show that Co is stabilizing layered structure and suppresses the movement of transition metal-ions into the inter-layer Li sites.

Therefore, in the light of above-mentioned studies, the motivation was to develop Co and Al doped layered $\text{LiNi}_0.6\text{Mn}_0.2\text{Fe}_0.2\text{O}_2$ (NMF) cathode materials using a simple sol-gel technique. Following the sol-gel synthesis procedure, a single-step heat treatment was carried out under an ambient atmosphere. The morphology and the structure of the prepared materials were examined using SEM and X-ray diffraction.

2. Experimental procedure

In this study, $\text{Li}_{1.05}(\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Fe}_{0.2})\text{O}_2$ (NMF622), Co-doped- $\text{Li}_{1.05}(\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Fe}_{0.2})\text{O}_2$ (Co-doped NMF622) and Al-doped $\text{Li}_{1.05}(\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Fe}_{0.2})\text{O}_2$ (Al-doped NMF622), were produced by a citric acid assisted sol-gel method. For this purpose, solution containing stoichiometric quantities of LiNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were mixed in the required proportions. The total concentration of the solution was kept at 0.8 M where citric acid was added to the aqueous solution as binder. As dopant 2 wt % Co was added for Co-doped NMF622 sample and 2 wt % Al were added for Al-doped NMF622 sample. Rather than being one mol, 0.5 % excess Li was added in order to overcome loss due to volatility of Li. The obtained gels were kept at 70°C for drying. The dried gels were pre-calcined at 450°C 4h and calcined at 800°C for 5h under an open atmosphere in order to achieve intended crystalline phases. The process is summarized in Fig. 1.

The crystal structure of the samples was investigated using X-ray diffractometer (XRD, D8 Advance, Bruker) using $\text{Cu-K}\alpha$ radiation (typically 40 kV, 40 mA). Lattice parameters, cell size and oxygen parameter (z) were obtained from the Rietveld refinement of X-ray data using MAUD software[32]. Synthesized powders were morphologically examined using field-emission scanning electron microscope (FEI Nova 430). Compositions were verified using the energy-dispersive spectroscopy (EDS) analysis. Electrical impedance spectroscopy (EIS) measurements were performed in the frequency range of 300 kHz to 3 mHz with a 10 mV AC amplitude.

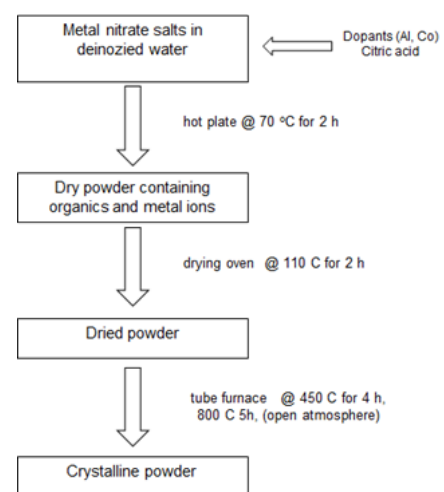


Figure 1. Schematic of sol-gel process.

3. Results and Discussion

Fig. 2 shows the X ray diffraction patterns of undoped NMF622, Co-doped NMF622 and Al-doped NMF622 cathodes after heat treatment at 850 °C 5h. The peaks

are indexed as layered oxide based on $R\bar{3}m$ structure.

Average crystallite sizes, lattice parameters, (a and c) were found by Rietveld refinement and are listed in Table 1. As a result of refinement, Fig. 3, diffraction peak positions fit with the position of hexagonal α -NaFeO₂ phase with layered structure with the refined % R_w values around 7. The lattice parameter value, c, were found 14.2831 Å for undoped case and 14.3255 Å, 14.2981 Å, for Co doped and Al doped cases, respectively. The % 0.2548 increase in the lattice parameter for Co case especially indicates the structure expand with the addition of Co. Due to larger lattice parameter in the c direction, comparatively better electrochemical performance is usually expected in the layered structures due to easier intercalation. The larger lattice parameter results in an increase in the Li gap, a gap between the transition metal-oxygen sandwich layers, indicating easier intercalation / deintercalation from the Li-ion diffusion perspective[33]. In both Al doped and Co doped case, dopant atoms incorporated into the structure forming a single phase and giving a single lattice parameter.

Oxygen atom positions found from Rietveld refinement are also given in Table 1. Li-gap was calculated using oxygen position parameters (z) and lattice parameter in c direction (c) using equation (1). The calculated Li-gap value indicates the distance between oxygen atoms, where Li intercalates/de-intercalates into the system.

