

SEARCH FOR NEW CATHODE COMPOSITIONS FOR MILDLY ACIDIC  
Zn-MnO<sub>2</sub> BATTERIES

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## ABSTRACT

### SEARCH FOR NEW CATHODE COMPOSITIONS FOR MILDLY ACIDIC Zn-MnO<sub>2</sub> BATTERIES

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This thesis focuses on finding a new MnO<sub>2</sub>-based cathode composition(s) for Zn-ion batteries. For this purpose combinatorial approach was employed using thick film cathodes deposited via magnetron sputtering. The system under study was MnO<sub>2</sub> alloyed with NaMnO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, NiO. For this purpose, four sputter targets were prepared. MnO<sub>2</sub> target was in 3-inch diameter placed in the central position and the other oxides were 2-inch in diameter placed 120° to one another forming a triangle. Substrates were 12.7 mm in diameter placed in a substrate magazine with a triangular geometry mimicking the targets underneath. A total of 36 cathode could be deposited in a single sputtering experiment each with a different composition.

A total of six experiments were carried yielding 216 cathodes. Cathodes were deposited on Ni foil used as a current collector. They were typically 3 μm thick with a mass varying from 0.23 to 2.38 mg. Cells used was of Swagelok type, anode was 300 μm thick Zn foil electrolyte was 2M ZnSO<sub>4</sub> + 0.1 M MnSO<sub>4</sub> aqueous solution.

The preliminary results indicated favorable results in Mn rich cathodes. As a result, out of six sets three set of cathodes were selected for detailed study.

Cyclic voltammetry as well as galvanostatic tests were carried for each cathode. Mn rich corner of the Bi-Mn-Ni ternary diagram where Na varied from 11 to 78% were mapped in terms of capacities, cyclic stability, and discharge plateau potential. Based on maps, three candidate compositions were selected with discharge capacities above 400 mAh/g. These are  $\text{Bi}_{0.04}\text{Na}_{0.55}\text{Ni}_{0.04}\text{Mn}_{0.36}\text{O}_x$ ,  $\text{Bi}_{0.04}\text{Na}_{0.37}\text{Ni}_{0.06}\text{Mn}_{0.53}\text{O}_x$  and  $\text{Bi}_{0.02}\text{Na}_{0.63}\text{Ni}_{0.02}\text{Mn}_{0.33}\text{O}_x$ . Further work is needed to check the full potential of the selected cathodes.

Keywords:  $\text{MnO}_2$  cathodes, Zinc-ion battery, Combinatorial deposition, Magnetron sputtering

## ÖZ

### HAFİF ASİDİK Zn-MnO<sub>2</sub> PİLLER İÇİN YENİ KATOT BİLEŞİMLERİNİN ARAŞTIRILMASI

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Bu tez, Zn-iyon piller için yeni bir MnO<sub>2</sub> bazlı katot bileşimleri bulmaya odaklanmaktadır. Bu amaçla magnetron sıçratma yoluyla biriktirilen kalın film katotları kullanılarak eşzamanlı üretim yaklaşımı kullanıldı. İncelenen sistem, NaMnO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, NiO ile alaşımlanmış MnO<sub>2</sub>'dir. Bu amaçla dört sıçratma diski hazırlanmıştır. MnO<sub>2</sub> diski 3 inç çapında merkezi konuma yerleştirilmiş ve diğer oksitler 2 inç çapında ve birbirine 120°'lik açılarla üçgen oluşturacak şekilde yerleştirilmiştir. 12,7 mm çapındaki altlıklar, üçgen geometriye sahip bir altlık tutucu haznesine yerleştirilmiştir. Her biri farklı bir bileşime sahip tek bir sıçratma deneyinde toplam 36 katot biriktirilmiştir.

Altı deney yapılarak 216 katot elde edilmiştir. Katotlar, akım toplayıcı olarak kullanılan Ni folyo üzerine kaplanmıştır. Kaplamalar tipik olarak 0,23 ila 2,38 mg arasında değişen bir kütle ile 3 µm kalınlığındadır. Kullanılan hücreler Swagelok tipindedir. Anot olarak 300 µm kalınlığında Zn folyo ve elektrolit olarak 2M ZnSO<sub>4</sub> + 0.1 M MnSO<sub>4</sub> sulu çözeltisi kullanılmıştır.

Ön sonuçlara göre Mn bakımından zengin katotlar olumlu sonuçlar verdiği gözlemlenmiştir. Sonuç olarak, detaylı çalışma için altı setten üç set katot seçilmiştir.

Her katot için döngüsel voltametri ve galvanostatik testler gerçekleştirilmiştir. Na'nın %11 ila %78 arasında değiştiği Bi-Mn-Ni üçlü diyagramının Mn açısından zengin köşesi, kapasiteler, döngüsel kararlılık ve deşarj plato potansiyelleri açısından haritalanmıştır. Haritalara dayalı olarak, 400 mAh/g'ın üzerinde deşarj kapasitelerine sahip üç aday kompozisyon seçilmiştir. Bunlar  $\text{Bi}_{0.04}\text{Na}_{0.55}\text{Ni}_{0.04}\text{Mn}_{0.36}\text{O}_x$ ,  $\text{Bi}_{0.04}\text{Na}_{0.37}\text{Ni}_{0.06}\text{Mn}_{0.53}\text{O}_x$  ve  $\text{Bi}_{0.02}\text{Na}_{0.63}\text{Ni}_{0.02}\text{Mn}_{0.33}\text{O}_x$ 'dir. Seçilen katotların tam potansiyelini kontrol etmek için daha fazla çalışmaya ihtiyaç duyulmaktadır.

Anahtar Kelimeler:  $\text{MnO}_2$  katot, Çinko-iyon pil, Eşzamanlı üretimli çöktürme, Magnetron sıçratmalı çöktürme



Dedicated to a sustainable future on the planet Earth

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I wish a sustainable future to my country Republic of Turkey.

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## CHAPTER 1

### INTRODUCTION

Energy demand of the world has been increasing. Oil, coal, and natural gas have been the primary energy sources for decades. Fossil fuels have met the energy demands very well for long time. However, those energy sources are carbon-based fuels. This leads air pollution by carbon emission. To meet extreme energy demand by fossil fuels creates excessive carbon emission. Renewable energy sources are quite vital for the sustainable, clean, and environmentally friendly future. However, they are available for limited time during a day. For instance, solar energy can be stored only sun is available during the day. The energy must be stored while they are available to use later when energy is needed. Energy storage systems are important to store energy from renewable sources.

There are several types of energy storage systems. Magnetic storage systems have very low storage time between 1 and 60 seconds. Dams are the mechanic energy storage systems. They can store energy about 2700 MW. However, it requires an area that geographically available. Besides, this method is not suitable for mobile devices. Batteries are most suitable for both mobile and grid storage.

Manganese oxide has been widely used since the first batteries were invented. Structurally modified  $\text{MnO}_2$  is a quite attractive material to make primary Zn- $\text{MnO}_2$  batteries not just rechargable but also improve the voltage profile. In addition, Mn and Zn are appealing materials with their abundancy and low cost. Zn/ $\text{MnO}_2$  batteries will be a good fit for grid energy storage systems to make them widespread in use. For this aim, modifying of  $\text{MnO}_2$  cathode is quite vital.

In this study,  $\text{MnO}_2$  cathodes were modified by doping agents. For this purpose, combinatorial approach with RF magnetron sputtering were used to find a new  $\text{MnO}_2$

composition. Targets were home-made. They were prepared from several metal oxides. First, manganese oxide, nickel oxide and bismuth oxide powders were solid-state synthesized. Then, home-made sputter targets were shaped from those powders by sintering process. The synthesized pure powders were pelletized in deformable PTFE rings. Sintered were made at several different temperatures and durations to find the best sintering condition. Homogenous grain size distribution is important to have a stable deposition rate during sputtering. The optimum internal structure with good sintering manner was investigated by scanning electron microscopy. X-ray diffraction phase analysis is made for both precursor oxides and targets to investigate existing phases. Maud software is used for Rietveld quantitative analyses.

Home-made targets were in the RF magnetron sputter device with proper angles and substrate to target distance. Manganese oxide-based cathode materials were grown on nickel substrates as thick films (1000 to 3000 nm). Manganese based cathodes with several range of compositions were formed by altering wattage (rate) of the targets. Active material weight was kept over 0.5 mg by coating for 15 hours or more.

Batteries were assembled as as-sputtered cathodes, zinc anode, PP separator and Zn/Mn sulfate electrolyte. Electrochemical characterizations were performed for each composition. Cyclic voltammetry was used to identify both electrochemical reactions and voltage range. Capacity and cycling performance of the batteries were also investigated to define the high-performance cathode with the best electrochemically active composition.

## CHAPTER 2

### LITERATURE REVIEW

Development of sustainable energy has attracted considerable attention due to environmental concerns caused by fossil fuels. Thus, we have seen a rapid rise of renewable energy, namely solar and wind energy. However, renewable energy sources are intermittent in its nature and require storage. From this perspective, secondary batteries such as Li-ion, and similar are suitable as storage devices. Lithium-ion batteries have good cycle stability and high energy density, but they are quite expensive. In addition, the lack of lithium sources and safety problems limit their use especially for large scale storage applications.

Zn-MnO<sub>2</sub> are known for a long time as primary battery. An advantage of this battery is their low cost which is just a fraction of that of Li-ion batteries. Active materials Zn and MnO<sub>2</sub> are abundant and low cost, and they are environmentally friendly.

In 1968, Kang et al. [1] first showed reduction of MnO<sub>2</sub> to Mn (III) oxide and afterwards to Mn (II) oxide in KOH electrolyte with Zn anode. Mn (II) oxide rechargeable to an inactive phase of Mn (III) oxide. They also found that only MnOOH is reversible to MnO<sub>2</sub> while Mn<sub>2</sub>O<sub>3</sub> is partially oxidases to MnO<sub>2</sub> back[1]. In 1981, Kordesch et al. [2] showed second step reaction that MnOOH to Mn(OH)<sub>2</sub> occurs at low voltage under 0.9 V. They also indicated second step reaction is irreversible and it is increased when KOH concentration is higher.

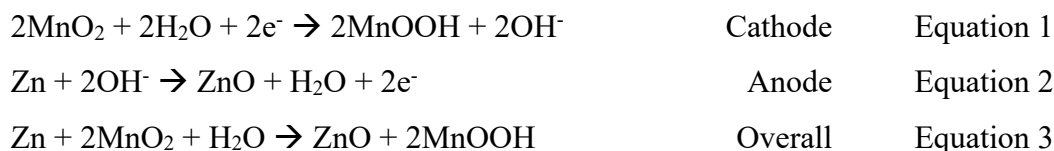
Zn has low cost, non-toxicity and theoretically is capable of yielding a capacity of 820 mAh/g and 5854 mAh/cm<sup>3</sup>[3]. For cathode, MnO<sub>2</sub>, the theoretical capacity of 308 mAh/g for one electron exchange which doubles the capacity if two electrons exchange were taking place.

Because of the attractive properties of Zn-MnO<sub>2</sub>, recent effort has concentrated on ways of making Zn-MnO<sub>2</sub> rechargeable. There are two approaches in these efforts. One concentrates on the traditional battery, i.e., using alkaline electrolyte and try to make the battery rechargeable. The alternative approach makes use of mildly acidic electrolyte and try to impart rechargeability with as high capacity as possible. The current thesis adopts the second approach and tries to develop new cathode chemistries for mildly acidic Zn-MnO<sub>2</sub> batteries.

## 2.1 Zn/MnO<sub>2</sub> Batteries

Zn-MnO<sub>2</sub> batteries are still in mass production as primary batteries. Electrolytic manganese dioxide (EMD) which is  $\gamma$ -MnO<sub>2</sub> is the primary battery cathode active material, and the electrolyte is aqueous KOH. Reaction mechanisms of both anode and cathode are shown on Equations [1-3]. As shown on Equation 1, upon discharge MnO<sub>2</sub> is reduced to MnOOH involving 1 electron exchange.

Reactions in KOH aqueous electrolyte:



If reduction continues to 2 electrons exchange, MnOOH is further reduced to spinel Mn<sub>3</sub>O<sub>4</sub> phase as shown on Equation 4. This second reaction is not reversible and thus, hinders the rechargeability.



A number of studies [4][5] were conducted in recent years to make the alkaline batteries rechargeable by modifying cathode[4]. Yadav et al. [4], improved

rechargeability and reached 2 electrons exchange by making  $\text{Mn}(\text{OH})_2$  reversible with the addition of  $\text{Cu}^{2+}$  and  $\text{Bi}_2\text{O}_3$ . Hertzberg et al. [5] studied with alkaline electrolyte KOH and LiOH mixing. 1M KOH + 3M LiOH aqueous solution was the best electrolyte for  $\text{Bi}_2\text{O}_3$  added  $\beta\text{-MnO}_2/\text{Zn}$  foil cell. LiOH addition prevents the formation of  $\text{ZnMn}_2\text{O}_4$  phase.

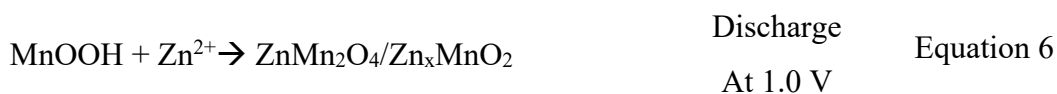
Due to problems faced in alkaline batteries, in 1987, Shoji et al. [6] was the first who pointed out that  $\text{Zn-MnO}_2$  batteries could be made rechargeable using mildly acidic electrolyte. Discharge capacity of the galvanic cell increases with increase in the concentration of  $\text{ZnSO}_4$ . Cell was made with  $\gamma\text{-MnO}_2$  cathode. They found cell is rechargeable more than 30 times. When cell cycle between 0.9 V and 1.7 V, it showed 100% coulombic efficiency with average discharge voltage of about 1.3 V[6].

Xu et al. [7] were first time discovered  $\text{Zn}^{2+}$  ions move in the mildly acidic aqueous electrolyte  $\text{Zn-MnO}_2$  battery and named it as zinc-ion battery due to  $\text{Zn}^{2+}$  ion move between electrodes.

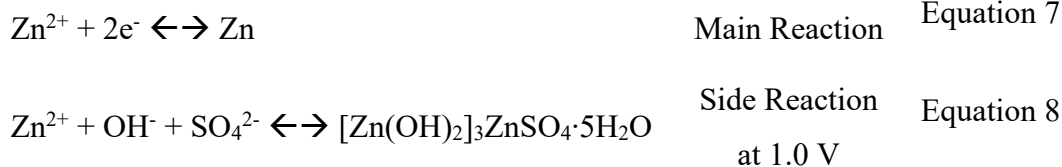
According to Sun et al. [8] in mildly acidic conditions showed  $\text{H}^+$  and  $\text{Zn}^{2+}$  co-insertion mechanism when mildly acidic electrolyte is used. XRD study showed  $\text{H}^+$  insertion is the main reaction during discharge to 1.3 V,  $\text{MnOOH}$  phase forms, while discharging to 1.0 V results as  $\text{ZnMn}_2\text{O}_4$  which shows the Zn insertion[8]. Reaction mechanisms of both anode and cathode in mildly acidic electrolyte are shown on Equations [5-8].

Reactions in mildly acidic aqueous electrolyte:

Cathode:



Anode:



### 2.1.1 Anode

McLarnon et al. [9] reported that the fundamental problem of Zn electrode are shape change and the formation of undesired morphologies such as dendrites, filamentary growths and nodules. They addressed those problems due to high solubility of Zn in common electrolytes and rapid electrochemical kinetics of Zn. Shin et al. [10] explained the dendritic growth in alkaline electrolyte. The oxidized  $\text{Zn}^{2+}$  ions form  $\text{Zn}(\text{OH})_4^{2-}$ -based phases due to the abundance of hydroxide ions around anode material. These zincate ions diffuse away from anode surface due to concentration gradient that yields loss of active material. In addition, zincate ions precipitate as ZnO when the local solubility limit of zincate is reached. Those precipitates yield as dendritic growth and/or passivation, damaging the rechargeability of batteries that operate in alkaline aqueous electrolytes.

Zn anodes are used in the form of either Zn powder or foil. In case powders, the electrodes are prepared as composite of Zn and ZnO using Teflon as binder [4]. An anode using a gelling agent (Carbopol 940) with Zn powder, Indium-Acetate and KOH solution was also reported [11]. Powder form of Zn is used for alkaline media, while in the case of mildly acidic media the anode was mostly Zn foil.

According to Shin et al. [10] in mildly acidic media, pH 4-6 window permits  $\text{Zn}^{2+}$  ions to remain in their ionized form. Using salts such as  $\text{ZnSO}_4$  or  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ , reversible Zn plating/stripping becomes possible to certain extent. In this fashion, recharging the battery becomes much easier by means of ionization of zinc metal.



When pH is lowered, it increases the potential for hydrogen evolution reaction, as predicted by the Nernst equation and the resulting Pourbaix diagram. This implies that low pH solutions are more sensitive to the hydrogen evolution reaction during a cathodic step [10].

As reported by Shin et al. [10] Zn is relatively stable in aqueous media, and the spontaneous formation of a solid electrolyte interface (SEI) layer is insignificant. They further stated that the absence of a SEI layer creates its own problems. SEI layer is a passivation layer that hinders unwanted side reactions. Further Zn is sensitive to some degree of the HER in aqueous media that consumes electrolyte solvent and corrodes the metal surface.

A number of attempts were made so as to improve the anode performance [12]-[13]. They can be categorized as (i) electrolyte formulation [12], (ii) electrode modification [14]-[15], and (iii) host development [13]. For electrolyte formulation, Zhang et al. [12] have used a number of mildly acidic electrolytes using  $\text{ZnCl}_2$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{ZnSO}_4$ , or  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ . They found that reversible reactions were possible sulfate-based and zinc triflate-based electrolytes, while nitrate-based and chloride-based electrolytes were unsuitable for reversible deposition/dissolution mechanism. They also found that 3M Zn-triflate electrolyte exhibited high stability. However, Zn-triflate salt was not enough on its own to meet the expectations in terms of performance and cycle life. In addition, its high cost compared to  $\text{ZnSO}_4$  was detrimental as a choice [10].

In electrode modification, Li et al. [14] used carbon-zinc composites in place of Zn powder. Unmodified Zn anode were made up of Zn powder, acetylene-black and PVDF binder in weight ratio of 7:2:1, while modified Zn anode were prepared mixing Zn powder with activated carbon plus acetylene-black and PVDF binder in weight ratio of 5.8:1.2:2:1. Both modified and unmodified electrodes delivered initial capacity of 170 mAh/g ( $\text{MnO}_2$ ). With unmodified Zn anode the capacity was reduced to 100 mAh/g after 60<sup>th</sup> cycle, while that of modified anode was significantly higher at 150 mAh/g. Li et al assigned this improvement to the suppression of the

zinc hydroxide sulfate ( $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot n\text{H}_2\text{O}$ ) (ZHS) formation brought about by activated carbon, which was an inactive phase. They further showed with XRD study that showed, deposition of zinc hydroxide sulfate preferentially occurs in the pores of activated carbon rather than on the surface of Zn particles.

Number of studies were conducted to coat Zn anode so as to improve its performance. Kang et al. [16] have tape casted nano- $\text{CaCO}_3$  slurry on Zn foil with PVDF binder as surface layer. The electrolyte was 3M  $\text{ZnSO}_4$ +0.1M  $\text{MnSO}_4$  aqueous solution and the cathode was  $\text{MnO}_2$ . They reported a discharge capacity of 200 mAh/g after 1000 cycles which was better than the bare Zn anode which delivered an initial discharge capacity of 175 mAh/g but faded to 100 mAh/g after 1000 cycles.

Zhao et al. [17] used atomic layer deposition to apply ultra-thin (8 nm) amorphous  $\text{TiO}_2$  coating on Zn anode. They found that the cell with pristine Zn delivered capacity around 75 mAh/g ( $\text{MnO}_2$ ) for 350 cycles, while the cell with modified Zn delivered 150 mAh/g capacity for 1000 cycles. They explained that the coating suppresses the gas evolution, corrosion process and enhance the  $\text{Zn}^{2+}$  ion transportation. The electrolyte was 3M  $\text{Zn}(\text{SO}_3\text{CF}_3)_2$  aqueous solution and  $\text{MnO}_2$  were used as the cathode. Xie et al. [15] applied 3D-nanoporous ZnO coating on Zn foil. The coating accelerated the kinetic of  $\text{Zn}^{2+}$  ion rather than the hydrated zinc. Modified anode had a capacity of 212 mAh/g ( $\text{MnO}_2$ ) and showed no capacity fading after 500 cycles at 500 mA/g.

Cui et al. [18] ion beam sputtered gold nanoparticles on Zn foil. The electrolyte was 3M  $\text{ZnSO}_4$  aqueous solution. Cells with both bare Zn and gold coated delivered initial capacity of 200 mAh/g ( $\text{MnO}_2$ ). However, cell with bare Zn failed after 500 cycles, while gold coated kept working over 2000 cycles. The improvement was explained based on gold nanoparticles acting as nucleation sites for ZHS-based phase.

Zhao et al. [19] studied polyamide coating on Zn anode. The electrolyte was 2M  $\text{ZnSO}_4$  + 0.1M  $\text{MnSO}_4$  aqueous solution. Cells with both bare Zn and polyamide

coated delivered initial capacity of 175 mAh/g ( $\text{MnO}_2$ ). However, cell with bare Zn had rapid capacity fading through 200 cycles, while polyamide coated kept capacity over 150 mAh/g for 1000 cycles.

Thus, it can be concluded that the coatings work as a protective layer on the Zn anode surface that prevents side reactions and dendritic growths.

In host development, the active material is loaded in a host. Li et al. [13] compared Cu foil, Cu foam or Ni foam as host material. Zn were electrodeposited on the host material. They assembled cells with  $\beta\text{-MnO}_2$  cathode and  $2\text{M ZnSO}_4 + 0.1\text{M MnSO}_4$  aqueous electrolyte. Cell with Cu foam had a capacity of 206 mAh/g ( $\text{MnO}_2$ ) showed the best cyclic stability after 500 cycles at 1000 mA/g. This is followed by Cu foil where the capacity faded to 100 mAh/g at 500<sup>th</sup> cycle. These compared with zinc flake anode where the fade in capacity was 50 mAh/g at 500<sup>th</sup> cycle. Ni foam anode was even worse than Zn flake in that it was subject to capacity fading down to 50 mAh/g at 300<sup>th</sup> cycle. The main advantage of using host is that it offers higher capacity and coulombic efficiency due to modification of surface area or physicochemical alteration of the pre-existing surfaces.

