Effects of Zinc-ion Substitution on the Structure and Electrical Conductivity of Sodium-Nickel-Manganese Materials as Cathode Materials

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Abstact: Sodium is one of the new materials to replace Lithium in battery manufacture. For this reason, further research is needed to explore this new material and its composition that meets the cathode material standards. This research aims to synthesize and characterize the Sodium- Nickel-Manganese material with the Zn^{2+} combination, which is expected to be used as a battery cathode material. The characterization used is XRD, SEM, and LCR-meter. In this research, we succeeded in synthesizing and characterizing Sodium-Nickel-Manganese material with a particle size of around 250-500 nm. Characterization using LCR meter obtained conductivity values of 6.77×10^{-6}, 7.46×10^{-4} and 5.45×10^{-2}S/cm at 100 Hz, 1.86×10^{-6}, 8.75×10^{-4} and 1.16 S/cm at 1.5 KHz, 1.7×10^{-6}, 9.45×10^{-4} and 1.51 S/cm at 3 KHz, for Zn^{2+} substitution with x=0.1, 0.15, and 0.20, respectively.

Keywords: Battery, Cathode, Nanoparticle, Na-NM, Zinc Substitutions.

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I. INTRODUCTION

Currently, the batteries used in electrical equipment are still dominated by lithium batteries to store electrical energy. However, it is predicted that sodium batteries will soon replace lithium batteries due to the predicted availability of Lithium only for the next 50 years [1].

It can certainly make the price of Lithium will soar expensive. In recent years, scientists have conducted a series of studies on the possibility of using a new material to replace Lithium in battery manufacture. One material that is a good candidate for large-scale energy storage is sodium [2-14]. Sodium was chosen because its characteristics are close to Lithium, cheap, and abundant. The availability of sodium is very abundant and available in various parts of the world. One of the research results has successfully produced a sodium-ion battery that can store as much energy as a lithium-ion battery. The results of this study represent a significant leap forward in the production of sodium-ion batteries [9]. Thus, batteries based on sodium materials need to be developed to meet battery production needs in the future.

The radius of sodium cations is larger than Lithium, so modification of battery components is required [15]. One of the downsides to sodium-ion batteries is that they are a bit heavier than lithium-ion batteries. However, this is not a problem because sodium batteries can be used as standby storage. For this reason, further research is needed to explore new materials and suitable compositions that meet the cathode material standards. In this paper, we composed samples of $NaNi_{1\text{-}2x}Mn_xZn_xO_2$ with variations x = 0.10, 0.15, and 0.20 and substituted zinc ions for Mn to improve the material's characteristics crystal structure, surface morphology, and electrical conductivity.

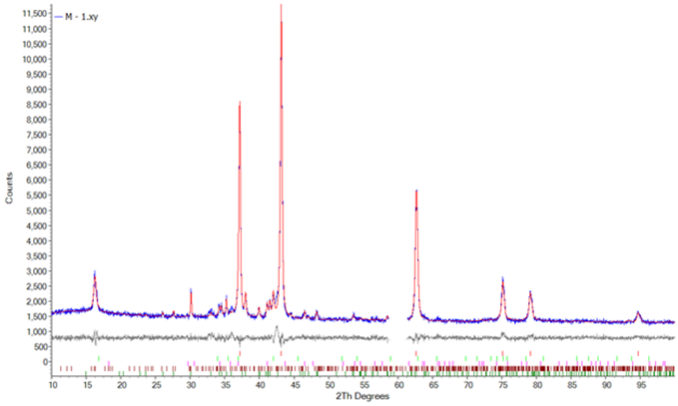
II. MATERIALS AND METHODS

Samples of $NaNi_{1\text{-}2x}Mn_xZn_xO_2$, with x = 0.10-0.20 as the battery cathode material, were prepared from Na_2O, NiO, $MnCO_3$, and Zn_xO_2/O_3 materials, each with >99% purity. The mixture of these ingredients was put into a stainless-steel vial and then processed through the solid-state reaction method using high-energy milling (750 rpm) for 50 hours. After that, it was heated at 800°C or 200°C/10 minutes heating rate for 2 hours in the open air in the form of pellets pressed with a pressure of 5 tons, then characterized.