The hexagonal setting of the $R\bar{3}m$ space group, with Li to be at 3b sites and transition metal atoms to be at 3a sites. The calculated Li gap values are also added to Table 1. Among undoped and doped NMF622 samples,

the Co-doped NMF622 has the maximum Li-gap value which is 2.3423 Å. As this value become higher, it is expected to have faster lithium-ion diffusion. These values indicate that within these samples it would be expected that Co-doped sample should have better electrochemical performance.

$$Li - gap = \frac{c}{3} - \left(\frac{2}{3} - 2.z\right).c \quad (1)$$

Song et al.[34] claimed that larger ratios of c/a bring greater degrees of crystallinity and stability of the NCA with layered structure. From c/a values (Table 1) we can think that especially Al-doped NMF the system become more stable compared to undoped sample. The splitting of (006)/(102) and (108)/(110) doublets can be indication of layered structure formation in the XRD spectrum. As can be seen from the X ray diffractogram, Fig. 2, in the synthesized samples these doublets, especially (108)/(110) one, can be separated. Further interpretation can be made as extended calcination of the synthesized samples can further separate these peak doublets forming well defined hexagonal layered structure[35].

The ratio of the I(003)/I(104) peaks in the diffraction pattern has been sign of the partial interchange of occupancy of the Li-sites and transition metal ions, so-called cation mixing[36]. The ratio of I(003)/I(104) being larger than 1.2, it is claimed that the cation mixing is small. The ratio lower than 1.2 is seen to be the indication of large extent of cation mixing. The values obtained in this study is well below the targeted ratio which can indicate some amount of cation mixing in the structure. Among samples, Co-doped NMF622 has higher I(003)/I(104) ratio (0.85) and can be expected to have lower cation mixing.

Table 1. Oxygen positions and lattice parameters of layered LiNi₆Mn₂Fe₂O₂ cathode materials derived from Rietveld analysis.

Sample (NMF-622)	a (Å)	c (Å)	c/a	I(003)/I(104)	Oxygen parameter (z)	Li gap (Å)	Crystallite size (nm)	% R _w
Un doped	2.9062	14.2831	4.863	0.7509	0.2589	2.127	68.5	5.82
Co-doped	2.9036	14.3255	4.921	0.8505	0.2515	2.342	55.91	6.1643
Al-doped	2.8961	14.2981	4.920	0.7112	0.2593	2.116	63.8	7.17

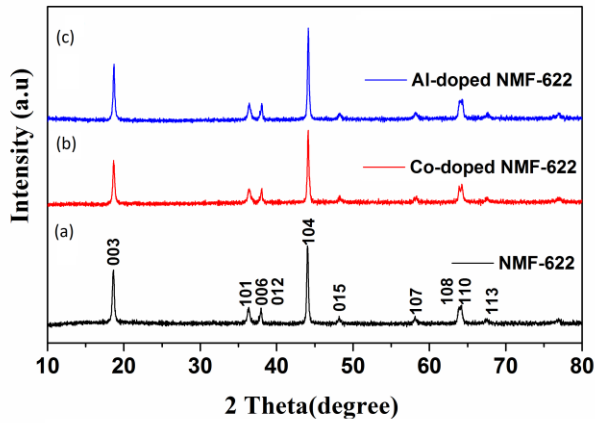


Figure 2. XRD spectrum of layered $\text{Li}(\text{Ni}_6\text{Mn}_2\text{Fe}_2)\text{O}_2$ (NMF) cathode materials using sol gel method and calcined at $850\text{ }^\circ\text{C}$ for 5h (a) undoped (b) Co-doped (c) Al-doped.

Table 2. Calculated and obtained compositions for synthesized samples.

Sample (NMF-622)	Mn (at %)	Fe (at %)	Ni (at %)	dopant (at %)
undoped	20.52	19.23	60.26	-
Co doped	20.28	20.99	56.45	2.28
Al doped	20.12	20.41	57.13	2.35

Composition of the undoped, Al doped, and Co doped systems was determined using the energy dispersive spectroscopy. The results are given in Table 2 and it can be claimed that they are in good agreement with the

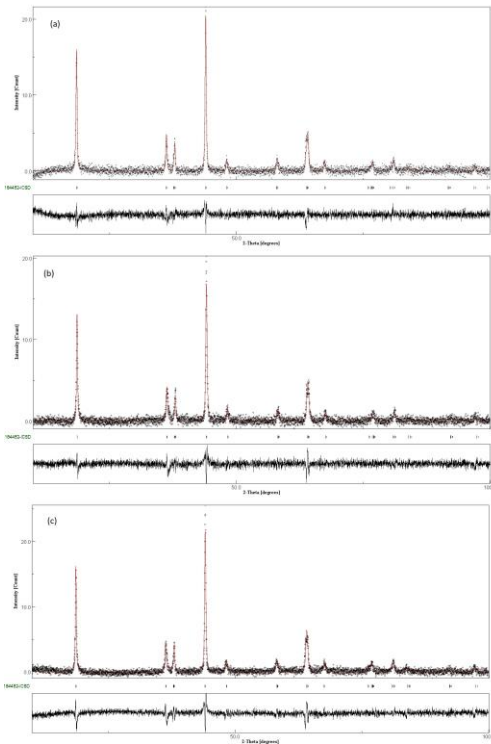


Figure 3. Refined XRD spectrum of $\text{Li}(\text{Ni}_6\text{Mn}_2\text{Fe}_2)\text{O}_2$ (NMF) (a) undoped (b) Co-doped and (c) Al-doped.