### 2.1.2 Electrolyte

For Zn- $\text{MnO}_2$  batteries, alkaline, mildly acidic, and non-aqueous ionic liquids are the main electrolytes that have been investigated. For alkaline electrolyte, KOH, LiOH and NaOH are commonly used. However, the use KOH common electrolyte for primary Zn- $\text{MnO}_2$  battery is quite problematic in the case of rechargeable Zn- $\text{MnO}_2$ [20][21].

Hertzberg et al. [5] studied LiOH addition to KOH electrolyte. They found that 1M KOH + 3M LiOH aqueous solution was the best electrolyte. The cathode was  $\text{Bi}_2\text{O}_3$  modified  $\beta\text{-MnO}_2$  while anode was Zn foil. Battery delivered almost double specific capacity at C/3 rate compared to other mixing ratios. Capacity remained over 100

mAh/g at C/3 for 60 cycles. Hertzberg et al. claimed that LiOH addition prevented the formation of  $\text{ZnMn}_2\text{O}_4$  phase.

Yuan et al. [22] studied 6M NaOH alkaline electrolyte where the cathode was  $\text{Na}_{0.44}\text{MnO}_2$  and the anode was Zn foil. Cells were cycled between 1.1 V and 1.95 V which delivered a capacity of 79 mAh/g. When the same cell was cycled between 0.3 V and 1.95 V, the capacity was 345 mAh/g.  $\text{Na}_{0.559}\text{MnO}_2$  had a phase transition below 1.1V to  $\text{Mn}(\text{OH})_2$  which was not reversible for this case and causes severe capacity fading.

Pan et al. [20] compared  $\text{ZnSO}_4+\text{MnSO}_4$  aqueous electrolytes with that of KOH.  $\text{ZnSO}_4+\text{MnSO}_4$  electrolyte had a better performance, lower polarization and stable behavior compared to KOH electrolyte. In this study, they found that Zn anode in KOH permanently transformed to ZnO after few cycles. In contrast, Zn in mildly acidic  $\text{ZnSO}_4$  electrolyte survived over 400 hours without oxidation.

Pan et al. [20] stated that the addition of  $\text{MnSO}_4$  helps prevent or minimize the dissolution of cathode active material  $\text{MnO}_2$  during discharge. Chamoun et al. [23] reports that 0.1M  $\text{MnSO}_4$  addition decreases the capacity decay quite significantly. Zhang et al. [24] tested  $\text{ZnSO}_4+\text{MnSO}_4$  electrolytes in different mixing ratios. 2M  $\text{ZnSO}_4 + 0.1\text{M MnSO}_4$  solution gives the better electrochemical behavior compared to other mixtures. There are more papers related with these electrolyte compositions. Huang et al. used  $\text{MnSO}_4$  addition up to 0.5M with 2M  $\text{ZnSO}_4$  [25]. They discovered that ZHS is also disappeared when reacts with the  $\text{Mn}^+$  ions in electrolyte to form a new reversible phase  $\text{ZnMn}_3\text{O}_7$ .

Zhang et al. [21] compared a number of electrolytes in a cell where cathode was pyrolusite  $\beta\text{-MnO}_2$  and the anode was Zn foil operated between 0.8 V and 1.9 V. The electrolytes were 45% KOH, 3M  $\text{ZnSO}_4$ , 3M  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  and 3M  $\text{Zn}(\text{CF}_3\text{SO}_3)_2\text{-}0.1\text{M Mn}(\text{CF}_3\text{SO}_3)_2$  aqueous electrolytes. Battery with KOH has severe capacity fading to 100 mAh/g after few cycles, meanwhile  $\text{ZnSO}_4$  and  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  faded down to 100 mAh/g after 60 cycles. The performance showed significant

improvement with 3M  $Zn(CF_3SO_3)_2$  - 0.1M  $Mn(CF_3SO_3)_2$  where the capacity remained over 200 mAh/g for 100 cycles at 0.65C.

Table 2.1 Summary of capacities of Zn-MnO<sub>2</sub> cell with hybrid electrolyte

Cathode	Electrolyte	Capacity (mAh/g)	Voltage Range (V)	Ref.
$\alpha$ -MnO <sub>2</sub>	Hybrid 1M NaOH and 0.01M Zn(AC) <sub>2</sub> 2M ZnSO <sub>4</sub> + 0.1M MnSO <sub>4</sub>	282 @200	1.4-2.2	Fan et al. [26]
Electrodeposited $\epsilon$ -MnO <sub>2</sub>	<b>Anode:</b> 6M KOH, 0.2M ZnO and 5mM vanillin solutions <b>Cathode:</b> 2.5M H <sub>2</sub> SO <sub>4</sub> and 0.5M MnSO <sub>4</sub>	600 @100	1-3	Zhong et al. [27]
Electrodeposited $\epsilon$ -MnO <sub>2</sub>	<b>Anode:</b> 6M KOH, 0.2M ZnO and 5mM vanillin solutions <b>Cathode:</b> 2.5M H <sub>2</sub> SO <sub>4</sub> and 0.5M MnSO <sub>4</sub>	600 @1000	1-3	Zhong et al. [27]

Fan et al [26] used a hybrid electrolyte using a nafion membrane where the electrolyte was 1M NaOH and 0.01M Zn(AC)<sub>2</sub>) for the anode and -mild (2M ZnSO<sub>4</sub> + 0.1M MnSO<sub>4</sub> for cathode . Cathode was  $\alpha$ -MnO<sub>2</sub>. The battery was cycled between 1.4 V and 2.2 V with an average discharge voltage of 1.7 V. The cell delivered an initial discharge capacity of 282 mAh/g at 200 mA/g which increased to 428 mAh/g after 80 cycles.

Zhong et al. [27] have used a decoupled electrolyte comprising three chambers. The chamber was for anode (Zn foil) with alkaline electrolyte made up of KOH, ZnO and vanillin solutions. The chamber for cathode was acidic with H<sub>2</sub>SO<sub>4</sub> and MnSO<sub>4</sub> electrolyte. In-between the two chambers were K<sub>2</sub>SO<sub>4</sub> electrolyte with selective ion

membranes. The battery exhibits an open-circuit voltage of 2.83 V (the conventional Zn-MnO<sub>2</sub> batteries deliver 1.5 V). The capacity was 600 mAh/g.

Han et al. [28] studied non-aqueous acetonitrile-Zn(TFSI)<sub>2</sub> in  $\delta$ -MnO<sub>2</sub>/Zn foil cell. Cell delivered a capacity of 123 mAh/g at C/10 for 125 cycles. They showed that 0.2 mol of Zn<sup>2+</sup> ions inserted per one mole of MnO<sub>2</sub> during discharge. Contact loss of active material, electrolyte decomposition and Mn dissolution were the main reason of capacity fading.

### 2.1.3 Cathode

Manganese is a transition metal that has several stable oxide phases (MnO, Mn<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>) and crystallizes in a wide range of crystal structures and multivalent phases due to different valance states of Mn: Mn<sup>2+</sup>, Mn<sup>3+</sup>, Mn<sup>4+</sup>, and Mn<sup>7+</sup>[29]. Diverse Mn-based cathode materials have been investigated for rechargeable zinc-ion batteries. This include  $\alpha$ -MnO<sub>2</sub>,  $\beta$ -MnO<sub>2</sub>,  $\gamma$ -MnO<sub>2</sub>, Akhtenskite-type MnO<sub>2</sub>, as well as Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, ZnMn<sub>2</sub>O<sub>4</sub>, NaxMnO<sub>2</sub>.

The most common structures in the manganese dioxide system are the rutile-type  $\beta$  phase, hollandite-type  $\alpha$ , ramsdellite-type R, birnessite-type  $\delta$ , spinel-type  $\lambda$ , and  $\gamma$ , which is an intergrowth of  $\beta$  and R with various fractions of  $\beta$ /R domains and twinning[30]. Most manganese oxide mineral structures are frame of MnO<sub>6</sub> octahedra which shares edges and/or corners in many combinations, giving rise to a large number of polymorphs[36]. Among them 14 crystal structures having nominal composition MnO<sub>2</sub>, natural or synthetic, have been cited in the literature[37]. The realization of each of these polymorphs is dependent on the type of linkage between the fundamental octahedral units in the crystallographic structure. Pyrolusite,  $\beta$ -MnO<sub>2</sub> having single chains of edge-linked octahedra share corners with neighboring chains to form a framework structure containing tunnels with square cross section that are one octahedron by one octahedron (1 x 1). Pyrolusite crystallizes in the tetragonal crystal system and the c axis is parallel to the chain and the tunnel

direction[38]. Ramsdellite is a metastable form of  $\text{MnO}_2$ . The crystal structure is built of double chains of  $\text{MnO}_6$  octahedra. The double chains consist of two adjacent single chains that shares edges. They link corners with each other to form a framework having rectangular-shaped tunnels that are  $1 \times 2$  octahedra on a side[39]. Further, an  $\alpha$ - $\text{MnO}_2$  (hollandite) cathode possessing  $2 \times 2$  tunnels (size  $\sim 4.6 \text{ \AA}$ ), while todorokite-type  $\text{MnO}_2$  has larger tunnels  $3 \times 3$  (size  $\sim 7.0 \text{ \AA}$ ), the low temperature  $\gamma$ - $\text{MnO}_2$  has randomly arranged intergrowth  $1 \times 1$  (size  $\sim 2.3 \times 2.3 \text{ \AA}$ , pyrolusite) and  $1 \times 2$  (size  $\sim 2.3 \times 4.6 \text{ \AA}$ , ramsdellite) tunnel blocks[40].  $\text{MnO}_6$  octahedra which shares edges gives rise to a layered  $\delta$ - $\text{MnO}_2$ . Crystal structures of manganese oxides are shown in Figure 2.1.

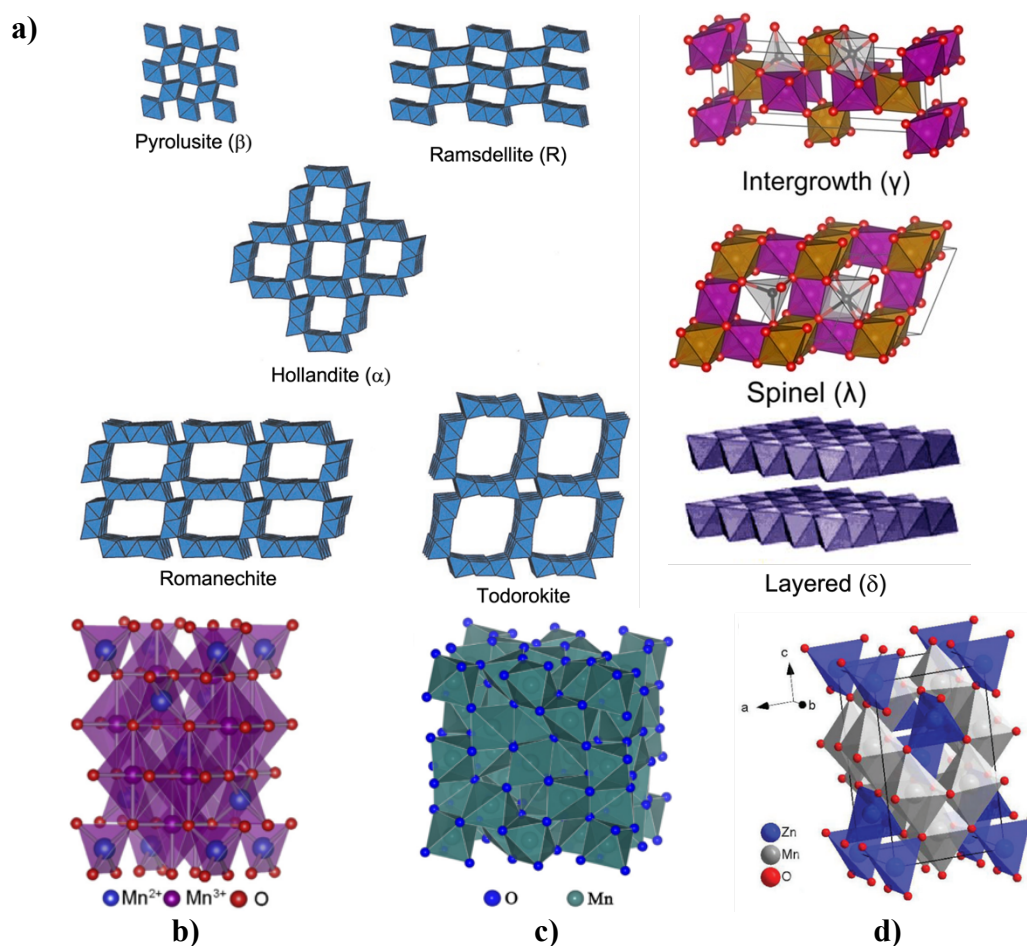


Figure 2.1 Crystal structures of **a)**  $\text{MnO}_2$  polymorphs [30][31][32], **b)** tetragonal spinel- $\text{Mn}_3\text{O}_4$  [33], **c)**  $\alpha$ - $\text{Mn}_2\text{O}_3$  [34], **d)** tetragonal spinel- $\text{ZnMn}_2\text{O}_4$  [35].

Table 2.2 Summary of capacities of  $\alpha$ -MnO<sub>2</sub> cathodes with Zn foil anode

Cathode	Electrolyte	Capacity (mAh/g)	Voltage Range (V)	Ref.
$\alpha$ -MnO <sub>2</sub>	1M ZnSO <sub>4</sub>	210 @C/2 130 @6C	1-1.9	Xu et al. [7]
$\alpha$ -MnO <sub>2</sub> nanofiber	2M ZnSO <sub>4</sub> + 0.1M MnSO <sub>4</sub>	285 @C/3 260 @C	1-1.8	Pan et al. [20]
$\alpha$ -MnO <sub>2</sub> nanorod CNT	2M ZnSO <sub>4</sub> + 0.1M MnSO <sub>4</sub>	282 @C 100 @9C	0.85-1.9	Li et al. [41]
$\alpha$ -MnO <sub>2</sub> Fiber (+10% C)	2M ZnSO <sub>4</sub> + 0.2M MnSO <sub>4</sub>	330 @500 mA/g	0.9-1.8	Gao et al. [42]
$\alpha$ -MnO <sub>2</sub> Fiber (+30% C)	2M ZnSO <sub>4</sub> + 0.2M MnSO <sub>4</sub>	140 @500 mA/g	0.9-1.8	Gao et al. [42]

Studies making use of  $\alpha$ -MnO<sub>2</sub> as cathode are collected in Table 2.2. Here the specific capacity ranges from 200 to 300 mAh/g (MnO<sub>2</sub>). Xu et al. [7] used 1M ZnSO<sub>4</sub> electrolyte without additives and cycled the cell between 1.0 V and 1.9 V. The batteries delivered an initial capacity of 210 mAh/g at 0.5C which was reduced to 100 after 100 cycles.

Pan et al. [20] studied the effect of MnSO<sub>4</sub> addition to the electrolyte. The cathode was  $\alpha$ -MnO<sub>2</sub> nanofiber which gave an initial capacity of 285 and 260 at C/3 and C respectively. The capacity at 5C was 161 mAh/g. The battery has yielded an impressive capacity retention of 92% after 5000 cycles. Authors attributed this to the beneficial effect of MnSO<sub>4</sub> addition to the electrolyte.

Gao et al. [42] used tetragonal  $\alpha$ -MnO<sub>2</sub> fiber as cathode and so as to improve its conductivity they have added acetylene black from 10 up to 40 wt.%. The electrolyte was 2M ZnSO<sub>4</sub> + 0.2M MnSO<sub>4</sub>. With 10% acetylene black, the battery delivers quite



a high capacity, namely 330 mAh/g at 500 mA/g, but the performance was not stable as the capacity faded rapidly with cycling. In terms of cyclic stability 30% acetylene black was found to be the best where the capacity after 300 cycles was 140 mAh/g. They also showed that  $H^+$  from the water is firstly inserted into  $\alpha$ - $MnO_2$ , resulting in the enrichment of  $OH^-$  and the formation of  $[Zn(OH)_2]_3ZnSO_4 \cdot 5H_2O$ . Then the  $Zn^{2+}$  is intercalated into  $\alpha$ - $MnO_2$ , resulting in the formation of  $ZnMn_2O_4$ . Zinc hydroxide sulfate (ZHS) were formed at 0.9 V during discharge.

Table 2.3 Summary of capacities of  $\gamma$ - $MnO_2$  cathodes with Zn foil anode

Cathode	Electrolyte	Capacity (mAh/g)	Voltage Range (V)	Ref.
$\gamma$ - $MnO_2$	1M $ZnSO_4$	210 @C/2 130 @6C	1-1.9	Alfaruqi et al. [40]

$\gamma$ - $MnO_2$  as cathode was investigated by Alfaruqi et al. [40]. The electrolyte was 1M  $ZnSO_4$ . The battery delivered an initial capacity of 285 mAh/g at 0.5 mA/cm<sup>2</sup>. They showed via an in-stu XRD measurements that  $\gamma$ - $MnO_2$  undergoes phase transition during discharge and new phases form close to 1.0 V, i.e.,  $\gamma$ - $MnO_2$  transforms to a spinel-type  $ZnMn_2O_4$  and two new intermediary phases  $\gamma$ - $Zn_xMnO_2$  (tunnel-type), and layered  $Zn_yMnO_2$  (layered- type). Parent  $\gamma$ - $MnO_2$  phase formed back when the battery charged to 1.8 V.

Table 2.4 Summary of capacities of  $\beta$ -MnO<sub>2</sub> cathodes with Zn foil anode

Cathode	Electrolyte	Capacity (mAh/g)	Voltage Range (V)	Ref.
$\beta$ -MnO <sub>2</sub>	2M ZnSO <sub>4</sub>	~260 @200	1-1.9	Li et al. [43]
$\beta$ -MnO <sub>2</sub>	2M ZnSO <sub>4</sub> + 0.1M MnSO <sub>4</sub>	~300 @200	1-1.9	Li et al. [43]
Commercial $\beta$ -MnO <sub>2</sub>	3M ZnSO <sub>4</sub> + 0.1M MnSO <sub>4</sub>	200 @100 150 @500	0.8-1.8	Han et al. [44]
Oxygen defected $\beta$ -MnO <sub>2</sub>	3M ZnSO <sub>4</sub> + 0.1M MnSO <sub>4</sub>	300 @100 200 @500	0.8-1.8	Han et al. [44]
$\beta$ -MnO <sub>2</sub> nanorod	1M ZnSO <sub>4</sub> + 0.2M MnSO <sub>4</sub>	275 @100 135 @200	1-1.8	Islam et al. [45]

Batteries making use of  $\beta$ -MnO<sub>2</sub> cathodes are reported in Table 2.4. Li et al. [43] used  $\beta$ -MnO<sub>2</sub> with 2M ZnSO<sub>4</sub> electrolyte. The initial capacity was close to 260 mAh/g at 200 mA/g which faded rapidly to below 50 mAh/g after 200 cycles. They explained that the fading occurs due to (i) the existence of the inert layer Zn<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>.H<sub>2</sub>O and ZnMn<sub>2</sub>O<sub>4</sub> hindering the electrochemical reaction, (ii) the dissolution of active material during discharge process leading to the capacity loss, (iii) release of gasses in the charging process resulting in poor contact and expansion of the battery. The battery performed significantly better with 2M ZnSO<sub>4</sub> + 0.1 M MnSO<sub>4</sub>. The capacity increased with cycling to 400 mAh/g at 25<sup>th</sup> cycle and then then stabilizes to 300 mAh/g for 200 cycles. Lie et al further claimed that the addition of sodium trimetaphosphate (0.3 wt.%) to electrolyte hinders the formation of Zn<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>.H<sub>2</sub>O and help, improve the cyclic stability.

Han et al. [44] examined oxygen defected  $\beta$ -MnO<sub>2</sub> as cathode. They reported an initial capacity of 302 mAh/g at 50 mA/g. The capacity at 500 mA/g was initially close to 200 mAh/g which was retained 94% after 300 cycles. These values compare

with commercial  $\beta$ -MnO<sub>2</sub> where the capacity was 206 mAh/g at 50 mA/g with 78% capacity retention.

Table 2.5 Summary of capacities of  $\delta$ -MnO<sub>2</sub> cathodes with Zn foil anode

Cathode	Electrolyte	Capacity (mAh/g) Rate (mA/g)	Voltage Range (V)	Ref.
nanoflake $\delta$ -MnO <sub>2</sub>	1M ZnSO <sub>4</sub>	4 <sup>th</sup> cycle 252 @83 100 <sup>th</sup> cycle 112 @83	1-1.8	Alfaruqi et al. [46]
nanosheet $\delta$ -MnO <sub>2</sub>	1M ZnSO <sub>4</sub> +	133 @100 86 @500	1-1.8	Guo et al. [47]
$\delta$ -MnO <sub>2</sub>	0.1M MnSO <sub>4</sub> 2M ZnSO <sub>4</sub> +	100 @100	1-1.8	Guo et al. [48]
Na intercalated $\delta$ -MnO <sub>2</sub>	0.2M MnSO <sub>4</sub> 2M ZnSO <sub>4</sub> +	278 @C 106 @20C	0.95-1.85	Wang et al. [49]
Hollow $\delta$ -MnO <sub>2</sub>	1M ZnSO <sub>4</sub> +	405 @C/2 305 @C	1-1.8	Guo et al. [50]
	0.2M MnSO <sub>4</sub>			

Batteries with  $\delta$ -MnO<sub>2</sub> cathodes are reported in Table 2.5. Alfaruqi et al. [46] used  $\delta$ -MnO<sub>2</sub> nanoflake cathode with 1M ZnSO<sub>4</sub> electrolyte. Cell delivered initial capacity of 112 mAh/g and reached 252 mAh/g at 4<sup>th</sup> cycle at 83 mA/g rate. The capacity then decreased down to 112 mAh/g at 100<sup>th</sup> cycle. During discharge they found that the layered  $\delta$ -MnO<sub>2</sub> undergoes a structural transformation to spinel-type ZnMn<sub>2</sub>O<sub>4</sub> with Mn(III) state and an intermediary Mn(II) phase of layered  $\delta$ -Zn<sub>x</sub>MnO<sub>2</sub>.