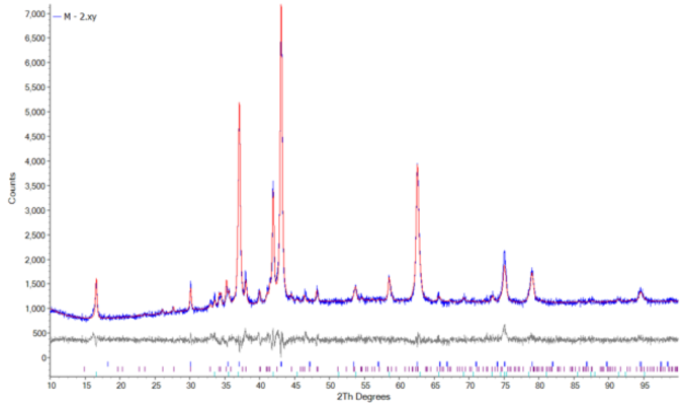
X-ray diffractometer (XRD) Philips PW1710 type was used with Cu-K radiation with a wavelength of 1.5406 from a diffraction angle of 2θ = 20°-80° to characterize the phase formation and crystal structure formed. SEM type-JEOL, JED 2300 was used to see the shape and morphology of the granules, while the material's electrical conductivity is characterized by LCR-meter HIOKI-5020 type.

III. RESULTS AND DISCUSSION

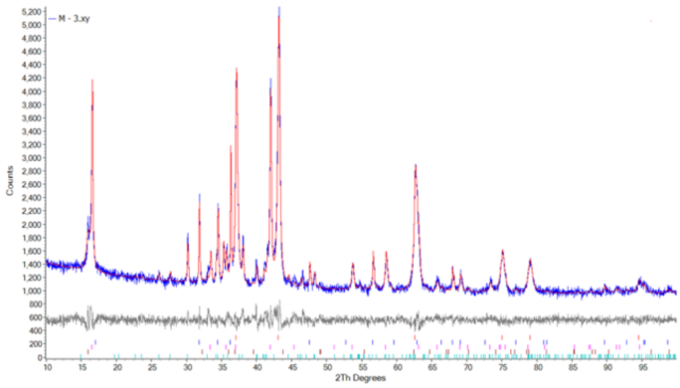
Fig. 1 shows the diffraction patterns in the $NaNi_{1\text{-}2x}Mn_xZn_xO_2$ samples with x=0.10, 0.15, and 0.20. It can be seen from the XRD results that all samples are not in



(a) M-1

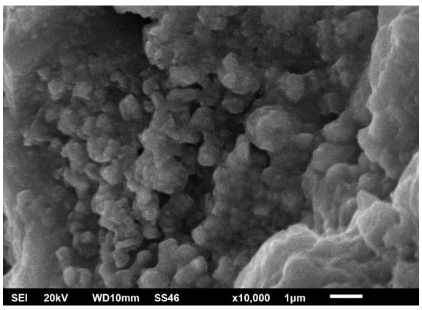


(b) M-2

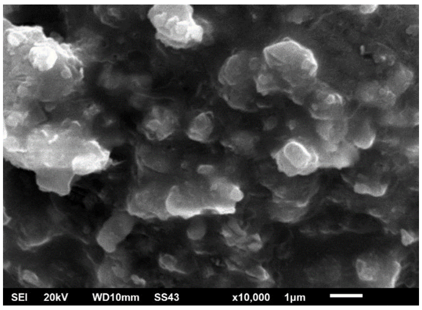


(c) M-3

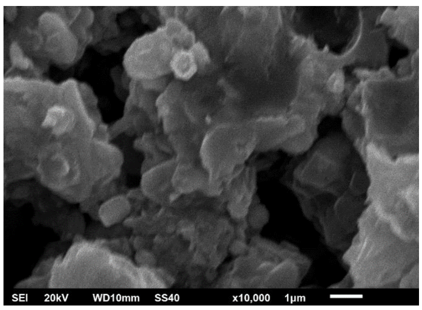
FIG. 1: Diffraction patterns of $NaNi_{1-2x}Mn_xZn_xO_2$ samples with x= 0.10, 0.15, and 0.20



(a) M-1



(b) M-2



(c) M-3

FIG. 2: Surface morphology of $NaNi_{1-2x}Mn_xZn_xO_2$ samples with x= 0.10, 0.15, 0.20

the same phase. Several phases appear as impurity phases which are NiO (11,01%), MnZnO (6,31%) and $NaMnO_2$ (0,11%). Not all constituent materials have appropriately reacted to form the $NaNi_{1-2x}Mn_xZn_xO_2$ phase. It is due to the less high heating temperature and less long duration-the temperature and duration of sintering influence phase formation [16]. Previous studies reported that biphasic materials were produced at low temperatures from 800 to 850°C [17]. And to get a single phase, heating is carried out at 850°C for 8 hours [18]. The sample shows peaks consistent with the Rhombohedral structure with the R-3m space group. Table I shows the Rietveld refined result of the samples. As shown in Table I, the cell volume increased in the presence of Zn^{2+} substitutions. It is in line with Tianyue Tong et al. report [19].