designed composition. Based on these results, the compositions of the synthesized cathode materials are

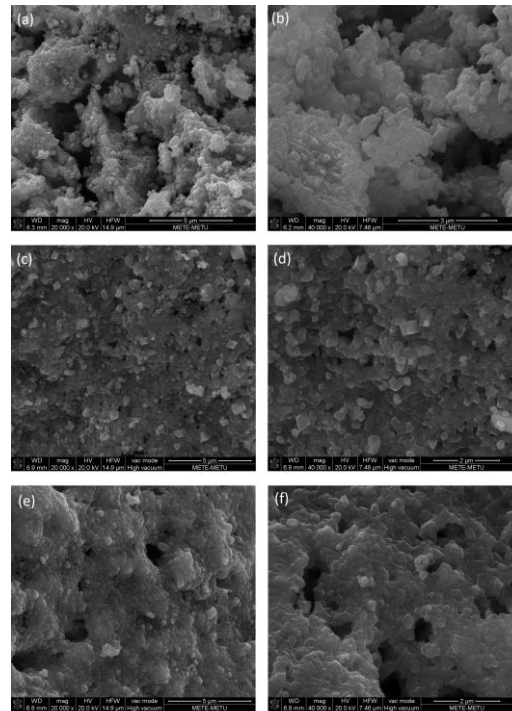


Figure 4. SEM images of $\text{Li}(\text{Ni}_6\text{Mn}_2\text{Fe}_2)\text{O}_2$ (NMF) (a),(b) undoped (c),(d) Co-doped and (e),(f) Al-doped samples.

found to be $\text{Li}_{1.05}(\text{Ni}_{0.60}\text{Mn}_{0.21}\text{Fe}_{0.19})\text{O}_2$ for undoped, $\text{Li}_{1.05}(\text{Ni}_{0.57}\text{Mn}_{0.20}\text{Fe}_{0.21})\text{O}_2$ for Co-doped, $\text{Li}_{1.05}(\text{Ni}_{0.57}\text{Mn}_{0.20}\text{Fe}_{0.21})\text{O}_2$ for Al-doped samples. The intended ratio of the components for the cathode material are found to be close to the determined one.

The SEM pictures of NMF cathode active materials at two magnifications are given in Fig. 4. The particles are composed of polycrystalline aggregates with very fine morphology. The particle sizes are found to be around 150 nm to 400 nm.

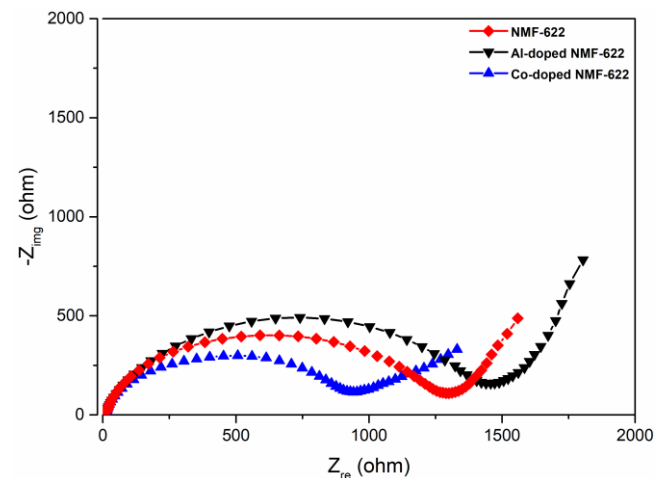


Figure 5. EIS graphs of NMF622, Al-doped NMF622 and Co-doped NMF622 samples.

The EIS spectra of NMF622, Co doped NMF622 and Al doped NMF622 samples are shown in Fig. 5. In interpretation of EIS for Li-ion batteries, common understanding is that there are several semicircles and a linear segment in spectrum. Semi-circuits in high and medium frequencies are primarily related to the resistive effects. As you can see from Fig. 5, Co doped-NMF622 sample had lower internal resistance. This lower internal resistance in Co doped NMF622 sample was a sign of a faster diffusion process[37-39]. In addition, Li-ion gap results (Table 1), it is found that Co-doped NMF622 had the largest Li-ion gap among our candidates. From the interpretation of these two results, Co-doped NMF622 the most promising candidate within our sample, which shows the possibility of the fastest Li ion intercalation with larger gap and small internal resistance.

4. Conclusion

In the current study, Co doped, Al doped and undoped NMF622 cathode material were synthesized by sol-gel method. The obtained powders were in the form of fine polycrystalline aggregates. XRD patterns revealed that intended crystal structure is obtained after the calcination heat treatment at 800 °C 5h. X-ray data especially [108]/[110] doublets show that structure was layered with hexagonal ordering. The change in the lattice parameter(c) and expansion in Li-gap indicate that within these samples it would be expected that Co-doped sample should have better electrochemical performance due to higher Li-gap. According the EIS results Co-doped sample is the electrochemically most promising sample due to lower internal resistance compared to Al doped and undoped NMF622 samples.

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