Wang et al. [49] used  $\delta$ -MnO<sub>2</sub> cathode pre-intercalated with Na and water molecules. The capacity was 278 mAh/g at 1C and 106 mAh/g at 20C. They reported an excellent capacity retention which was as high as 98% after 10000 cycles. This was attributed to smooth intercalation of Zn in the pre-intercalated layered structure. Guo

et al. [48] compared unmodified  $\delta$ -MnO<sub>2</sub> with  $\beta$ -MnO<sub>2</sub> and claim that  $\beta$ -MnO<sub>2</sub> electrode shows better cycling stability than  $\delta$ -MnO<sub>2</sub>, due to the stable 3D tunnel structure of the latter.

As seen in Table 2.5 highest capacity was obtained with a hollow  $\delta$ -MnO<sub>2</sub> cathode [50] prepared with a special technique. The electrolyte was 1M ZnSO<sub>4</sub> + 0.2M MnSO<sub>4</sub>. They reported a discharge capacity of 405 at C/2 and 305 at C. The cyclic stability of the battery was also quite acceptable preserving a capacity of ~300 mAh/g after 100 cycles.

Table 2.6 Summary of capacities of Mn<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub> and ZnMn<sub>2</sub>O<sub>4</sub> cathodes with Zn foil anode.

<b>Cathode</b>	<b>Electrolyte</b>	<b>Capacity (mAh/g)</b>	<b>Voltage Range (V)</b>	<b>Ref.</b>
Mn <sub>3</sub> O <sub>4</sub>	2M ZnSO <sub>4</sub>	120 @500	0.9-1.9	Hao et al. [33]
Mn <sub>3</sub> O <sub>4</sub>	0.5M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	100@100	0.8-1.9	Stoševski et al. [34]
Mn <sub>2</sub> O <sub>3</sub>	2M ZnSO <sub>4</sub>	148 @ 100	1-1.9	Jiang et al. [34]
Mesoporous Amorphous Manganese Oxide	2M ZnSO <sub>4</sub>	225 @100 till 110 <sup>th</sup> cycle 100 @100 after 200 <sup>th</sup> cycle:	1-1.85	[51]
ZnMn <sub>2</sub> O <sub>4</sub>	1M ZnSO <sub>4</sub> + 0.1M MnSO <sub>4</sub>	225 @100	1-1.8	[52]

Manganese oxides other than MnO<sub>2</sub> were also used as cathodes for the Zn batteries. Hao et al. [33] used Mn<sub>3</sub>O<sub>4</sub> as cathode material for mildly acidic battery using 2M ZnSO<sub>4</sub> electrolyte. Mn<sub>3</sub>O<sub>4</sub> transforms to Mn<sub>5</sub>O<sub>8</sub> during charging and keeping the battery at 1.9 V converts Mn<sub>5</sub>O<sub>8</sub> to Zn birnessite. The battery, cycled between 0.9 V and 1.9 V at 500 mA/g had an initial capacity of around 40 mAh/g increased up to

140 mAh/g till 50<sup>th</sup> cycle. The capacity was reduced to 120 mAh/g after 300 cycles. Stoševski et al. [53] in a similar study confirmed the phase transition of Mn<sub>3</sub>O<sub>4</sub> to birnessite MnO<sub>2</sub>. In addition, they found that for full activation of the battery with Mn<sub>3</sub>O<sub>4</sub> 50 cycles were required with ZnSO<sub>4</sub> electrolyte whereas with zinc triflate electrolyte 15 cycles were sufficient. Jiang et al. [34] used Mn<sub>2</sub>O<sub>3</sub> cathode material, which also transformed to Zn birnessite.

Wu et al. [51] propose used amorphous manganese oxide as cathode . The battery delivered a capacity of 225 mAh/g till around 110<sup>th</sup> cycle, but thereafter the capacity was reduced to 100 mAh/g after 200 cycles. This was attributed to the formation of woodruffite phase (ZnMn<sub>3</sub>O<sub>7</sub>·2H<sub>2</sub>O) which hinders the reversibility. Soundharrajan et al. [52] used ZnMn<sub>2</sub>O<sub>4</sub> microrods as cathode with 1M ZnSO<sub>4</sub> + 0.1M MnSO<sub>4</sub> electrolyte. The battery delivered 225 mAh/g at 100 mA/g for 200 cycles and the capacity retention was 80% after 1000 cycles.

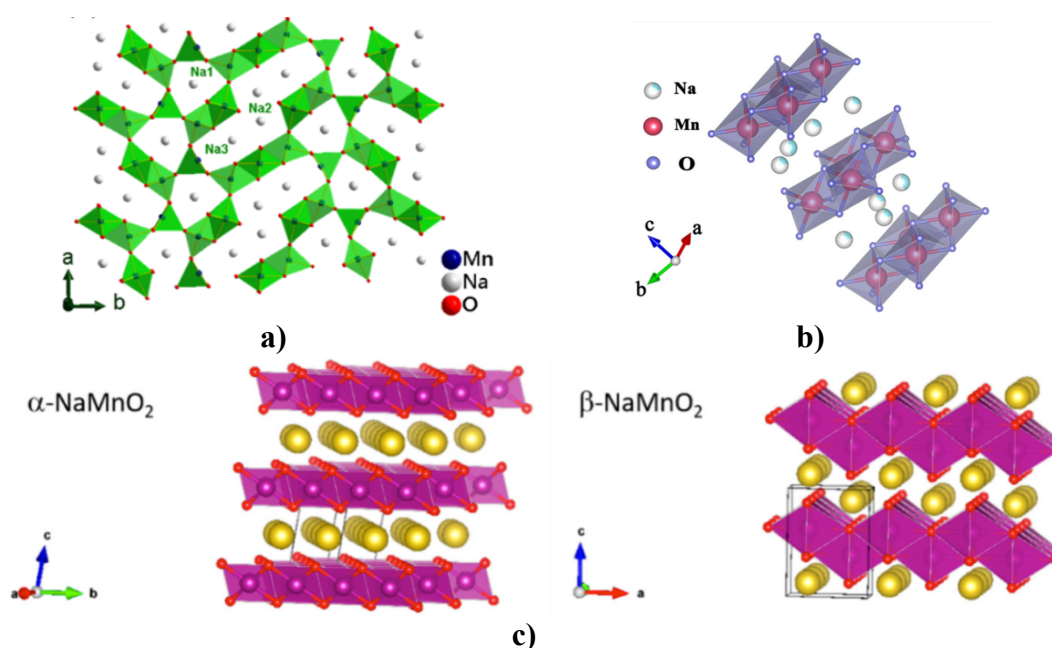


Figure 2.2 Crystal structure of Na<sub>x</sub>MnO<sub>y</sub> **a)** orthorhombic Na<sub>0.44</sub>MnO<sub>2</sub> [54], **b)** hexagonal Na<sub>0.7</sub>MnO<sub>2.05</sub> [55], **c)** monoclinic α-NaMnO<sub>2</sub> and orthorhombic β-MnO<sub>2</sub> [56].

Sauvage et al. [57] revealed that Na<sub>0.44</sub>MnO<sub>2</sub>, which is isostructural with Na<sub>4</sub>Mn<sub>4</sub>Ti<sub>5</sub>O<sub>18</sub>, crystallizes in an orthorhombic lattice cell (*Pbam* space group). The

manganese ions are located in two different environments: all  $\text{Mn}^{\text{IV}+}$  ions and half of the  $\text{Mn}^{\text{III}+}$  ions are in octahedral sites ( $\text{MnO}_6$ ), while the other  $\text{Mn}^{\text{III}+}$  ions are gathered in a square-pyramidal environment ( $\text{MnO}_5$ ). The latter forms edge-linked chains linked to two double and one triple octahedral chain by the vertices, leading to the formation of two types of tunnels. Crystal structure of sodium manganese oxides are shown in Figure 2.2. Sun et al. [55] described the  $\text{Na}_{0.7}\text{MnO}_{2.05}$  shows a layered structure composed of corner-sharing and edge-sharing  $\text{MnO}_6$  octahedra which each oxygen atom belongs to three manganese-oxygen octahedra, while the interlayer is filled by  $\text{Na}^+$ . Manzi et al. [56] reported that  $\text{NaMnO}_2$  crystallize in two different layered structure: (a) the low temperature  $\alpha$ - $\text{NaMnO}_2$  one stable between 600 and 850°C, and (b) the high temperature polymorph  $\beta$ - $\text{NaMnO}_2$  that is thermodynamically stable above 850°C. As seen on Figure 2.2, The  $\alpha$ - $\text{NaMnO}_2$  crystallizes in a monoclinic system ( $C2/m$  space group) with cell parameters  $a = 5.53 \pm 0.01$ ,  $b = 2.860 \pm 0.004$ ,  $c = 5.77 \pm 0.01$  Å, and  $\beta = 112^\circ$  [58]. This crystal structure is a classified O3 type: sodium ions occupy octahedral sites and share edges between the  $\text{MnO}_6$  octahedra, whereas  $\text{Mn}^{3+}$  ions are six-coordinated by oxygen atoms on planar triads with a stacking AB CA BC [59]. The  $\beta$ - $\text{NaMnO}_2$  crystallizes in an orthorhombic system with the space group  $Pmnm$  and cell parameters  $a = 4.77 \pm 0.01$ ,  $b = 2.852 \pm 0.003$ , and  $c = 6.31 \pm 0.02$  Å. In this structure, the  $\text{MnO}_6$  sheets buckle forming a peculiar packed layered structure where sodium ions are hexa-coordinated in the zig-zag interlayers [58].

Table 2.7 Summary of capacities of  $\text{Na}_x\text{MnO}_y$  cathodes with Zn foil anode

Cathode	Electrolyte	Capacity (mAh/g) Rate (mA/g)	Voltage Range (V)	Ref.
$\text{Na}_{0.44}\text{MnO}_2$	0.5M $\text{ZnSO}_4$ +	114 @4C	0.5-2	Wu et al. [60]
$\text{Na}_4\text{Mn}_9\text{O}_{18}$ CNT	1M $\text{Na}_2\text{SO}_4$ 0.5M $\text{ZnSO}_4$ +	53 @4C	1-1.85	Yin et al. [61]
$\text{Na}_{0.44}\text{MnO}_2$	6M NaOH	345 @C/2 79 @C/2	0.3-1.95 and 1.1-1.95	Yuan et al. [22]
$\text{Na}_{0.55}\text{Mn}_2\text{O}_4$ and $\text{Na}_{0.7}\text{MnO}_{2.05}$	3M $n(\text{CF}_3\text{SO}_3)_2$	250 @100 150 @500	0.95-1.85	Wang et al. [62]

There are also number of sodium bearing manganese oxide compounds used as cathodes. These are tabulated in Table 2.8. Wu et al. [60] studied  $\text{Na}_{0.44}\text{MnO}_2$  as cathode using 0.5M  $\text{ZnSO}_4$  + 1M  $\text{Na}_2\text{SO}_4$  as electrolyte. Cell delivered initial discharge capacity of 114 mAh/g at 4C, cycled between 0.5 V and 2.0 V. however rapid capacity fading occurs with cycling. Yuan et al. [22] studied 6M NaOH alkaline electrolyte with  $\text{Na}_{0.44}\text{MnO}_2/\text{Zn}$  foil cell. Cells were cycled between both 1.1-1.95 V and 0.3-1.95 V, and they delivered initial capacities of 79 mAh/g and 345 mAh/g, respectively.  $\text{Na}_{0.55}\text{MnO}_2$  below 1.1 V transforms to  $\text{Mn}(\text{OH})_2$  which is not reversible and causes severe capacity fading. Thus, upon cycling between 0.35 to 1.95 V, the capacity reduced to 30 mAh/g after 4 cycles. However, between 1.1 V and 1.95 V, there was no capacity fading and the cell delivered 79 mAh/g at C/2 for 50 cycles.

Wang et al. [62] used  $\text{Na}_{0.55}\text{Mn}_2\text{O}_4$  and  $\text{Na}_{0.7}\text{MnO}_{2.05}$  as a mixture for cathode. The electrolyte was 3M  $n(\text{CF}_3\text{SO}_3)_2$ . The cell delivered a discharge capacity of 250 mAh/g at 100 mA/g. The cell tested at 1A/g had a capacity of 80 mAh/g an excellent cycling stability with a capacity retention of 83% after 800 cycles.

Number of compounds were used as additive during cathode preparation. Yu [63] claimed that incorporation of Bi into  $\text{MnO}_2$  was beneficial during the synthesis. Yu further explained that  $\text{Bi}^{3+}$  ions are much larger than  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  which as a result prevents spinel  $\text{Mn}_3\text{O}_4$  formation. Minakshi et al. [64] made a various levels of  $\text{TiS}_2$  and  $\text{Bi}_2\text{O}_3$  addition to  $\gamma\text{-MnO}_2$  for an alkaline battery using  $\text{LiOH}$  electrolyte so as to prevent  $\text{Mn}_3\text{O}_4$  formation. A mixture of  $\text{Bi}_2\text{O}_3$  (3%) +  $\text{TiS}_2$  (2%) was the best in terms of performance followed by  $\text{Bi}_2\text{O}_3$  (5%),  $\text{TiS}_2$  (5%), and the plain  $\gamma\text{-MnO}_2$ . Yadav et al. [4] investigated Cu addition during the synthesis of layered  $\delta\text{-MnO}_2$ .  $\text{Bi}_2\text{O}_3$  addition was made to the cathode slurry. The electrolyte was  $\text{KOH}$  (25 wt.%), the battery cycled. They report a capacity of 607 mAh/g for 90 cycles. They claim that Cu stabilizes the layered (birnessite) structure while the  $\text{Bi}_2\text{O}_3$  prevents the formation of irreversible phase of  $\text{Mn}_3\text{O}_4$ . Ni and Co doping are investigated by Biswal et al. in  $\text{Zn/MnO}_2$  battery [65]. With Co doped 2 wt.%, a capacity of 670 mAh/g was reported. With Ni doped 1 wt.% the initial capacity was 395 mAh/g. According to Sokolowski et al. [66] different dopants stabilize different  $\text{MnO}_2$  polymorphs;  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  stabilize  $\gamma\text{-MnO}_2$ ,  $\text{Cr}^{3+}$  stabilizes layered  $\delta\text{-MnO}_2$  (birnessite).

To summarize, manganese oxides generally suffer from two major problems when used as the cathode materials for aqueous rechargeable zinc-ion batteries: 1) Phase transitions taking place during cycling leading to the formation of irreversible phases. 2) Mn dissolution into electrolyte affecting the chemistry of the cathode.



## CHAPTER 3

### PREPARATION OF SPUTTER TARGET FOR THICK FILM CATHODE DEPOSITION

In this chapter details with preparing to active material synthesis are given which are used in sputter target preparation. This involves the preparation of fine oxide powders which are then pressed and sintered to obtain sputter targets in 2-inch diameter.

#### 3.1 Materials and Methods

##### 3.1.1 Synthesis of metal oxide powders

Precursors used in active material synthesis were Mn, Bi and Ni nitrates. Pure oxides were synthesized via a calcination treatment. All calcination were carried out in a muffle furnace with a heating rate of 10°C/min. Where complex oxides were synthesized e.g.,  $\text{Na}_{0.7}\text{MnO}_2$ . The precursors were mixed in stoichiometric proportions and then subjected to calcination treatment. Oxides and carbonates when processed were dried in a furnace at 100°C before they were ball milled. The ball milling was carried out with Retsch PM 400 Ma-Type at 120 rpm for 4 hours.

##### 3.1.2 Preparation of sputter targets

A few drops of water were added to powders and mixed thoroughly before compaction (6 g powder 0.4 cc DI water). The compaction was carried out using a deformable die [67] made up of PTFE ring typically 65 mm inside diameter , 5 mm wall thickness, 5 mm high. The powders were filled into the ring and compacted under 100 MPa pressure. Green body was then removed from the ring and placed in

a muffle furnace for sintering. Heating rate was 10°C/min Following sintering, the resulting disc which was slightly larger than 50 mm was grinded so as to reduce its diameter to 50 mm. MnO<sub>2</sub> target which was 3-inch in diameter were procured from Changsha Xinkang Advanced Materials Co., Ltd.

### 3.1.3 Structural Characterization

Phase analysis of synthesized powders and targets were investigated by Rigaku DMAX2200 or Bruker D8 Advance X-ray diffractometer. 20 mm pellets were used to investigate phase and microstructure after sintering process. Rigaku and Bruker X-ray diffractometer were used with Cu-K<sub>α</sub> radiation ( $\lambda=1.5406\text{\AA}$ ) at 30 kV acceleration and 40 mA current. Diffraction patterns were scanned between 5° and 85° with scan speed of 1°/min and step size of 0.02°. Where necessary, the X-ray diffraction pattern were refined by Rietveld refinement technique using Maud software [68].

FEI Nova NanoSEM scanning electron microscopy (SEM) with SE and EDS detector were used to investigate microstructure. SE detector was used for imaging with 20 kV acceleration voltage. 30 kV acceleration voltage were used for EDS analysis.

## 3.2 Results and Discussions

### 3.2.1 NaMnO<sub>2</sub>

So as to synthesize NaMnO<sub>2</sub>, first Mn<sub>2</sub>O<sub>3</sub> powder was synthesized. For this purpose manganese (II) nitrate tetrahydrate (Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Merck 98.5%) was calcined at various temperatures, 285°C, 325°C, 400°C, 450°C ve 600°C, in air. XRD pastern of calcined powders are given in Figure 3.1. As seen in the pattern MnO<sub>2</sub> phase co-exist with Mn<sub>2</sub>O<sub>3</sub>. When calcined at 600°C for a duration of 5 hours, the resulting powder was Mn<sub>2</sub>O<sub>3</sub>.

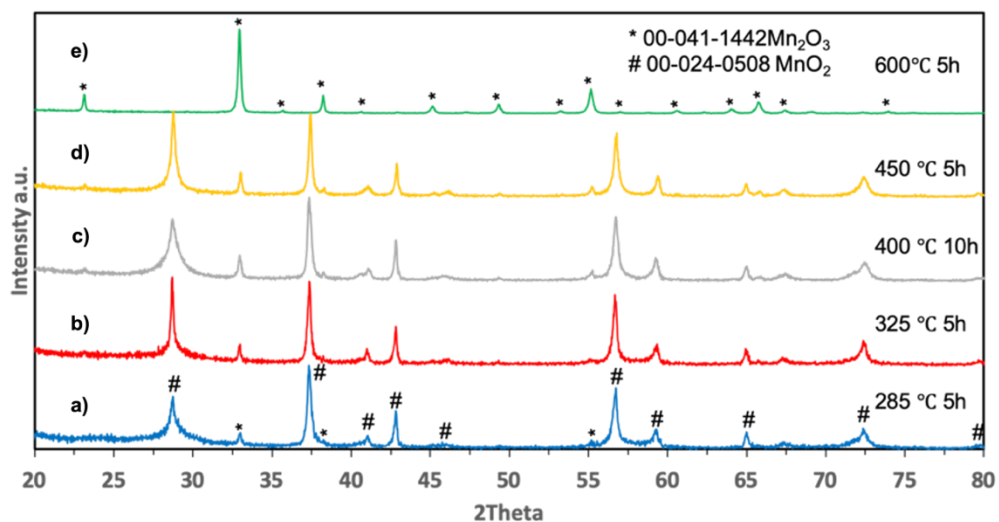


Figure 3.1 XRD pattern of calcined manganese nitrate at different temperatures **a)** 285°C, **b)** 325°C, **c)** 400 °C, **d)** 450 °C, **e)** 600°C

So as to synthesize  $\text{NaMnO}_2$ ,  $\text{Mn}_2\text{O}_3$  synthesized at 600°C for 5 hours are mixed with stoichiometric proportion of  $\text{Na}_2\text{CO}_3$  (99.9% Merck) and ball milled for 4 hours. The mixture was then calcined at 850°C and 950°C for 9, 12 and 15 hours. XRD pattern of the powders synthesized at 850°C are given in Figure 3.2. It is seen that  $\alpha\text{-NaMnO}_2$  is the dominant phase after 9 hours calcination. As the duration is increased the relative proportion of  $\beta\text{-Na}_{0.7}\text{MnO}_2$  increases. There are also minor phases as shown in Figure 3.2.

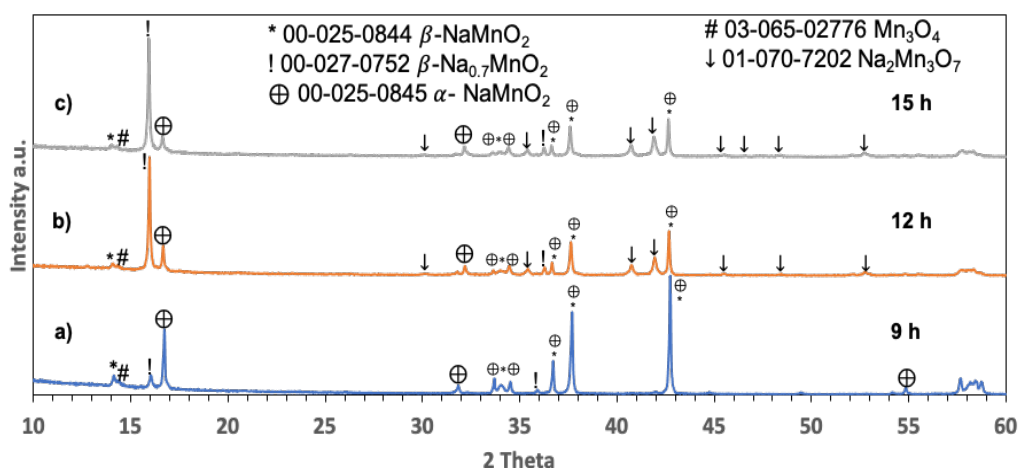


Figure 3.2 XRD pattern of powder synthesis of  $\text{NaMnO}_2$  at 850°C for **a)** 9h, **b)** 12h, **c)** 15h.