The surface morphology of the sample is shown in Fig. 2. The sample has heterogeneous grains according to the surface morphology of the sample, and the particles experience agglomeration. We assume that because the sample is hygroscopic, it also affects the morphology of the sample. The average particle size obtained is around 250-500 nm. Meanwhile,

TABLE I: Rietveld refined result of $NaNi_{1-2x}Mn_xZn_xO_2$ with x= 0.10, 0.15, dan 0.20

Phase	$NaNi_{1-2x}Mn_xZn_xO_2$	x = 0.10	x=0.15	x = 0.20
Space Group		R-3m	R-3m	R-3m
Cell Mass		187.488	326.000	326.000
Cell Volume (^{3})		119.62736	120.41(3)	120.70(3)
Crystal Density (g/cm^3)		2.603	4.4959(12)	4.4851(12)
Lattice Parameters:	a ()	2.9533337	2.9474(3)	2.9437(4)
	c ()	15.8370703	16.005(3)	16.083(2)
Rexp		2.49	2.88	2.86
Rwp		3.22	3.80	3.72
GoF		1.29	1.32	1.30

TABLE II: The conductivity of the sample with Zinc substitutions

x	Frequency (Hz)	Conductivity (S/cm)
0.1	100	6.77×10^{-6}
	1.5×10^3	1.86×10^{-6}
	3×10^3	1.7×10^{-6}
0.15	100	7.46×10^{-4}
	1.5×10^3	8.75×10^{-4}
	3×10^3	9.45×10^{-4}
0.20	100	5.45×10^{-2}
	1.5×10^3	1.16
	3×10^3	1.51

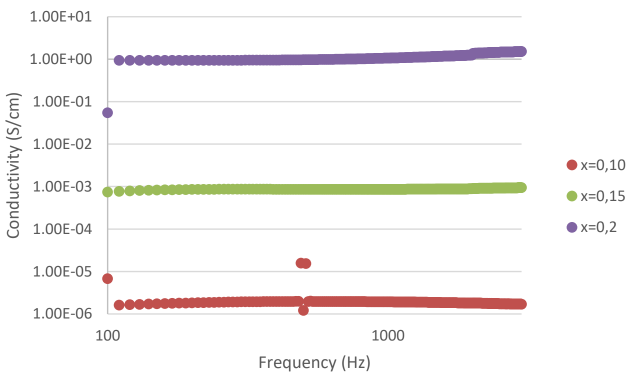


FIG. 3: LCR measurement results for sample $NaNi_{1-2x}Mn_xZn_xO_2$ with x= 0.10, 0.15, and 0.20

Qianjiang et al. obtained an average particle size of about 2 m [20], and Mahesh et al. produced a sample particle size of 100-200 nm [21]. Meanwhile, Kang Du et al. obtained a particle size of around 1-3 m [22]. As per our previous report, the size of the particle affects the conductivity. The larger the particle size, the greater the conductivity. One that influences this is the sample heating temperature [16, 23].

The results of the LCR measurements can be seen in Fig. 3. The best results for the conductivity obtained were at the composition x=0.2, i.e., 5.45×10^{-2} S/cm at 100 Hz, 1.16 S/cm at 1.5 KHz dan 1.51 S/cm at 3 KHz. It is in line with the result obtained by Chi Li et al. that the Zn_2^+ substitutions affect the increases in conductivity values [24, 25]. Of the effective way to increase the conductivity value of Natrium-Nickel-Manganese material, Zn^{2+} substitution can be considered to do [26, 27].

IV. CONCLUSION

The cathode material for a Sodium-Nickel-Manganese battery with Zn^{2+} substitution has been successfully synthesized and characterized. The average particle size obtained is around 250-500 nm, has heterogeneous grains, and the particles experience agglomeration. The conductivity values of the samples with x=0.1, 0.15, and 0.2 are 6.77×10^{-6}, 7.46×10^{-4} and 5.45×10^{-2}S/cm at 100 Hz, 1.86×10^{-6},8.75×10^{-4} and 1.16 S/cm at 1.5 KHz, 1.7×10^{-6}, 9.45×10^{-4} and 1.51 S/cm at 3 KHz. The Zn^{2+} substitution affects an increase of the conductivity value and reduces the particle sizes to the nanoscale. For further research, it is suggested to use other methods and variations of Zn^{2+} composition in preparing samples, such as the sol-gel or co-precipitation methods.

Acknowledgments

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