In Figure 3.3, phases in the case of calcination at 950°C are similar. After 9 hours of calcination, the relative amount of phases  $\alpha$ -NaMnO<sub>2</sub> and  $\beta$ -NaMnO<sub>2</sub> were similar. With prolonged sintering  $\beta$ -NaMnO<sub>2</sub> transforms to  $\beta$ -Na<sub>0.7</sub>MnO<sub>2</sub> and its fraction increases. So as to obtain  $\beta$ -NaMnO<sub>2</sub> instead of  $\beta$ -Na<sub>0.7</sub>MnO<sub>2</sub> the experiment was repeated with excess Na<sub>2</sub>CO<sub>3</sub>. The patterns are given in Figure 3.4. It is seen that with 10% excess Na<sub>2</sub>CO<sub>3</sub>, the synthesized powder is made up of  $\alpha$ -NaMnO<sub>2</sub> with some minor phases.

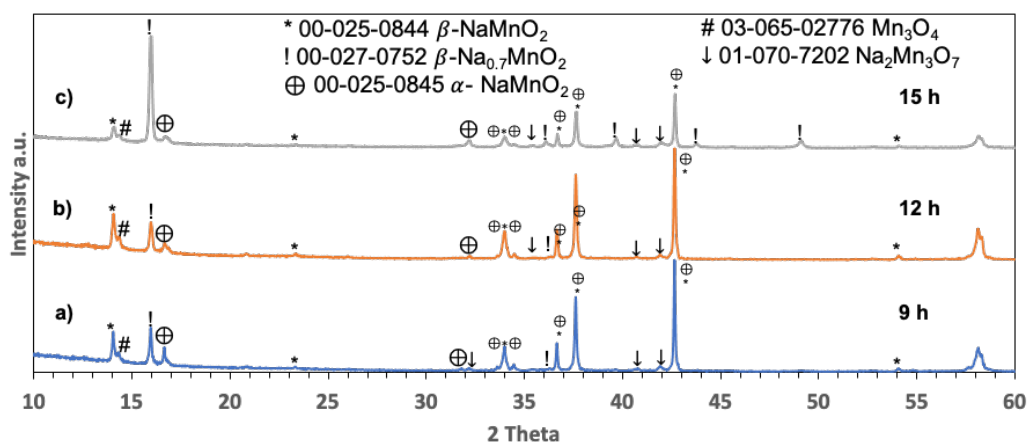


Figure 3.3 XRD pattern of powder synthesis of NaMnO<sub>2</sub> at 950°C for a) 9h, b) 12h, c) 15h

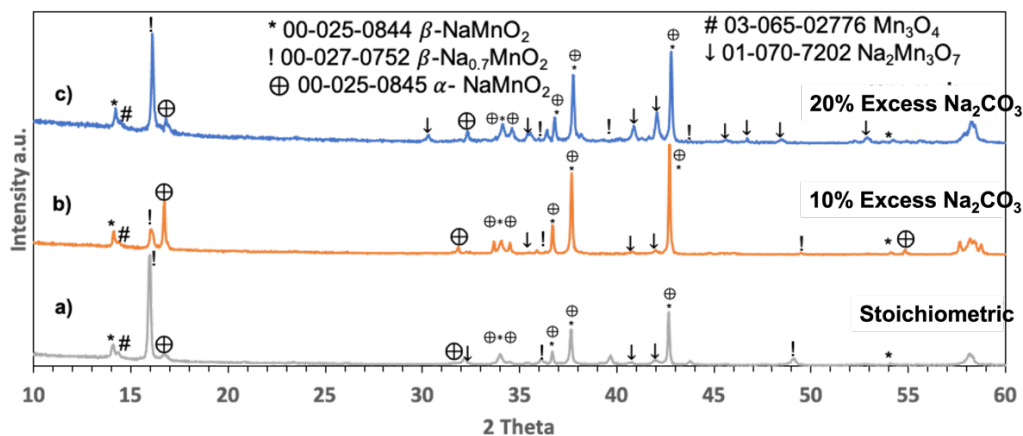


Figure 3.4 XRD pattern of powder synthesis of NaMnO<sub>2</sub> at 950°C a) stoichiometric, b) 10% excess Na<sub>2</sub>CO<sub>3</sub>, c) 20% excess Na<sub>2</sub>CO<sub>3</sub>

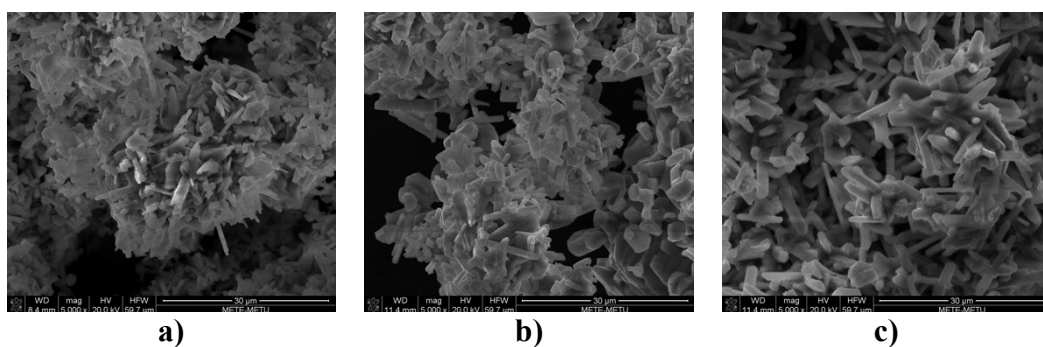


Figure 3.5 SEM images of as-synthesized powders for 15 hours at **a)** 850°C, **b)** 950°C **c)** 950°C with 10% excess  $\text{Na}_2\text{CO}_3$

Representative SEM images recorded from synthesized powders are given in Figure 3.5. It is seen that the powders are needle like and morphologically are all similar to one another. EDS analysis taken from Figure 3.5 (c) which refers to the sample with 10%  $\text{Na}_2\text{CO}_3$  addition yield  $\text{Na}:\text{Mn} = 0.48:0.52$  which is quite close to  $\alpha\text{-NaMnO}_2$  powder.

Powders with 10%  $\text{Na}_2\text{CO}_3$  addition was synthesized at 950°C for 15 hours. A total of 10 gram of  $\alpha\text{-NaMnO}_2$  was synthesized. They were pressed to 20 mm diameter disc and sintered at 1350°C at 5, 10, 15 hours. XRD pattern of the resulting pellet are given in Figure 3.6. It is seen that after 5 hours of sintering there are two phases in the pellet;  $\alpha\text{-NaMnO}_2$  which was the starting phase of the powders and  $\beta\text{-NaMnO}_2$  plus  $\beta\text{-Na}_{0.7}\text{MnO}_2$ . With prolonged sintering the latter phase becomes more dominant such that after 15 hours of sintering the pellet was totally made of  $\beta\text{-Na}_{0.7}\text{MnO}_2$ . SEM image of the sintered pellet is given in Figure 3.7 (a). It is seen that the structure is fully dense.

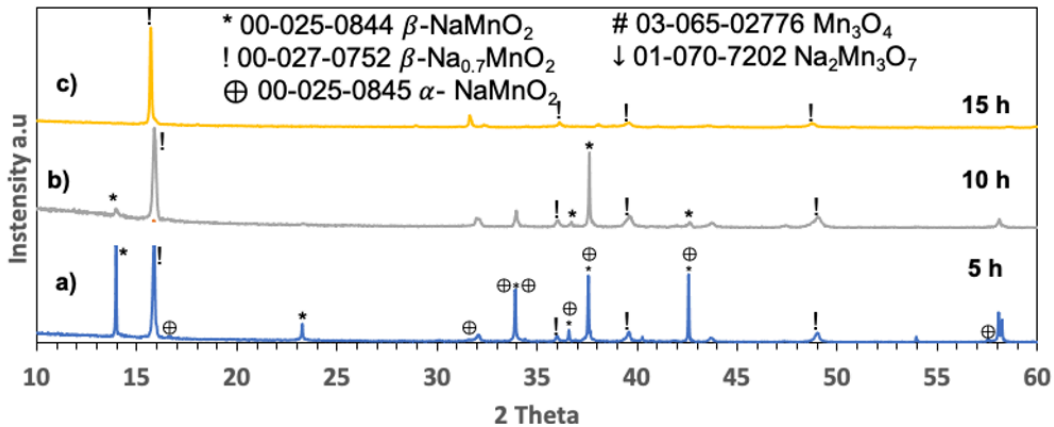


Figure 3.6 XRD pattern of sintered  $\text{NaMnO}_2$  targets at  $1350^\circ\text{C}$  for a) 5h, b) 10h, c) 15h

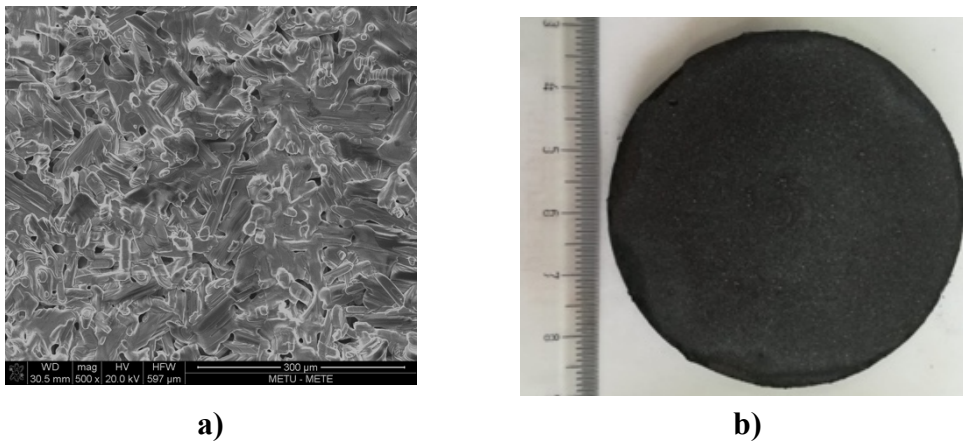


Figure 3.7  $\text{Na}_{0.7}\text{MnO}_2$  sputter target sintered at  $1350^\circ\text{C}$  a) SEM micrograph b) sputter target

Having determined the conditions of sintering, noting that little shrinkage takes place in sintering, the powders were pressed into 55 mm diameter Teflon ring and sintered in the same conditions. The resulting pellet is shown in Figure 3.7 (b). This pellet was reduced in diameter to 50 mm by grinding its periphery.

### 3.2.2 $\text{Bi}_2\text{O}_3$

$\text{Bi}_2\text{O}_3$  was synthesized from Bismuth oxynitrate ( $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$ , 71% Bi basis Merck). For this purpose, Bismuth oxynitrate powders were placed in a crucible and calcined in air. XRD pattern of the powder resulting from calcination at  $600^\circ\text{C}$  after 1.5 hours is given in Figure 3.8. The pattern was compatible with  $\text{Bi}_2\text{O}_3$  (pdf card

no. 00-027-0052). Cell parameters as derived from XRD pattern using a related CIF file via Rietvelt refinement were  $a=5.859\text{\AA}$ ,  $b=8.171\text{\AA}$ ,  $c=7.517\text{\AA}$ . Representative SEM images recorded from synthesized powders are given in Figure 3.9.

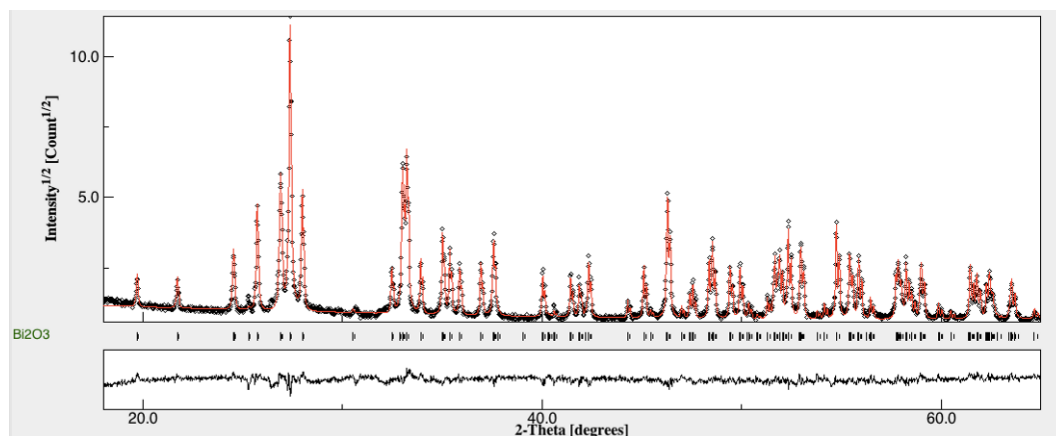


Figure 3.8 XRD pattern of as-synthesized  $\text{Bi}_2\text{O}_3$  powder at  $600^\circ\text{C}$

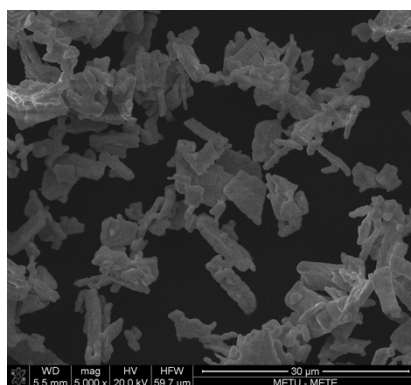


Figure 3.9 SEM image of synthesized  $\text{Bi}_2\text{O}_3$  powder

For target making small pellets 20 mm in diameter were pressed and sintered at  $600^\circ\text{C}$ . XRD pattern was very similar to that given in Figure 3.8. SEM micrograph after sintering is given in Figure 3.10 (a) where the structure is almost fully dense.

Having determined the sintering conditions powders calcined at  $600^\circ\text{C}$  were pressed into a Teflon ring of 65 mm in diameter and the pellet was sintered at  $600^\circ\text{C}$  for 5 hours. The resulting pellet was ground at its periphery so that its diameter was 50 mm. A photograph of  $\text{Bi}_2\text{O}_3$  sputter target produced in this way is shown in Figure 3.10 (b).

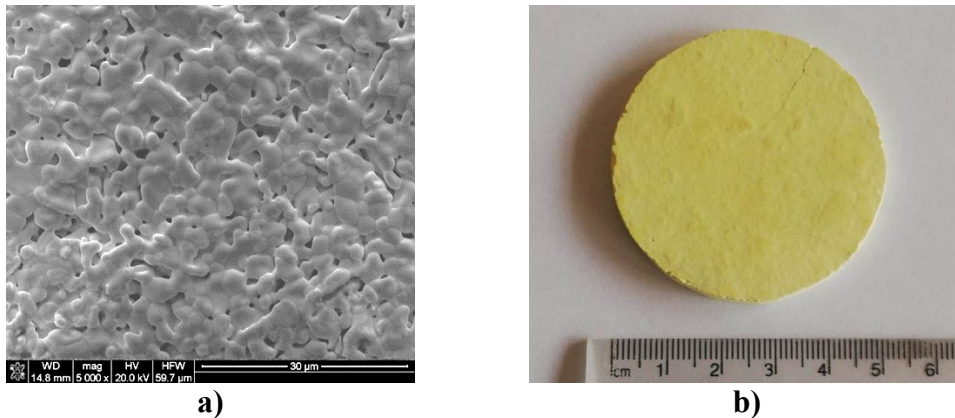


Figure 3.10 Bi<sub>2</sub>O<sub>3</sub> sputter target sintered at **a)** SEM image (20 mm pellet), **b)** sputter target

### 3.2.3 NiO

NiO was synthesized from nickel (II) nitrate hexahydrate ((Ni(NO)<sub>3</sub>.6H<sub>2</sub>O, Merck 99%). For this purpose, nickel nitrate powders were placed in a crucible and calcined in air. XRD pattern of the powder resulting from calcination at 800°C after 1 hour is given in Figure 3.11. The pattern was compatible with cubic NiO (pdf card no. 04-001-9373). Cell parameters as derived from XRD pattern using a related CIF file via Rietvelt refinement were a=4.179Å. Representative SEM images recorded from synthesized powders are given in Figure 3.12.

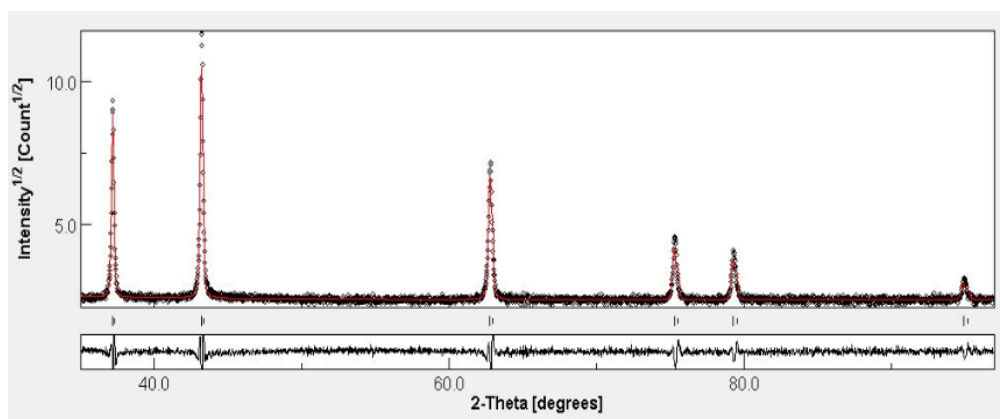


Figure 3.11 XRD pattern of as-synthesized NiO powder at 800°C



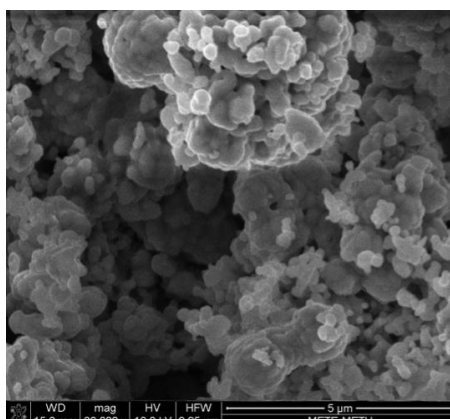
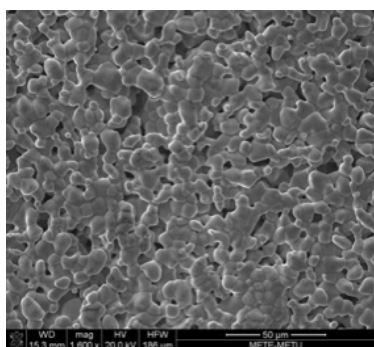
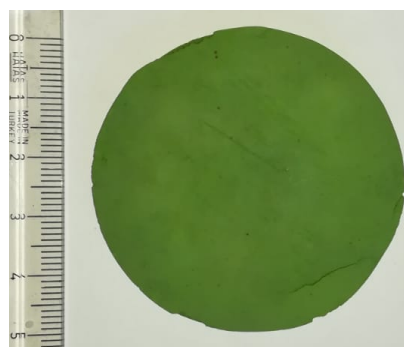


Figure 3.12 SEM image of synthesized NiO powder

For target making small pellets 20 mm in diameter were pressed and sintered at 1250°C. XRD pattern was very similar to that given in Figure 3.11. SEM micrograph after sintering is given in in Figure 3.13 (a) where the structure is almost fully dense. Having determined the sintering conditions, powders calcined at 800°C were pressed into a Teflon ring of 65 mm in diameter and the pellet was sintered at 1250°C for 7 hours. The resulting pellet was ground at its periphery so that its diameter was 50 mm. A photograph of NiO sputter target produced in this way is shown in Figure 3.13 (b).



**a)**



**b)**

Figure 3.13 **a)** SEM image of sintered NiO (20 mm pellet) in air, **b)** 2-inch NiO target

### **3.3 Summary**

Active materials were synthesized successfully and discs of  $\text{Na}_{0.7}\text{MnO}_2$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{NiO}$  in 2-inch diameter were successfully produced by sintering the pressed pellets at elevated temperature. In addition to these discs, the use was made of  $\text{MnO}_2$  disc in 3-inch in diameter which was procured from Changsha Xinkang Advanced Materials Co., Ltd.

## CHAPTER 4

### COMBINATORIAL DEVELOPMENT OF $\text{MnO}_2$ -BASED CATHODES FOR Zn- $\text{MnO}_2$ BATTERIES

#### 4.1 Introduction

Batteries are normally prepared by slurry method, i.e., anode and cathodes were prepared as slurry and applied to current collectors. Solid state batteries are somewhat different as a certain fraction of them are prepared via PVD methods [69]. Zhou et al. [69] reported that battery components of anode, cathode and electrolyte can be deposited layer by layer to make all-solid-state battery with thickness less than  $20 \mu\text{m}$ . Thus, energy dense batteries can be produced without using conductive additive or binders. Lobe et al. [70] summarized the PVD process in which material is deposited from the gas phase. Its main advantage is the creation of dense solid layers with a tunable thickness, adjustable and controlled composition, crystallinity, and crystal orientation. Further, the contamination is minimal due to the absence of organic reactants, and there is the option to sequentially deposition of several materials.

Combinatorial approach based on sputter deposition were investigated for Li-ion batteries [71]-[72]. Exploring the different methods of film deposition, Bouwman et al. [71] stated that for  $\text{LiCoO}_2$  films deposited by radiofrequency (RF) sputtering exhibited an  $a$ -axis orientation while those deposited by PLD showed a  $c$ -axis orientation. Whitacre et al. [73] combinatorial sputter deposited cathode, anode, and electrolyte with different compositions. This simultaneous approach allowed many solid-state micro-batteries that had  $\text{Li}_y\text{Mn}_x\text{Ni}_{2-x}\text{O}_4$  cathodes, where  $x$  varied from 0.2 to 1.8 and  $y$  varied from 2.7 to 3.7 in the as-deposited films. Meanwhile lithium phosphorus oxynitride was used as electrolyte and evaporated Li metal was the anode. Cathode with composition of  $\text{LiMn}_{1.4}\text{Ni}_{0.6}\text{O}_4$  had both the highest specific

capacity and longest high-potential discharge plateau. Finally, conventionally made cathode with same composition aggregated with similar result. Fleischauer et al. [72] combinatorial sputtered Si anodes for Li-ion batteries. They deposited Si on a lead patterned circuit having 64 channels of 5 mm diameter of contact pads. Depending on the distance, capacity per unit area of the electrode changed. The near to target, higher areal capacity obtained. They showed that combinatorial deposited 64 cells assembly in 10 min which equals to assembly of two conventionally made coin cell.

Hanak [74] studied combinatorial sputtering with very interesting targets. They made a twofold circular target half is material A and other half is material B or threefold circular target with three portions of material. Another target was made as circular target that include smaller circular target in it with different material. Hatchard et al. [75] studied combinatorial sputtering with multiple sputter target.

For MnO<sub>2</sub>, changing sputtering parameters different microstructures and/or different phases can be made. Borysiewicz et al. [76] studied relationship between process conditions and structural properties for MnO<sub>2</sub>. For 0, 1 and 5 sccm oxygen flow, when chamber pressure increased deposition rate decreases for all conditions. MnO<sub>2</sub> target were used. A composition of  $\lambda$ -MnO<sub>2</sub>/ $\gamma$ -MnO<sub>2</sub> was found for no oxygen content. Meanwhile, the composition changed to  $\beta$ -MnO<sub>2</sub>/ $\gamma$ -MnO<sub>2</sub> for intermediate oxygen content, and  $\gamma$ -MnO<sub>2</sub> phase was dominating when largest oxygen content was present. LIN et al. [77] studied sputtering of MnO<sub>2</sub> thin film by using Mn target. Increasing oxygen content was yielded as Mn<sub>2</sub>O<sub>3</sub> formation and increasing sputtering time was yielded as needle shape of grains.

In our lab, Pişkin et al. and Sarı et al. have used combinatorial approach to determine compositions suitable for hydrogen separation membranes [78][79][80] and cathodes for intermediate temperature solid oxide fuel cells [67].

In this chapter cathodes for Zn-MnO<sub>2</sub> batteries were sputter deposited in Bi<sub>2</sub>O<sub>3</sub>-Na<sub>0.7</sub>MnO<sub>2</sub>-NiO ternary system. The aim was to identify cathode compositions with superior electrochemical performance.

## 4.2 Experimental Procedure

### 4.2.1 Sputter deposition of cathodes

Vacuum chamber used for sputter deposition was 500x500x500 mm, Figure 4.1. The chamber incorporates a total three peripheral sputter guns in 2-inch diameter placed at a circle of 350 mm and 120° apart. The chamber also incorporates a central gun in 3-inch in diameter.

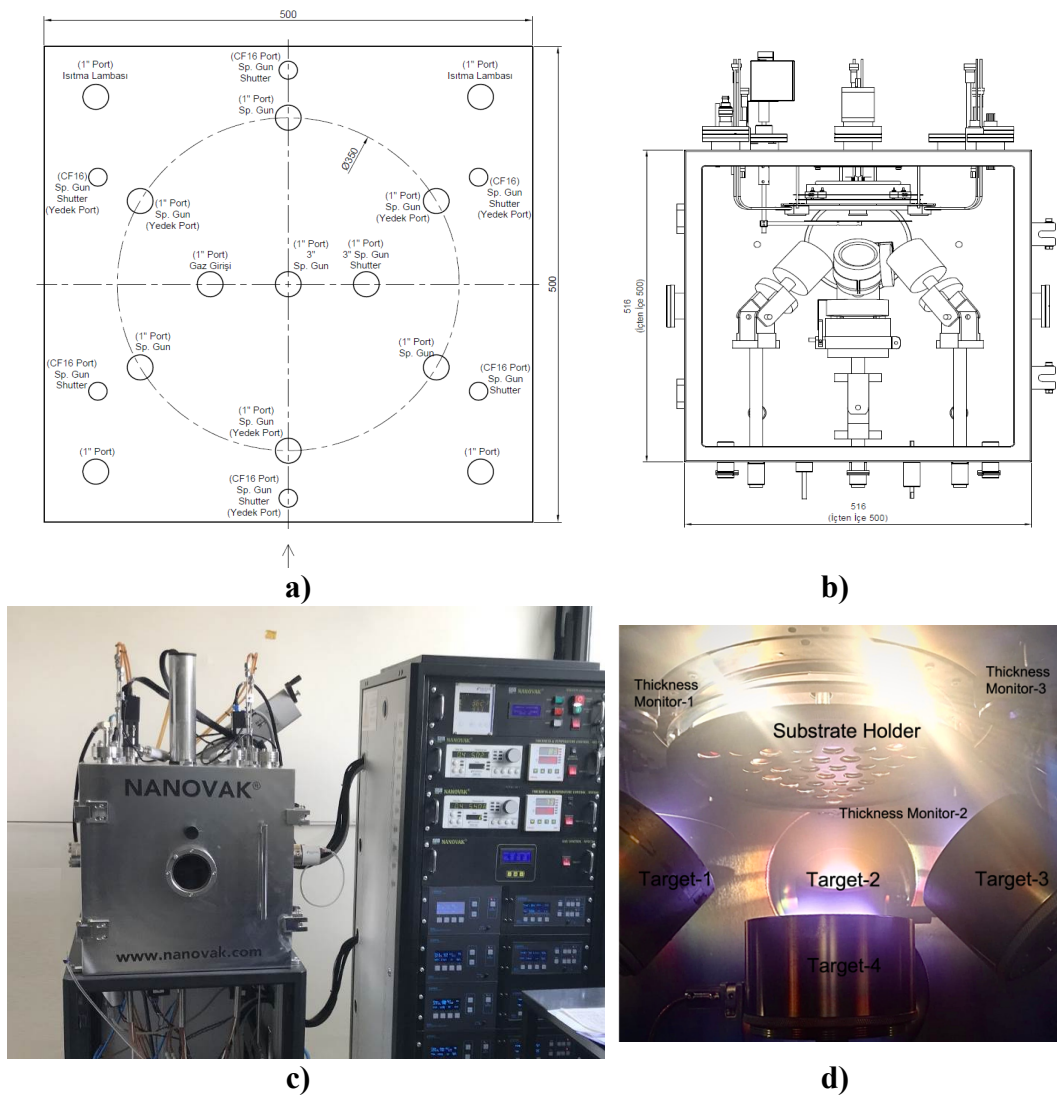


Figure 4.1 Technical drawing of Nanovak magnetron sputtering **a)** top view, **b)** side view and photograph of the machine **c)** outside, **d)** inside view

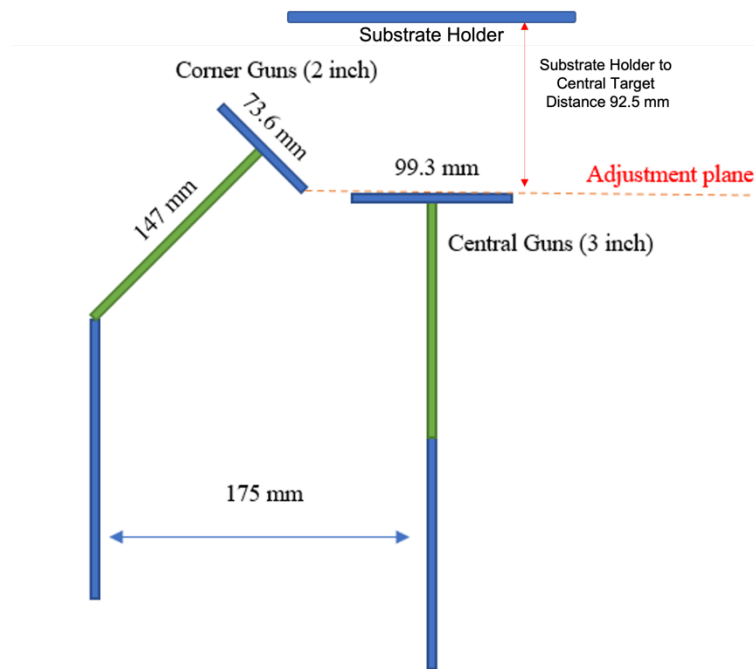


Figure 4.2 Gun positions

The guns were aligned in the following manner. First the height of the central gun was adjusted such that the distance to the substrate plane was 92.5 mm. Then peripheral guns were tilted as shown in Figure 4.2 i.e., the lower edge of the peripheral target holder was just touching the central target plane. In this position the tilt angle was 45°. Samples were placed in a substrate magazine at the substrate plane, Figure 4.3. As seen in Figure 4.3, the substrates were 12.7 mm in diameter in a triangular geometry. A total 36 substrates could be loaded on the substrate magazine. The alignment of the peripheral guns was also checked with sensors placed closed to the corners of the triangle: The rotation of the gun was made such that two sensors away from the gun reads the same deposition rate.

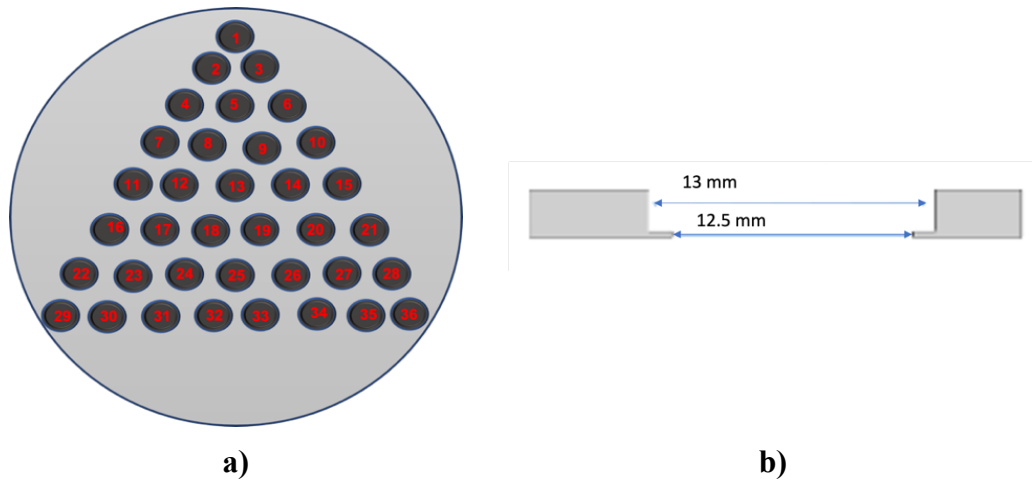


Figure 4.3 Schematic presentation of sample holder **a)** top view, **b)** side view

Having placed the targets in their gun and substrates to the sample magazine, the experiment was initiated by taking the chamber under vacuum. Once the base pressure reached  $10^{-7}$  Torr, sputtering gas of high purity argon (99.999%, Linde Gaz Inc.) and high purity oxygen (99.999%, Linde Gaz Inc.) were fed with 10 and 13 sccm, respectively. The total chamber pressure was kept at  $10^{-3}$  Torr and gas pressure was kept at 5 mTorr. Once the chamber pressure and argon pressure stabilize, targets were started with proper power settings increases with 0.5 W/sec. Increasing the power load slow protects the targets since they all were ceramic which having insulating behavior. Finally, targets and sample shutters were turned on, respectively.

The experiment first involved the determination of tooling factor. Once gun positions were fixed, tooling factor of thickness monitors were calibrated. Thickness sensor calculation includes materials density, z-ratio, and tooling factor. Materials density and z-ratio are material dependent variables. Therefore, tooling factor should be calibrated. For this purpose, sputtering was made for each target. Glass substrate was selected. Initial tooling factor set as 100. Argon flow set as 10 sccm and oxygen flow set as 13 sccm. Total chamber pressure was kept as 3 mTorr. 130 min and 360 min coating were made for peripheral and central guns, respectively. Thickness monitor value is recorded. Then real thickness was measured under SEM. Finally, tooling

factor were corrected. For tooling factor determination of the thickness monitor for NiO target, materials density, z-ratio, and tooling factor were set as 7.450, 1 and 100, respectively. After 130 min deposition, measured thickness was  $\approx 100$  nm under SEM and sensor thickness was 150 nm. Therefore, tooling factor was set as 66.7.

## **4.2.2 Material Characterization**

### **4.2.2.1 Structural Characterization**

Structural analysis of sputtered cathodes was carried out X-ray diffraction using Rigaku DMAX2200 or Bruker D8 Advance X-ray diffractometer. Rigaku and Bruker X-ray diffractometer were used with Cu-K $_{\alpha}$  radiation ( $\lambda=1.5406\text{\AA}$ ) at 30 kV acceleration and 40 mA current. The scanning rate was 1 $^{\circ}$ /min with step size of 0.02 $^{\circ}$ .

Sputtered samples were also investigated with Scanning electron microscopy. For this purpose, FEI Nova NanoSEM was used (20 kV with SE detector). Where necessary the samples were investigated with EDS analysis. Weighing of sputtered samples were carried out using Sartorius CPA225D (0.01 mg sensitivity). Measurements were recorded when the balance was reliably stabilized.

### **4.2.2.2 Electrochemical Characterization**

Cells used for electrochemical characterization was of Swagelok type, Figure 4.4. MnO $_2$  based cathode sputtered on nickel disc 80  $\mu\text{m}$  thick and has a diameter of 12.7 mm in diameter was used as cathode. Anode was Zn foil 300  $\mu\text{m}$  thick (99.8% pure). Separator was 180  $\mu\text{m}$  thick Freudenberg FS 2226. Electrolyte was 2M ZnSO $_4$ +0.1M MnSO $_4$  in DI water. Current collectors in the Swagelok cell were 12.9 mm diameter stainless steel rods. Cell has a spring which keep the cell steady state. Spring has a rod diameter of 1 mm and diameter of 12.4 mm and height of 10.5 mm. Cells were assembled starting from cathode and separator first. Then 0.5 ml electrolyte were dripped and let the separator absorb. Finally, Zn foil anode were placed. Before



anode current collector rod, 10 mm height of stainless-steel rod and spring were placed, then cell closed by tighten the valves.

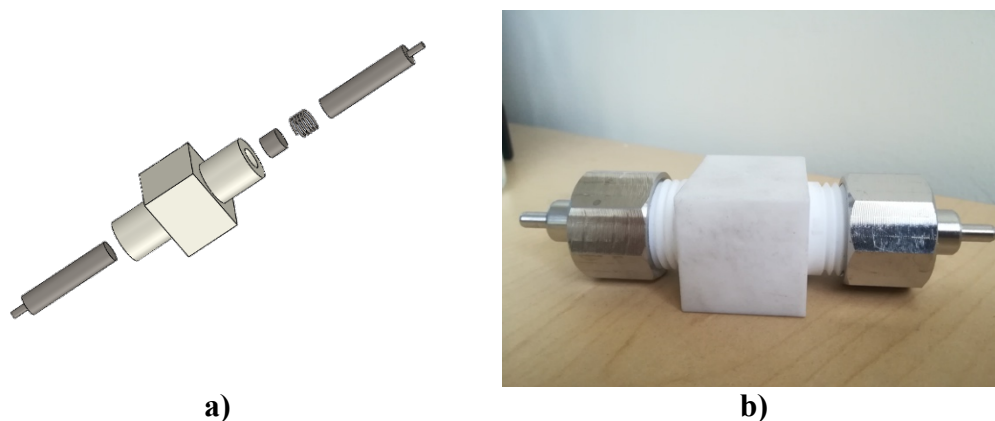


Figure 4.4 Swagelok type cell **a)** schematic view, **b)** photograph of the cell in as – assembled form

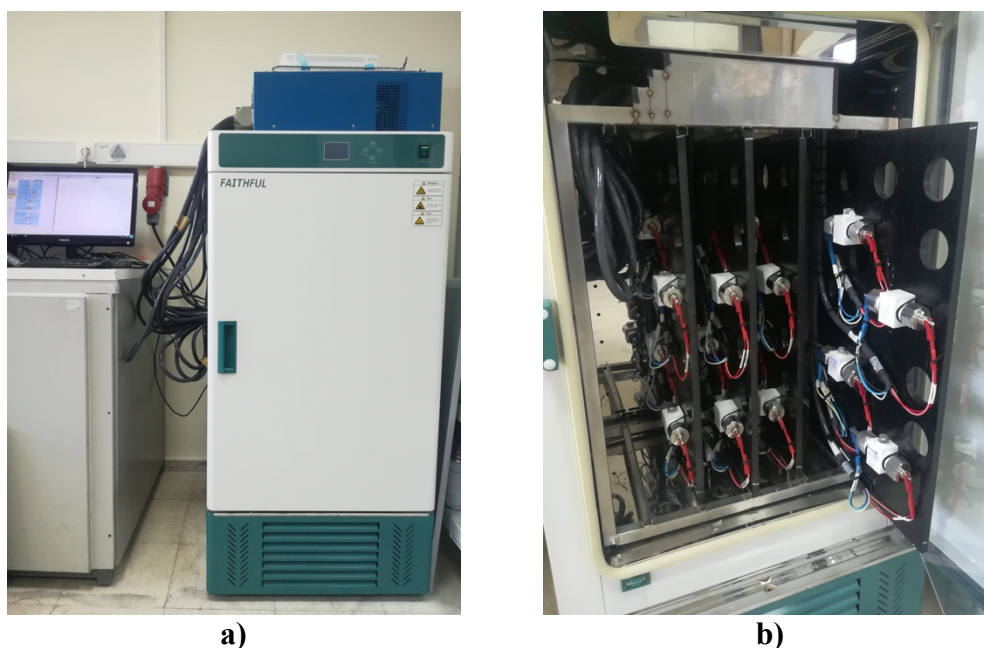


Figure 4.5 16 channel battery testing system **a)** cabin, **b)** sliding shelves with mounted cells inside the cabin

Electrochemical measurements were made with BioLogic MPG2 cell testing equipment, Figure 4.5. It incorporates total of 16 channels. Cyclic voltammetry (CV) was measured scanning between 1.0 V and 2.0 V with sweep rate of 2 mV/sec for 15 cycles. Galvanostatic testing were made between 1.0 V and 1.9 V for 50 cycles. Samples were investigated under constant current with rate of 61.6 mA/g. Having

reached the cut-off voltage, the cell rested for 5 minutes before continuing the test. Rate capability tests were carried out with rates of 61.6, 154, 308 and 616 mA/g each for 5 cycles each.

### **4.3 Combinatorial Development of MnO<sub>2</sub>-Based Cathodes**

#### **4.3.1 Compositional mapping**

Bi<sub>2</sub>O<sub>3</sub>, Na<sub>0.7</sub>MnO<sub>2</sub> and NiO targets 2-inch in diameter were placed in the peripheral guns and a MnO<sub>2</sub> target of 3-inch in diameter was placed in the central gun. Tooling factors which had been determined entered the respective channel of the thickness monitor. A total of 6 experiments were carried out using power settings as given in Table 4.1. The experiments were carried out first on aluminum substrate (200 μm thick) for a duration of 7 hours yielding 1.23 μm thick films. Then the experiment was repeated in the same conditions for nickel substrate (200 μm thick) for 17 hours where the thickness was approximately 3 μm (measured in the corners of the triangular substrate magazine).

A total of 36 cathodes deposited on aluminum substrate were characterized with EDS analysis. Three measurements were taken on the sample under low magnification each with a duration of 60 seconds. The compositions determined are shown plotted in Figure 4.6 (a) where the power settings of the targets were 30, 100, 100 and 100 W for Bi<sub>2</sub>O<sub>3</sub>, Na<sub>0.7</sub>MnO<sub>2</sub>, NiO and MnO<sub>2</sub>, respectively. Here each composition shown was such that atomic fractions of Bi, Ni and Na summed up to 1 and the atomic fraction of Mn was normalized accordingly. Thus, atomic fractions summed up for all elements when Mn was included were therefore greater than 1. As can be seen in Figure 4.6 (a), thin film cathodes are collected more towards the Na-Ni line. In order to obtain a more homogeneous distribution, a second experiment, i.e., Experiment B, was carried out in which the power setting of the Bi<sub>2</sub>O<sub>3</sub> target was reduced. The power setting of the subsequent four depositions is given in Table 4.1

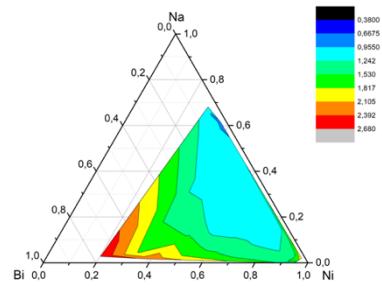
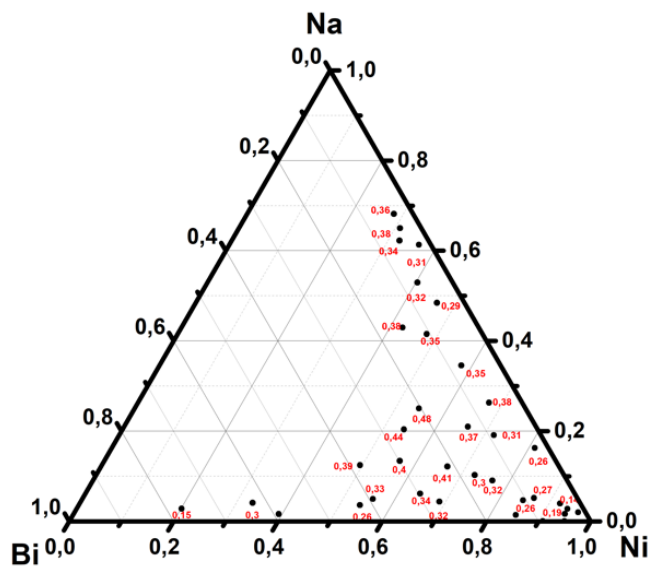
and were successful in yielding thin films with richer Na content. These are shown plotted in in Figure 4.6.

Table 4.1 Power parameters of different series of sputtering.

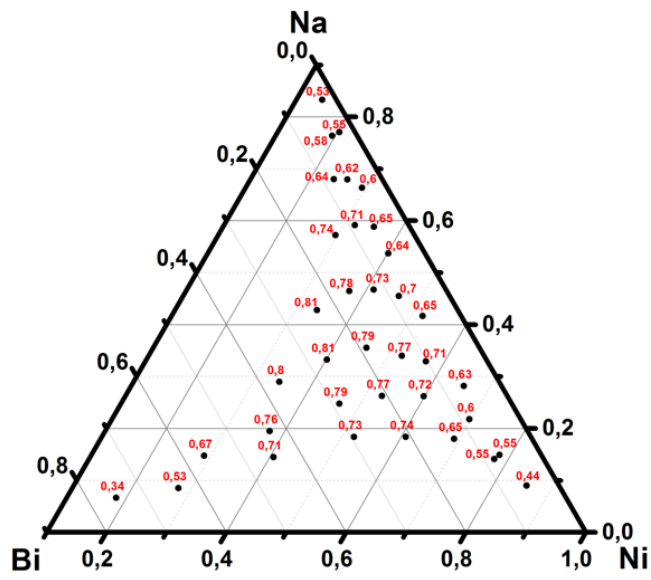
Experiment	Bi <sub>2</sub> O <sub>3</sub> (Watt)	Na <sub>0.7</sub> MnO <sub>2</sub> (Watt)	NiO (Watt)	MnO <sub>2</sub> (Watt)
A	30	100	100	100
B	20	100	50	120
C	15	100	25	120
D	15	100	35	120
E	10	50	25	120
F	10	25	25	120

With 6 sputter deposition experiment each producing 36 thin film electrodes, a total of 216 samples were fabricated. Since some samples were close to one another, a subset comprising a total of 108 samples were selected for detailed study. The selected compositions are shown plotted in Figure 4.7 as Bi-Na-Ni ternary diagram.

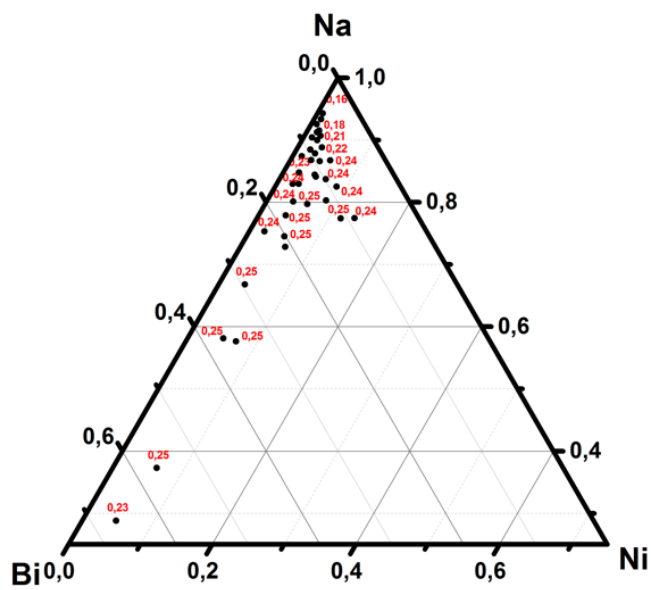
Even though the original aim was to examine the modification of MnO<sub>2</sub> with NiO, Bi<sub>2</sub>O<sub>3</sub> and Na bearing additives, it was found more useful to look at the chemistry change in Bi-Mn-Ni space. For this reason, the samples reported in Figure 4.7 are replotted in Figure 4.8 as Bi-Mn-Ni space. In particular, Mn corner in Bi-Mn-Ni space contain samples with attractive properties. For this reason, a portion of this space is redrawn in higher magnification in Figure 4.9. Chemical compositions of the samples within the magnified portion are tabulated in Table 4.2.



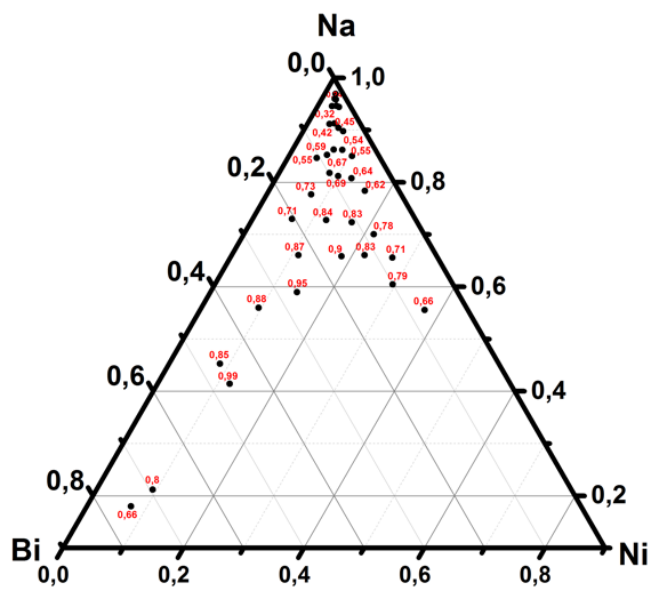
a)



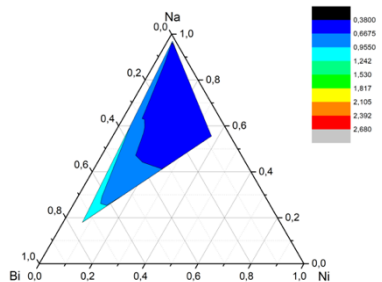
b)

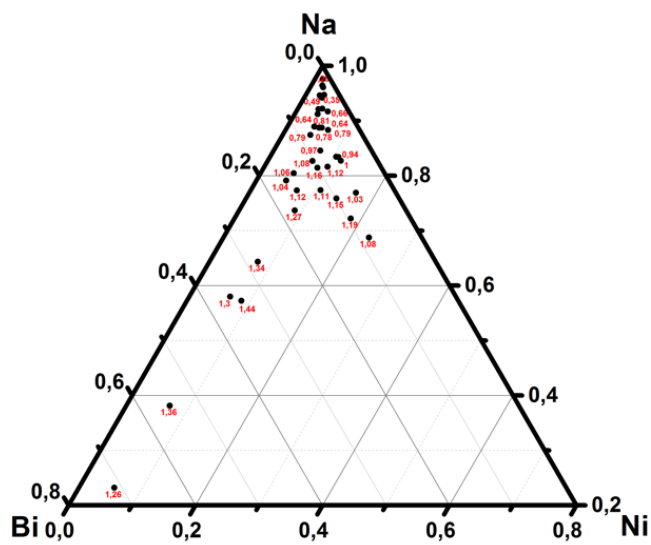


c)

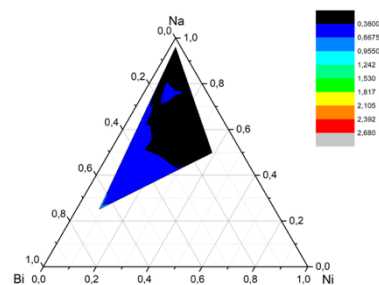


d)





e)



f)

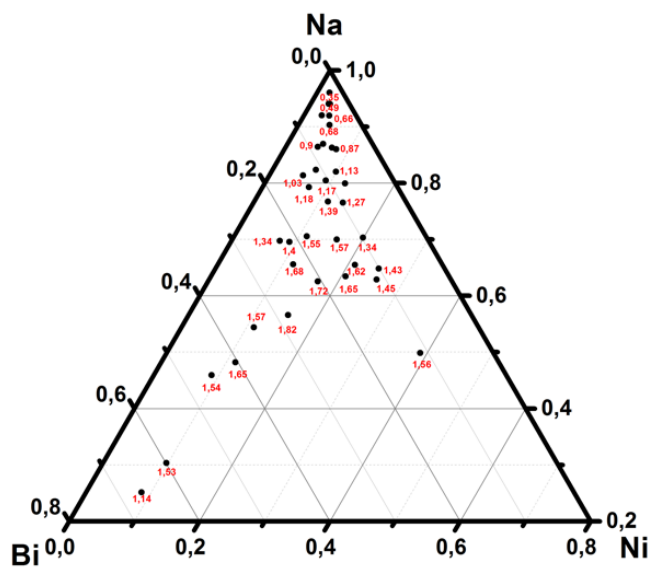


Figure 4.6 Composition distribution on Bi-Na-Ni ternary diagram. Power settings of targets  $\text{Bi}_2\text{O}_3\text{-Na}_{0.7}\text{MnO}_2\text{-NiO-MnO}_2$  were **a)** 30-100-100-100W, **b)** 20-100-50-120W, **c)** 15-100-25-120W, **d)** 15-100-35-120W, **e)** 10-50-25-120W, **f)** 10-25-25-120W. Mass distribution of sputter deposited layers are also shown at the side map for (a), (d) and (f)

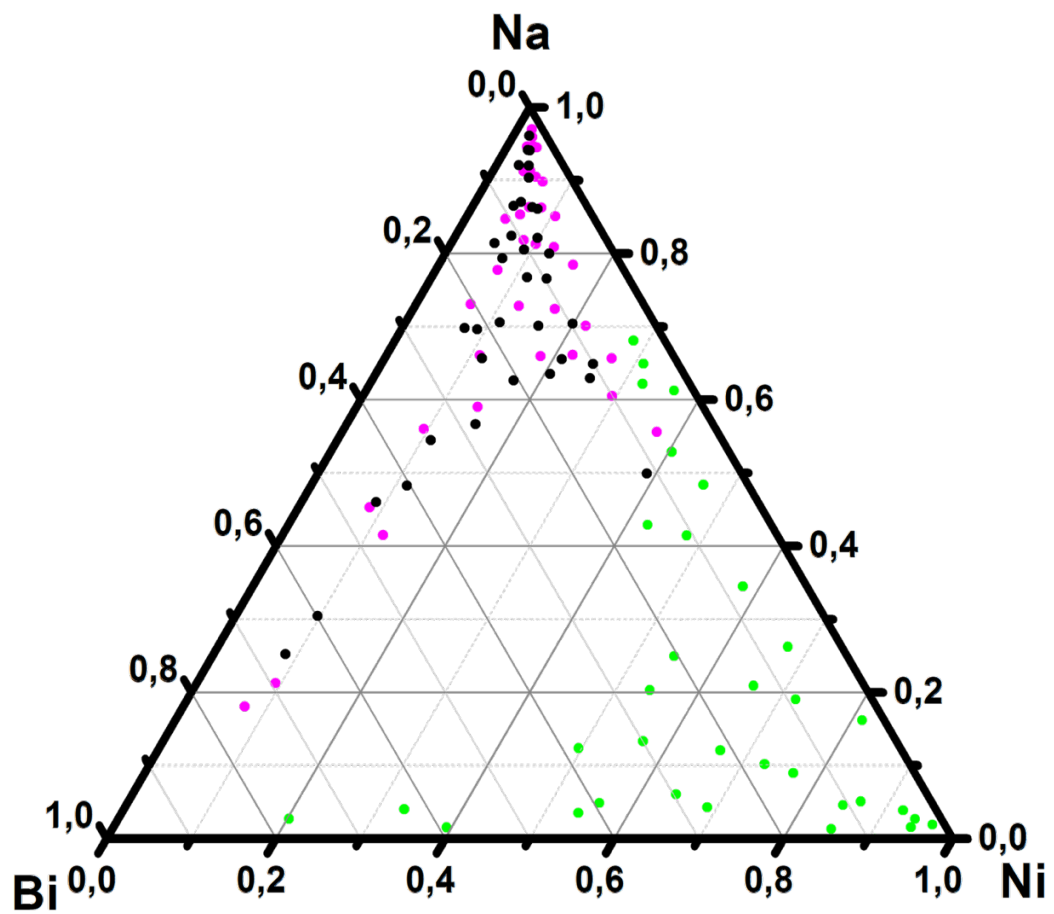


Figure 4.7 Samples on Bi-Na-Ni ternary from three different power combination sputter process (Green, magenta, and black are A, D and F, respectively)

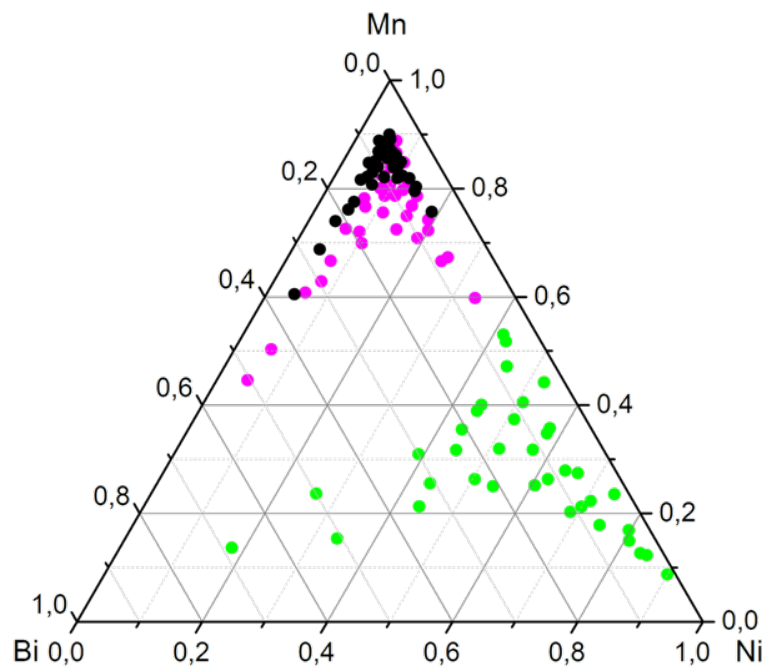


Figure 4.8 Samples on Bi-Mn-Ni ternary from three different power combination sputter process (Green, magenta, and black are A, D and F, respectively)

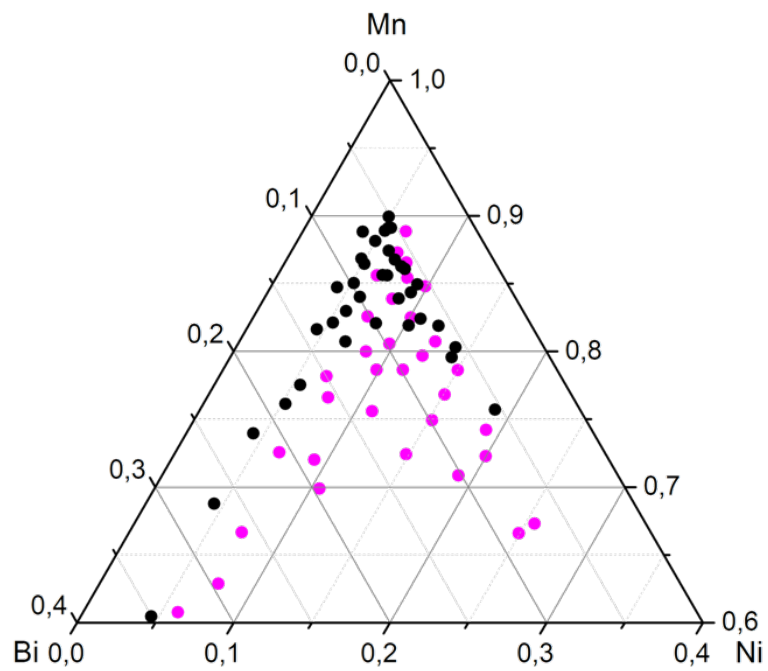


Figure 4.9 Bi-Mn-Ni ternary diagram for Mn-rich compositions



Table 4.2 List of material library that selected samples for Mn sides

Mass(mg)	Bi	Na	Ni	Mn	Formula
0.72	0.01	0.78	0.01	0.20	Bi <sub>0.01</sub> Na <sub>0.78</sub> Ni <sub>0.01</sub> Mn <sub>0.20</sub> O <sub>x</sub>
0.65	0.01	0.75	0.02	0.22	Bi <sub>0.01</sub> Na <sub>0.75</sub> Ni <sub>0.02</sub> Mn <sub>0.22</sub> O <sub>x</sub>
0.69	0.01	0.76	0.02	0.21	Bi <sub>0.01</sub> Na <sub>0.76</sub> Ni <sub>0.02</sub> Mn <sub>0.21</sub> O <sub>x</sub>
0.58	0.02	0.71	0.02	0.24	Bi <sub>0.02</sub> Na <sub>0.71</sub> Ni <sub>0.02</sub> Mn <sub>0.24</sub> O <sub>x</sub>
0.59	0.02	0.72	0.02	0.24	Bi <sub>0.02</sub> Na <sub>0.72</sub> Ni <sub>0.02</sub> Mn <sub>0.24</sub> O <sub>x</sub>
0.54	0.01	0.72	0.03	0.24	Bi <sub>0.01</sub> Na <sub>0.72</sub> Ni <sub>0.03</sub> Mn <sub>0.24</sub> O <sub>x</sub>
0.59	0.04	0.64	0.03	0.29	Bi <sub>0.04</sub> Na <sub>0.64</sub> Ni <sub>0.03</sub> Mn <sub>0.29</sub> O <sub>x</sub>
0.55	0.03	0.63	0.03	0.31	Bi <sub>0.03</sub> Na <sub>0.63</sub> Ni <sub>0.03</sub> Mn <sub>0.31</sub> O <sub>x</sub>
0.57	0.03	0.62	0.04	0.31	Bi <sub>0.03</sub> Na <sub>0.62</sub> Ni <sub>0.04</sub> Mn <sub>0.31</sub> O <sub>x</sub>
0.58	0.03	0.63	0.05	0.30	Bi <sub>0.03</sub> Na <sub>0.63</sub> Ni <sub>0.05</sub> Mn <sub>0.30</sub> O <sub>x</sub>
0.52	0.04	0.55	0.04	0.36	Bi <sub>0.04</sub> Na <sub>0.55</sub> Ni <sub>0.04</sub> Mn <sub>0.36</sub> O <sub>x</sub>
0.56	0.04	0.56	0.05	0.35	Bi <sub>0.04</sub> Na <sub>0.56</sub> Ni <sub>0.05</sub> Mn <sub>0.35</sub> O <sub>x</sub>
0.59	0.12	0.43	0.04	0.42	Bi <sub>0.12</sub> Na <sub>0.43</sub> Ni <sub>0.04</sub> Mn <sub>0.42</sub> O <sub>x</sub>
0.61	0.09	0.45	0.04	0.42	Bi <sub>0.09</sub> Na <sub>0.45</sub> Ni <sub>0.04</sub> Mn <sub>0.42</sub> O <sub>x</sub>
0.58	0.04	0.49	0.08	0.39	Bi <sub>0.04</sub> Na <sub>0.49</sub> Ni <sub>0.08</sub> Mn <sub>0.39</sub> O <sub>x</sub>
0.57	0.12	0.35	0.06	0.47	Bi <sub>0.12</sub> Na <sub>0.35</sub> Ni <sub>0.06</sub> Mn <sub>0.47</sub> O <sub>x</sub>
0.58	0.08	0.39	0.07	0.46	Bi <sub>0.08</sub> Na <sub>0.39</sub> Ni <sub>0.07</sub> Mn <sub>0.46</sub> O <sub>x</sub>
0.55	0.06	0.40	0.09	0.45	Bi <sub>0.06</sub> Na <sub>0.40</sub> Ni <sub>0.09</sub> Mn <sub>0.45</sub> O <sub>x</sub>
0.44	0.05	0.39	0.12	0.44	Bi <sub>0.05</sub> Na <sub>0.39</sub> Ni <sub>0.12</sub> Mn <sub>0.44</sub> O <sub>x</sub>
0.48	0.04	0.38	0.16	0.41	Bi <sub>0.04</sub> Na <sub>0.38</sub> Ni <sub>0.16</sub> Mn <sub>0.41</sub> O <sub>x</sub>
0.54	0.14	0.30	0.07	0.49	Bi <sub>0.14</sub> Na <sub>0.30</sub> Ni <sub>0.07</sub> Mn <sub>0.49</sub> O <sub>x</sub>
0.50	0.07	0.36	0.12	0.45	Bi <sub>0.07</sub> Na <sub>0.36</sub> Ni <sub>0.12</sub> Mn <sub>0.45</sub> O <sub>x</sub>
0.50	0.06	0.34	0.17	0.44	Bi <sub>0.06</sub> Na <sub>0.34</sub> Ni <sub>0.17</sub> Mn <sub>0.44</sub> O <sub>x</sub>
0.36	0.01	0.71	0.01	0.26	Bi <sub>0.01</sub> Na <sub>0.71</sub> Ni <sub>0.01</sub> Mn <sub>0.26</sub> O <sub>x</sub>
0.37	0.02	0.64	0.02	0.32	Bi <sub>0.02</sub> Na <sub>0.64</sub> Ni <sub>0.02</sub> Mn <sub>0.32</sub> O <sub>x</sub>
0.24	0.02	0.63	0.02	0.33	Bi <sub>0.02</sub> Na <sub>0.63</sub> Ni <sub>0.02</sub> Mn <sub>0.33</sub> O <sub>x</sub>
0.24	0.03	0.56	0.02	0.39	Bi <sub>0.03</sub> Na <sub>0.56</sub> Ni <sub>0.02</sub> Mn <sub>0.39</sub> O <sub>x</sub>
0.26	0.03	0.54	0.03	0.40	Bi <sub>0.03</sub> Na <sub>0.54</sub> Ni <sub>0.03</sub> Mn <sub>0.40</sub> O <sub>x</sub>
0.29	0.02	0.56	0.02	0.40	Bi <sub>0.02</sub> Na <sub>0.56</sub> Ni <sub>0.02</sub> Mn <sub>0.40</sub> O <sub>x</sub>
0.27	0.04	0.44	0.03	0.49	Bi <sub>0.05</sub> Na <sub>0.46</sub> Ni <sub>0.03</sub> Mn <sub>0.47</sub> O <sub>x</sub>
0.29	0.03	0.45	0.04	0.47	Bi <sub>0.04</sub> Na <sub>0.44</sub> Ni <sub>0.03</sub> Mn <sub>0.49</sub> O <sub>x</sub>
0.28	0.03	0.46	0.04	0.46	Bi <sub>0.03</sub> Na <sub>0.45</sub> Ni <sub>0.04</sub> Mn <sub>0.47</sub> O <sub>x</sub>
0.28	0.07	0.40	0.03	0.51	Bi <sub>0.03</sub> Na <sub>0.46</sub> Ni <sub>0.04</sub> Mn <sub>0.46</sub> O <sub>x</sub>
0.32	0.05	0.39	0.03	0.53	Bi <sub>0.07</sub> Na <sub>0.40</sub> Ni <sub>0.03</sub> Mn <sub>0.51</sub> O <sub>x</sub>
0.30	0.05	0.37	0.04	0.54	Bi <sub>0.05</sub> Na <sub>0.39</sub> Ni <sub>0.03</sub> Mn <sub>0.53</sub> O <sub>x</sub>
0.27	0.04	0.39	0.05	0.53	Bi <sub>0.05</sub> Na <sub>0.37</sub> Ni <sub>0.04</sub> Mn <sub>0.54</sub> O <sub>x</sub>
0.27	0.04	0.37	0.06	0.53	Bi <sub>0.04</sub> Na <sub>0.39</sub> Ni <sub>0.05</sub> Mn <sub>0.53</sub> O <sub>x</sub>
0.20	0.10	0.30	0.03	0.57	Bi <sub>0.04</sub> Na <sub>0.37</sub> Ni <sub>0.06</sub> Mn <sub>0.53</sub> O <sub>x</sub>
0.31	0.09	0.29	0.04	0.58	Bi <sub>0.10</sub> Na <sub>0.30</sub> Ni <sub>0.03</sub> Mn <sub>0.57</sub> O <sub>x</sub>
0.37	0.06	0.36	0.03	0.54	Bi <sub>0.09</sub> Na <sub>0.29</sub> Ni <sub>0.04</sub> Mn <sub>0.58</sub> O <sub>x</sub>
0.43	0.05	0.32	0.05	0.58	Bi <sub>0.06</sub> Na <sub>0.36</sub> Ni <sub>0.03</sub> Mn <sub>0.54</sub> O <sub>x</sub>
0.40	0.04	0.34	0.06	0.56	Bi <sub>0.05</sub> Na <sub>0.32</sub> Ni <sub>0.05</sub> Mn <sub>0.58</sub> O <sub>x</sub>
0.39	0.04	0.30	0.09	0.57	Bi <sub>0.04</sub> Na <sub>0.34</sub> Ni <sub>0.06</sub> Mn <sub>0.56</sub> O <sub>x</sub>
0.32	0.18	0.18	0.04	0.61	Bi <sub>0.04</sub> Na <sub>0.30</sub> Ni <sub>0.09</sub> Mn <sub>0.57</sub> O <sub>x</sub>
0.53	0.13	0.21	0.04	0.61	Bi <sub>0.18</sub> Na <sub>0.18</sub> Ni <sub>0.04</sub> Mn <sub>0.61</sub> O <sub>x</sub>
0.45	0.09	0.25	0.04	0.63	Bi <sub>0.13</sub> Na <sub>0.21</sub> Ni <sub>0.04</sub> Mn <sub>0.61</sub> O <sub>x</sub>
0.28	0.07	0.28	0.04	0.61	Bi <sub>0.09</sub> Na <sub>0.25</sub> Ni <sub>0.04</sub> Mn <sub>0.63</sub> O <sub>x</sub>

**Table 4.2 (cont'd)**

0.37	0.05	0.27	0.06	0.61	$\text{Bi}_{0.07}\text{Na}_{0.28}\text{Ni}_{0.04}\text{Mn}_{0.61}\text{O}_x$
0.32	0.05	0.25	0.08	0.62	$\text{Bi}_{0.05}\text{Na}_{0.27}\text{Ni}_{0.06}\text{Mn}_{0.61}\text{O}_x$
0.26	0.04	0.27	0.10	0.59	$\text{Bi}_{0.05}\text{Na}_{0.25}\text{Ni}_{0.08}\text{Mn}_{0.62}\text{O}_x$
0.57	0.24	0.12	0.04	0.61	$\text{Bi}_{0.24}\text{Na}_{0.12}\text{Ni}_{0.04}\text{Mn}_{0.61}\text{O}_x$
0.42	0.15	0.18	0.04	0.62	$\text{Bi}_{0.15}\text{Na}_{0.18}\text{Ni}_{0.04}\text{Mn}_{0.62}\text{O}_x$
0.31	0.10	0.20	0.05	0.65	$\text{Bi}_{0.10}\text{Na}_{0.20}\text{Ni}_{0.05}\text{Mn}_{0.65}\text{O}_x$
0.23	0.08	0.23	0.06	0.63	$\text{Bi}_{0.08}\text{Na}_{0.23}\text{Ni}_{0.06}\text{Mn}_{0.63}\text{O}_x$
0.31	0.06	0.24	0.08	0.62	$\text{Bi}_{0.06}\text{Na}_{0.24}\text{Ni}_{0.08}\text{Mn}_{0.62}\text{O}_x$
0.31	0.05	0.26	0.11	0.59	$\text{Bi}_{0.05}\text{Na}_{0.26}\text{Ni}_{0.11}\text{Mn}_{0.59}\text{O}_x$
0.28	0.04	0.19	0.15	0.61	$\text{Bi}_{0.04}\text{Na}_{0.19}\text{Ni}_{0.15}\text{Mn}_{0.61}\text{O}_x$

### 4.3.2 Structural Characterization

Cathodes deposited on Ni substrate were characterized with X-ray diffraction using Bragg-Brentano geometry. A typical spectrum recorded between  $10^\circ < 2\theta < 85^\circ$  is given in Figure 4.10. It is seen that there is a broad peak centered at  $2\theta \approx 16^\circ$  plus three well defined sharp peaks located at  $2\theta = 44.78^\circ$ ,  $52.06^\circ$  and  $76.47^\circ$ . These peaks refer to nickel which was used as substrate during the sputter deposition. Since the cathodes deposited are oxides, they are expected to produce peaks at low angles. For that reason, X-ray diffraction was confined to  $10^\circ < 2\theta < 44^\circ$ .

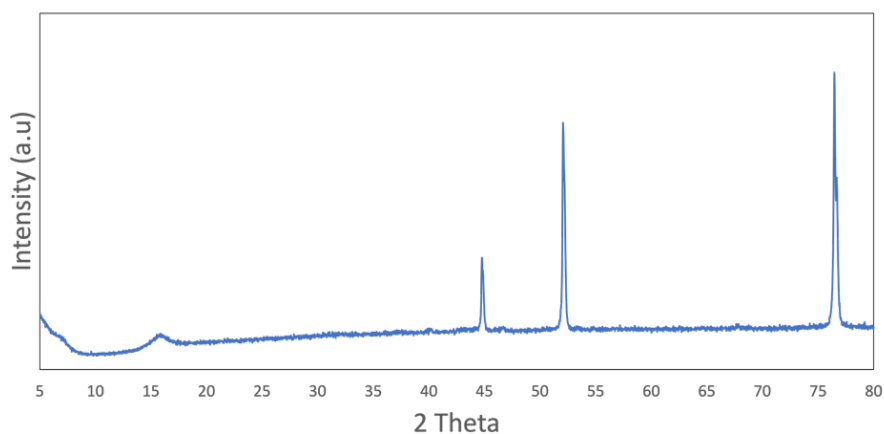


Figure 4.10 X-ray diffraction pattern of a cathode  $\text{Bi}_{0.03}\text{Na}_{0.50}\text{Ni}_{0.21}\text{Mn}_{0.26}\text{O}_x$  deposited on Ni Substrate. Sharp peaks are those of Ni substrate. The broad peak at  $2\theta = 16^\circ$  is from the cathode

Figure 4.11 shows typical XRD pattern recorded from the as deposited cathode. Figure 4.11 (a) refers to a sample close to  $\text{Bi}_2\text{O}_3$  corner of the ternary diagram. The pattern comprises a broad peak centered at  $2\theta \approx 28^\circ$ . Normally  $\text{Bi}_2\text{O}_3$  have their strongest peaks close to  $2\theta \approx 27^\circ$  and comprises other peaks located at  $2\theta = 22.7^\circ$ ,  $27.9^\circ$  and  $32.3^\circ$  (pdf card no. 00-027-0052). Therefore, the broad peak at  $2\theta = 28^\circ$  is consistent with an amorphous pattern formed by broadening of the  $\text{Bi}_2\text{O}_3$  peaks. The case close to  $\text{MnO}_2$  corner is similar, Figure 4.11 (b). Here there are two broad peaks centered on  $2\theta \approx 12.5^\circ$  (001) and  $25^\circ$  (002). The positions are consistent with  $\delta\text{-MnO}_2$  which have peaks at  $2\theta = 12.6^\circ$ ,  $2\theta = 25.3^\circ$  (pdf card no. 01-042-1317). Figure 4.11 (c) refers to a sample close equidistant to Ni and Mn corner. The pattern comprises a small hump at low angles plus a well-defined peak at  $2\theta \approx 40.5^\circ$ . The latter peak is close with that of NiO which normally occurs at  $2\theta = 43.2^\circ$  (pdf card no. 00-047-1049).

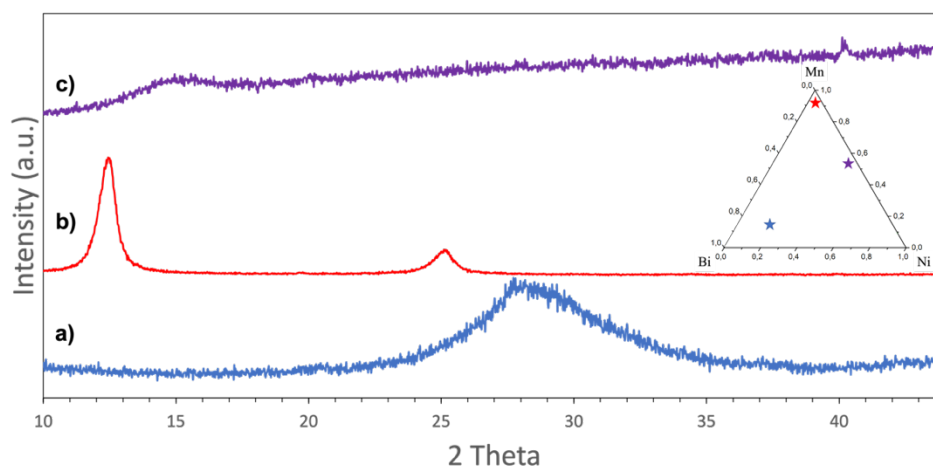


Figure 4.11 Typical XRD pattern of sputtered cathodes **a)** near Bi corner ( $\text{Bi}_{0.67}\text{Na}_{0.02}\text{Ni}_{0.17}\text{Mn}_{0.13}\text{O}_x$ ), **b)** near Mn corner ( $\text{Bi}_{0.01}\text{Na}_{0.71}\text{Ni}_{0.01}\text{Mn}_{0.26}\text{O}_x$ ), **c)** equidistant to Ni and Mn corner ( $\text{Bi}_{0.10}\text{Na}_{0.15}\text{Ni}_{0.48}\text{Mn}_{0.27}\text{O}_x$ )

After electrochemical testing which involved 50 cycles of charging and discharging, the cells were dismantled, and the cathodes were checked for their structure again using X-ray diffraction. A Typical SEM micrograph of a cathode under low magnifications given in Figure 4.12. It is seen that cathode which was continuous in

the as-deposited state were fragmented into islands during cycling, Figure 4.12 (b).

Figure 4.13 shows the structure of cycled cathodes at high magnifications.

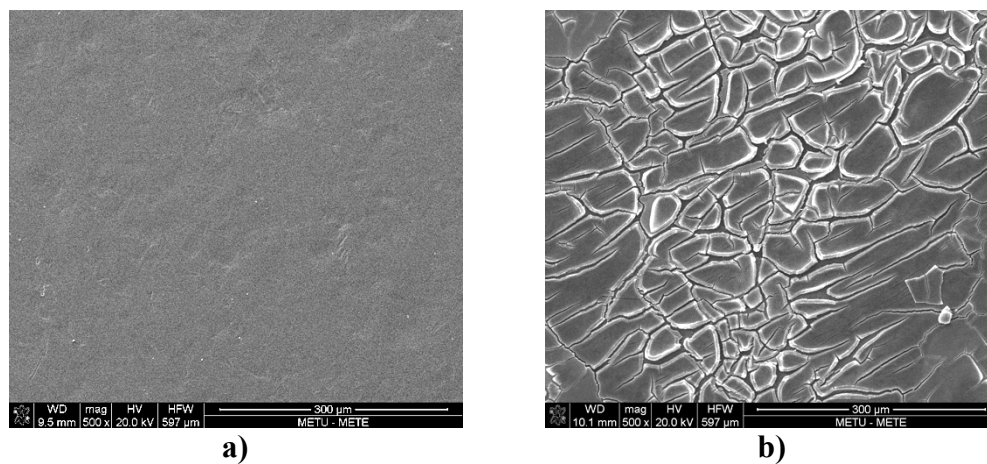


Figure 4.12 SEM image of a cathode ( $\text{Bi}_{0.02}\text{Na}_{0.71}\text{Ni}_{0.02}\text{Mn}_{0.24}\text{O}_x$ ) **a)** before cycling, **b)** after cycling

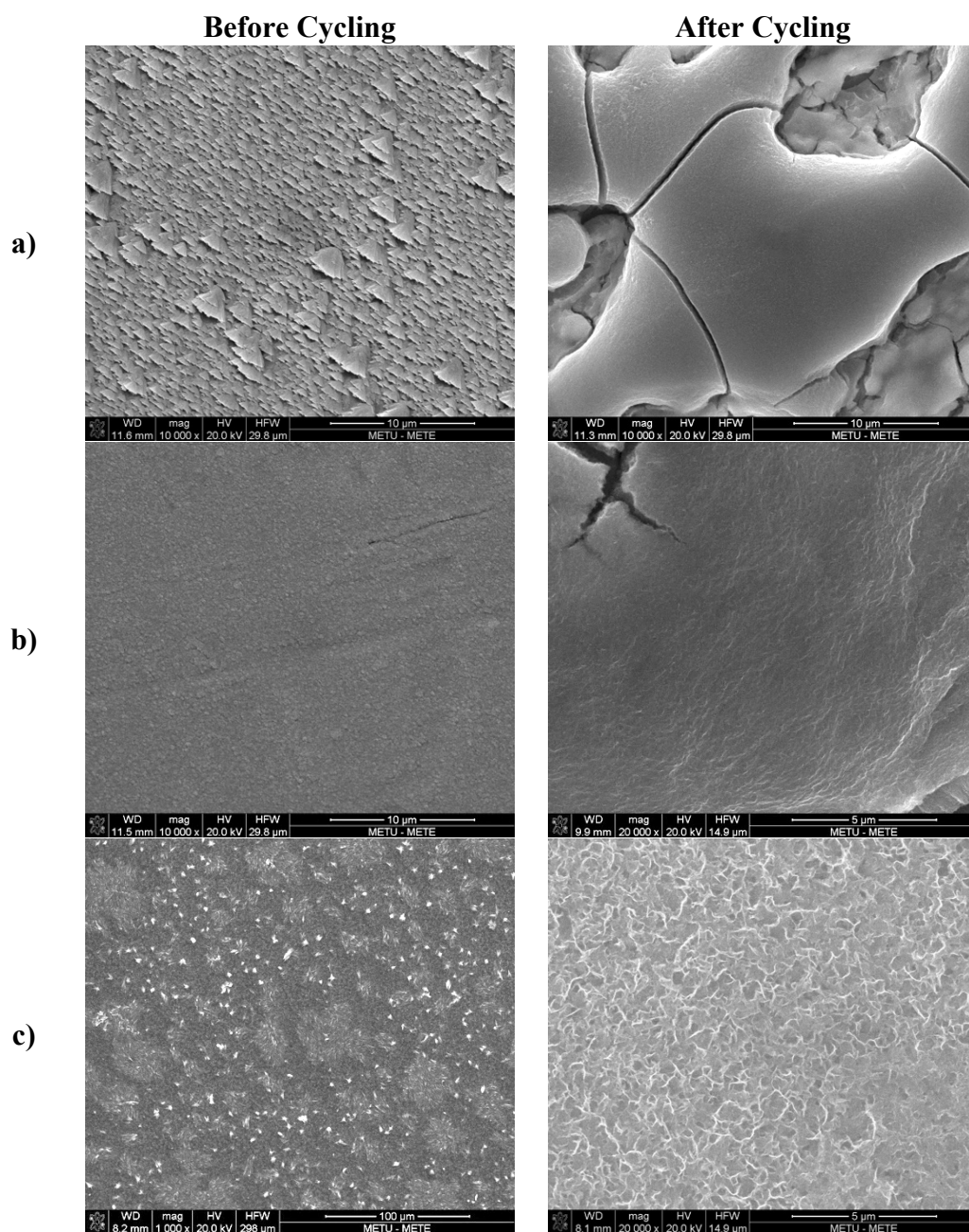


Figure 4.13 Typical characteristic of microstructural change after 50 cycles; **a)** Bi corner ( $\text{Bi}_{0.39}\text{Na}_{0.12}\text{Ni}_{0.05}\text{Mn}_{0.44}\text{O}_x$ ) **b)** Ni corner ( $\text{Bi}_{0.06}\text{Na}_{0.34}\text{Ni}_{0.17}\text{Mn}_{0.44}\text{O}_x$ ) **c)** Mn-side ( $\text{Bi}_{0.01}\text{Na}_{0.71}\text{Ni}_{0.01}\text{Mn}_{0.26}\text{O}_x$ )

Cycling also lead to changes in the crystal structure. Figure 4.14 shows cathodes with featureless XRD patterns in the as deposited state. As seen in Figure 4.14 (a) there is a slight hump formed at  $2\theta=12.5^\circ$ . In Figure 4.14 (b) and (c), there is a clear sign of crystallization with well-defined peak(s). Figure 4.14 (d) shows a fully

crystallized structure with well-defined peaks. The position of the peaks in the cycled cathode should be compared with a XRD pattern of  $\delta$ -MnO<sub>2</sub> given in Figure 4.15. It is seen that the peak positions seen in Figure 4.14 do match the positions in  $\delta$ -MnO<sub>2</sub> which has a layered structure.

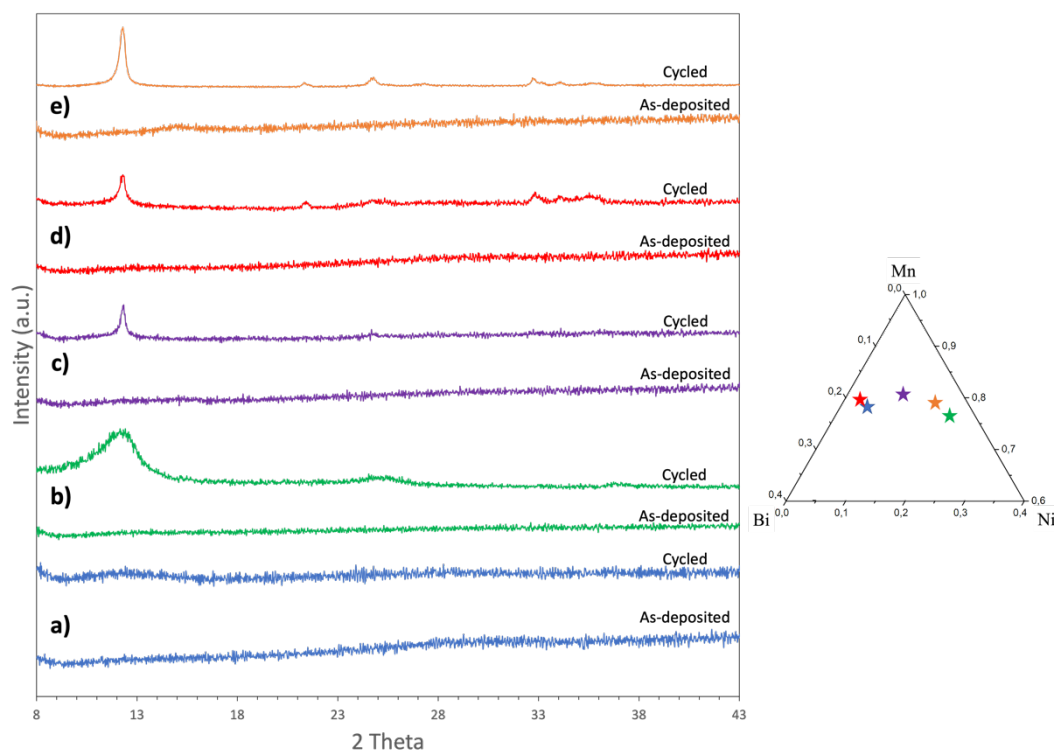


Figure 4.14 XRD pattern of cathodes before and after cycling; **a)** Bi<sub>0.09</sub>Na<sub>0.45</sub>Ni<sub>0.04</sub>Mn<sub>0.42</sub>O<sub>x</sub> **b)** Bi<sub>0.04</sub>Na<sub>0.19</sub>Ni<sub>0.15</sub>Mn<sub>0.61</sub>O<sub>x</sub> **c)** Bi<sub>0.04</sub>Na<sub>0.55</sub>Ni<sub>0.04</sub>Mn<sub>0.36</sub>O<sub>x</sub> **d)** Bi<sub>0.07</sub>Na<sub>0.55</sub>Ni<sub>0.03</sub>Mn<sub>0.35</sub>O<sub>x</sub>, **e)** Bi<sub>0.03</sub>Na<sub>0.55</sub>Ni<sub>0.07</sub>Mn<sub>0.35</sub>O<sub>x</sub>

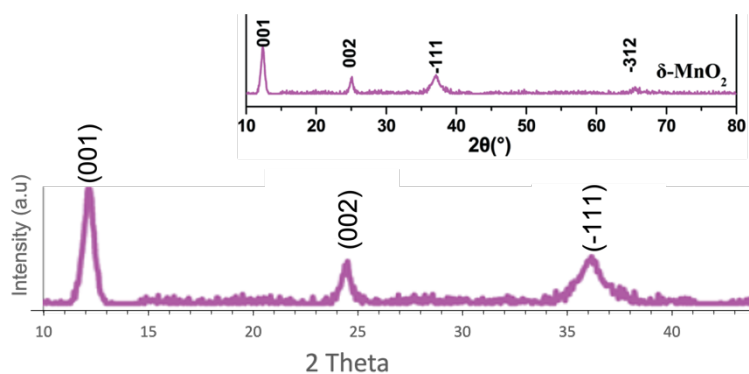


Figure 4.15 XRD pattern of  $\delta$ -MnO<sub>2</sub> [81]

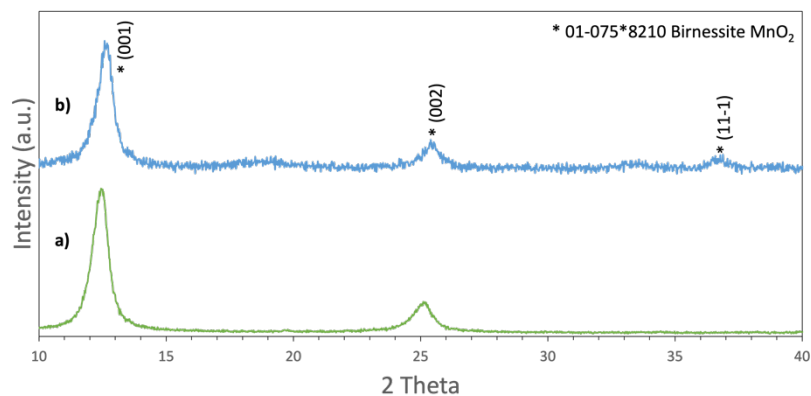


Figure 4.16 XRD pattern of a cathode ( $\text{Bi}_{0.01}\text{Na}_{0.71}\text{Ni}_{0.01}\text{Mn}_{0.26}\text{O}_x$ ) keeps the crystalline  $\delta\text{-MnO}_2$  phase; **a)** as-deposited, **b)** after 50 cycles

Similarly, Figure 4.16 refers to a cathode which was crystalline  $\delta\text{-MnO}_2$  in the as-deposited state and remained crystalline with cycling. There were also cathodes little affected by cycling. Figure 4.17 refers to a sample close to Bi corner where amorphous structure remained amorphous during cycling.

Although great majority of the cathodes after cycling were converted into layered crystalline structure, there were also exceptions. Figure 4.18 refers to an amorphous cathode in the as-deposited state, but after cycling it developed a well-defined crystal structure of ZHS and  $\text{Na}_4\text{Mn}_{12}\text{O}_{28}$  which peak positions totally different from those of  $\delta\text{-MnO}_2$ .

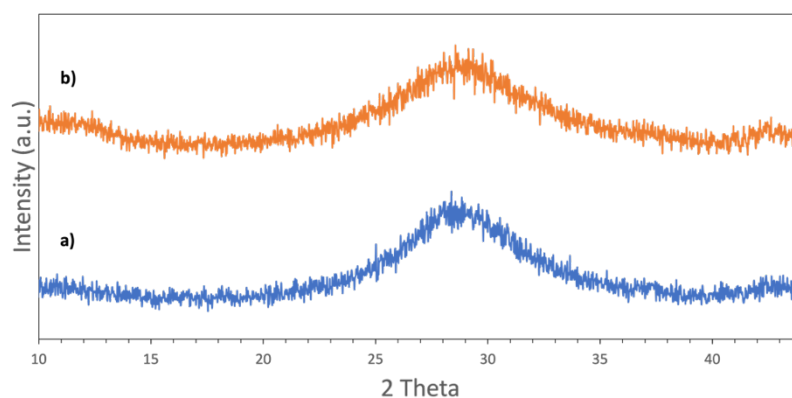


Figure 4.17 Amorphous tendency at Bi side; **a)** as-deposited, **b)** after 50 cycles

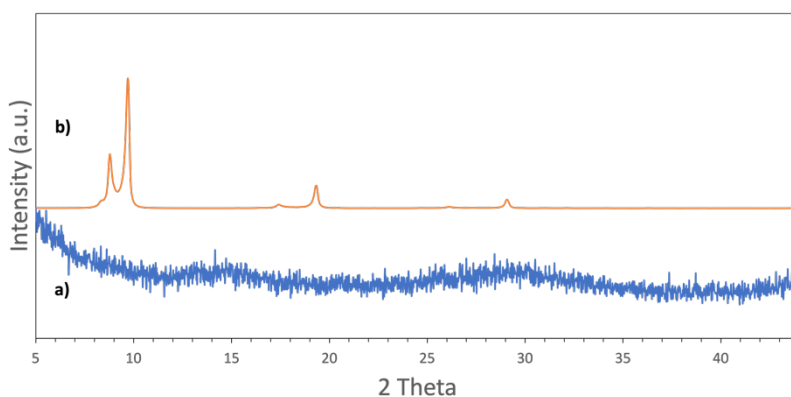


Figure 4.18 Crystallized as sodium manganese oxide hydrate and zinc hydroxide sulfate; **a)** as-deposited, **b)** after 50 cycles

### 4.3.3 Cyclic Voltammetry

Cyclic voltammetry experiments were carried on a cell where the anode was zinc sheet, and the electrolyte was 2M ZnSO<sub>4</sub> and 0.1M MnSO<sub>4</sub>. Voltammograms were recorded from 1.0 V to 2.0 V with a sweep rate of 2 mV/sec.

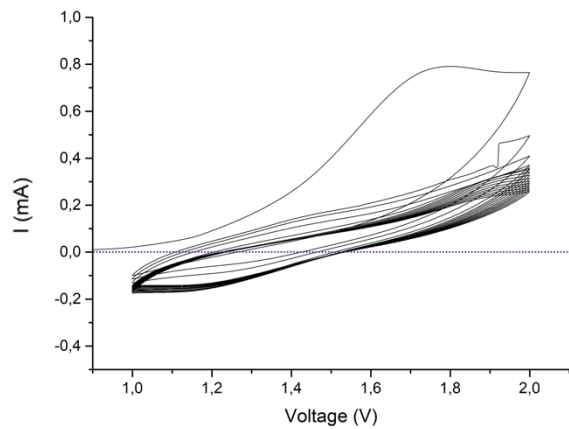
Typical examples are reported in Figure 4.19. The first curve refers to a bismuth rich cathode Bi<sub>0.45</sub>Na<sub>0.11</sub>Ni<sub>0.04</sub>Mn<sub>0.40</sub>O<sub>x</sub>. The initial curve showed an oxidation peak at 1.7 V, but subsequently the cathode became less active with a general drop in current. Figure 4.19 (b) refers to Bi<sub>0.09</sub>Na<sub>0.45</sub>Ni<sub>0.04</sub>Mn<sub>0.42</sub>O<sub>x</sub>. Here in the first cycle, there is an oxidation peak at 1.707 V and a shoulder at 1.802 V and reduction peaks at 1.278 V and 1.137 V. With cycling we see a single oxidation peak at 1.729 V, but this later stabilizes in a broad peak at 1.725 V. With cycling the reduction peaks deepens and stabilizes at 1.127 and 1.265 V. Figure 4.19 (c) refer to a cathode Bi<sub>0.01</sub>Na<sub>0.71</sub>Ni<sub>0.01</sub>Mn<sub>0.26</sub>O<sub>x</sub> which is rich in its Na content. There is a well-defined a single oxidation peak at 1.689 V and a well-defined reduction peak 1.218 V.

A voltammogram similar to Figure 4.19 (b) is given in Figure 4.20 (a). Here with cycling oxidation peaks move to higher voltages and reduction peaks does opposite and move to lower voltages with the result that rechargeability is adversely affected.

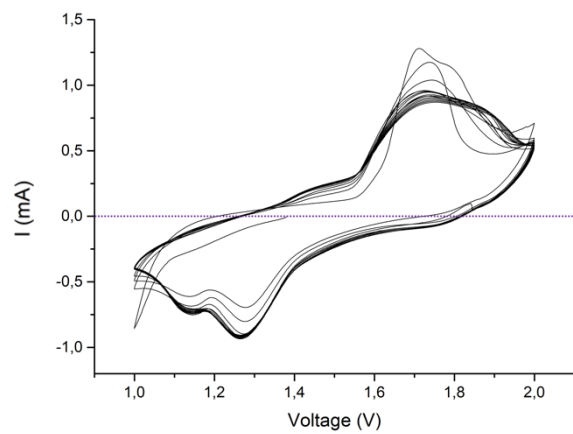


A voltammogram similar to that given above is given in Figure 4.20 (b). Here with cycling results in favorable change in peak positions. Accordingly, the oxidation peaks move to lower voltages and reduction peaks move to higher voltages with the net result that the voltage difference decreases with cycling.

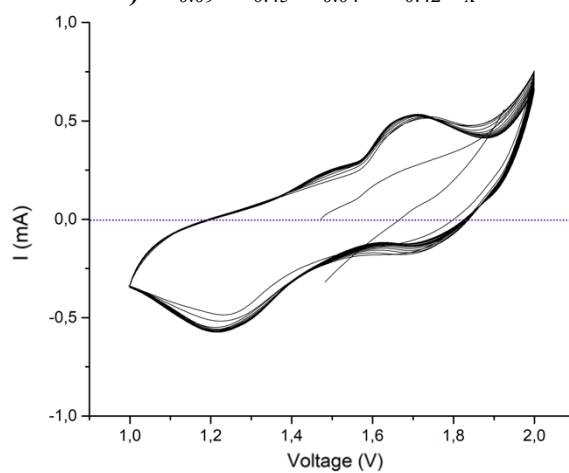
The peak positions for oxidation and reduction varies with compositions. The values after 10<sup>th</sup> cycle in Mn rich samples are tabulated in Table 4.3.



**a)  $\text{Bi}_{0.45}\text{Na}_{0.11}\text{Ni}_{0.04}\text{Mn}_{0.40}\text{O}_x$**



**b)  $\text{Bi}_{0.09}\text{Na}_{0.45}\text{Ni}_{0.04}\text{Mn}_{0.42}\text{O}_x$**



**c)  $\text{Bi}_{0.01}\text{Na}_{0.71}\text{Ni}_{0.01}\text{Mn}_{0.26}\text{O}_x$**

Figure 4.19 Typical examples of cyclic voltammograms in  $\text{MnO}_2$  based cathodes **a)**  $\text{Bi}_{0.45}\text{Na}_{0.11}\text{Ni}_{0.04}\text{Mn}_{0.40}\text{O}_x$ , **b)**  $\text{Bi}_{0.09}\text{Na}_{0.45}\text{Ni}_{0.04}\text{Mn}_{0.42}\text{O}_x$ , **c)**  $\text{Bi}_{0.01}\text{Na}_{0.71}\text{Ni}_{0.01}\text{Mn}_{0.26}\text{O}_x$

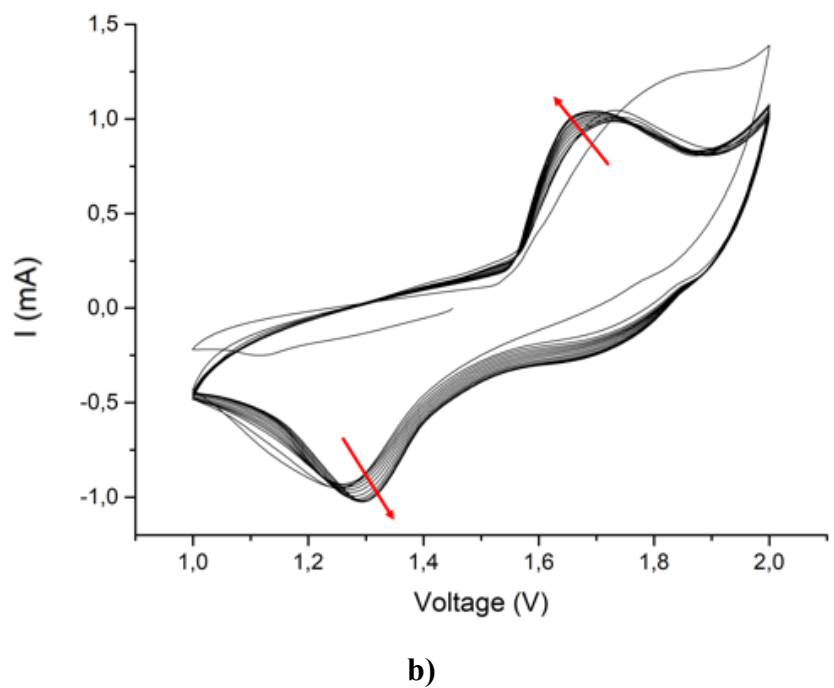
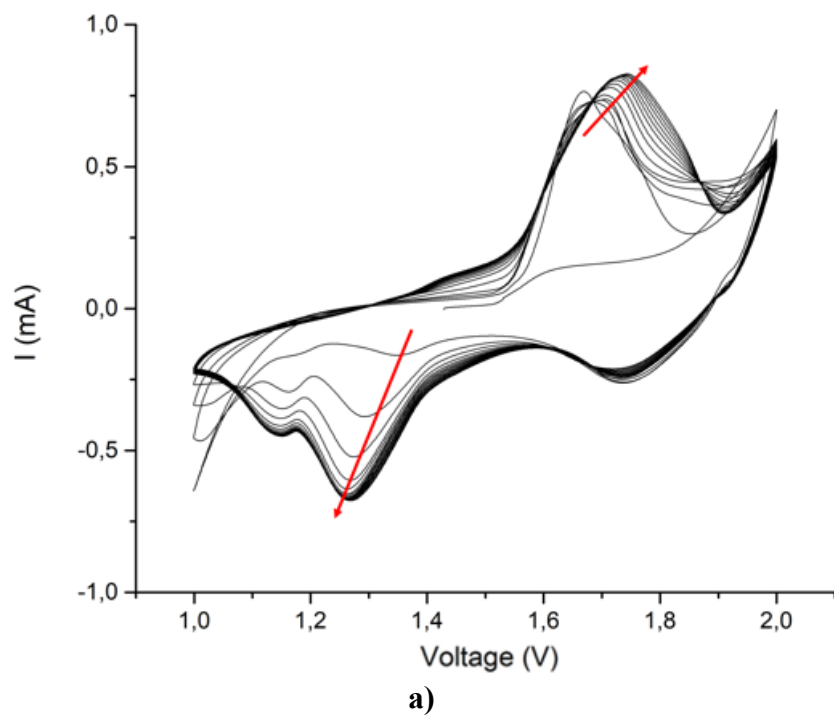


Figure 4.20 Typical CV profile of as-deposited cathodes **a)** increasing redox potential, **b)** decreasing redox potential

Table 4.3 List of cathodes with their oxidation and reduction peaks voltages

<b>Cathode Compositions</b>	<b>Oxidation Peak (V)</b>	<b>Reduction Peak (V)</b>	<b>Voltage Difference</b>
Bi <sub>0.03</sub> Na <sub>0.50</sub> Ni <sub>0.21</sub> Mn <sub>0.26</sub>	1.6873	1.31531	0.37199
Bi <sub>0.02</sub> Na <sub>0.47</sub> Ni <sub>0.28</sub> Mn <sub>0.23</sub>	1.85051	1.22081	0.6297
Bi <sub>0.03</sub> Na <sub>0.47</sub> Ni <sub>0.22</sub> Mn <sub>0.27</sub>	1.74123	1.27613	0.4651
Bi <sub>0.04</sub> Na <sub>0.38</sub> Ni <sub>0.36</sub> Mn <sub>0.22</sub>	1.76547	1.22146	0.54401
Bi <sub>0.11</sub> Na <sub>0.31</sub> Ni <sub>0.31</sub> Mn <sub>0.28</sub>	1.75856	1.27922	0.47934
Bi <sub>0.08</sub> Na <sub>0.31</sub> Ni <sub>0.35</sub> Mn <sub>0.26</sub>	1.70428	1.29392	0.41036
Bi <sub>0.05</sub> Na <sub>0.21</sub> Ni <sub>0.53</sub> Mn <sub>0.22</sub>	1.72379	1.2671	0.45669
Bi <sub>0.18</sub> Na <sub>0.14</sub> Ni <sub>0.38</sub> Mn <sub>0.30</sub>	1.80102	1.25409	0.54693
Bi <sub>0.02</sub> Na <sub>0.13</sub> Ni <sub>0.65</sub> Mn <sub>0.20</sub>	1.70723	1.27421	0.43302
Bi <sub>0.27</sub> Na <sub>0.09</sub> Ni <sub>0.36</sub> Mn <sub>0.28</sub>	1.79917	1.26747	0.5317
Bi <sub>0.15</sub> Na <sub>0.09</sub> Ni <sub>0.47</sub> Mn <sub>0.29</sub>	1.74472	1.28259	0.46213
Bi <sub>0.11</sub> Na <sub>0.07</sub> Ni <sub>0.58</sub> Mn <sub>0.25</sub>	1.69132	1.29526	0.39606
Bi <sub>0.07</sub> Na <sub>0.04</sub> Ni <sub>0.68</sub> Mn <sub>0.21</sub>	1.71325	1.28519	0.42806
Bi <sub>0.03</sub> Na <sub>0.03</sub> Ni <sub>0.77</sub> Mn <sub>0.16</sub>	1.71118	1.26518	0.446
Bi <sub>0.30</sub> Na <sub>0.04</sub> Ni <sub>0.42</sub> Mn <sub>0.25</sub>	1.6863	1.26557	0.42073
Bi <sub>0.22</sub> Na <sub>0.05</sub> Ni <sub>0.48</sub> Mn <sub>0.25</sub>	1.7605	1.27192	0.48858
Bi <sub>0.13</sub> Na <sub>0.08</sub> Ni <sub>0.56</sub> Mn <sub>0.23</sub>	1.7185	1.28661	0.43189
Bi <sub>0.04</sub> Ni <sub>0.81</sub> Mn <sub>0.15</sub>	1.70522	1.26922	0.436
Bi <sub>0.67</sub> Na <sub>0.02</sub> Ni <sub>0.17</sub> Mn <sub>0.13</sub>	1.7253	1.2862	0.4391
Bi <sub>0.34</sub> Na <sub>0.03</sub> Ni <sub>0.43</sub> Mn <sub>0.21</sub>	1.82188	1.22686	0.59502
Bi <sub>0.20</sub> Na <sub>0.03</sub> Ni <sub>0.52</sub> Mn <sub>0.24</sub>	1.74724	1.27586	0.47138
Bi <sub>0.11</sub> Na <sub>0.01</sub> Ni <sub>0.68</sub> Mn <sub>0.20</sub>	1.71865	1.28753	0.43112
Bi <sub>0.01</sub> Na <sub>0.02</sub> Ni <sub>0.88</sub> Mn <sub>0.09</sub>	1.74278	1.29722	0.44556
Bi <sub>0.02</sub> Na <sub>0.72</sub> Ni <sub>0.02</sub> Mn <sub>0.24</sub> O <sub>x</sub>	1.70771	1.28443	0.42328
Bi <sub>0.03</sub> Na <sub>0.63</sub> Ni <sub>0.03</sub> Mn <sub>0.31</sub> O <sub>x</sub>	1.65626	1.28909	0.36717
Bi <sub>0.03</sub> Na <sub>0.62</sub> Ni <sub>0.04</sub> Mn <sub>0.31</sub> O <sub>x</sub>	1.71036	1.27779	0.43257
Bi <sub>0.03</sub> Na <sub>0.63</sub> Ni <sub>0.05</sub> Mn <sub>0.30</sub> O <sub>x</sub>	1.71177	1.24007	0.4717
Bi <sub>0.05</sub> Na <sub>0.54</sub> Ni <sub>0.04</sub> Mn <sub>0.37</sub> O <sub>x</sub>	1.7316	1.26062	0.47098
Bi <sub>0.04</sub> Na <sub>0.55</sub> Ni <sub>0.04</sub> Mn <sub>0.36</sub> O <sub>x</sub>	1.72349	1.27585	0.44764
Bi <sub>0.04</sub> Na <sub>0.56</sub> Ni <sub>0.05</sub> Mn <sub>0.35</sub> O <sub>x</sub>	1.70764	1.27071	0.43693
Bi <sub>0.03</sub> Na <sub>0.55</sub> Ni <sub>0.07</sub> Mn <sub>0.35</sub> O <sub>x</sub>	1.7034	1.27136	0.43204
Bi <sub>0.09</sub> Na <sub>0.45</sub> Ni <sub>0.04</sub> Mn <sub>0.42</sub> O <sub>x</sub>	1.74223	1.26388	0.47835

**Table 4.3 (cont'd)**

Bi <sub>0.06</sub> Na <sub>0.49</sub> Ni <sub>0.05</sub> Mn <sub>0.40</sub> O <sub>x</sub>	1.7315	1.27902	0.45248
Bi <sub>0.04</sub> Na <sub>0.49</sub> Ni <sub>0.08</sub> Mn <sub>0.39</sub> O <sub>x</sub>	1.7184	1.2659	0.4525
Bi <sub>0.25</sub> Na <sub>0.24</sub> Ni <sub>0.05</sub> Mn <sub>0.46</sub> O <sub>x</sub>	1.816	1.25368	0.56232
Bi <sub>0.12</sub> Na <sub>0.35</sub> Ni <sub>0.06</sub> Mn <sub>0.47</sub> O <sub>x</sub>	1.88731	1.2153	0.67201
Bi <sub>0.08</sub> Na <sub>0.39</sub> Ni <sub>0.07</sub> Mn <sub>0.46</sub> O <sub>x</sub>	1.7506	1.26915	0.48145
Bi <sub>0.06</sub> Na <sub>0.40</sub> Ni <sub>0.09</sub> Mn <sub>0.45</sub> O <sub>x</sub>	1.70913	1.2881	0.42103
Bi <sub>0.05</sub> Na <sub>0.39</sub> Ni <sub>0.12</sub> Mn <sub>0.44</sub> O <sub>x</sub>	1.72556	1.28001	0.44555
Bi <sub>0.04</sub> Na <sub>0.38</sub> Ni <sub>0.16</sub> Mn <sub>0.41</sub> O <sub>x</sub>	1.78305	1.27675	0.5063
Bi <sub>0.14</sub> Na <sub>0.30</sub> Ni <sub>0.07</sub> Mn <sub>0.49</sub> O <sub>x</sub>	1.81173	1.27771	0.53402
Bi <sub>0.08</sub> Na <sub>0.36</sub> Ni <sub>0.10</sub> Mn <sub>0.47</sub> O <sub>x</sub>	1.8294	1.2887	0.5407
Bi <sub>0.07</sub> Na <sub>0.36</sub> Ni <sub>0.12</sub> Mn <sub>0.45</sub> O <sub>x</sub>	1.70481	1.27983	0.42498
Bi <sub>0.04</sub> Na <sub>0.33</sub> Ni <sub>0.22</sub> Mn <sub>0.40</sub> O <sub>x</sub>	1.77691	1.29086	0.48605
Bi <sub>0.01</sub> Na <sub>0.71</sub> Ni <sub>0.01</sub> Mn <sub>0.26</sub> O <sub>x</sub>	1.70804	1.21641	0.49163
Bi <sub>0.02</sub> Na <sub>0.64</sub> Ni <sub>0.02</sub> Mn <sub>0.32</sub> O <sub>x</sub>	1.73593	1.24059	0.49534
Bi <sub>0.02</sub> Na <sub>0.63</sub> Ni <sub>0.02</sub> Mn <sub>0.33</sub> O <sub>x</sub>	1.78829	1.23500	0.55329
Bi <sub>0.03</sub> Na <sub>0.56</sub> Ni <sub>0.02</sub> Mn <sub>0.39</sub> O <sub>x</sub>	1.74467	1.25906	0.48561
Bi <sub>0.03</sub> Na <sub>0.54</sub> Ni <sub>0.03</sub> Mn <sub>0.40</sub> O <sub>x</sub>	1.73215	1.26585	0.4663
Bi <sub>0.05</sub> Na <sub>0.46</sub> Ni <sub>0.03</sub> Mn <sub>0.47</sub> O <sub>x</sub>	1.77275	1.24851	0.52424
Bi <sub>0.03</sub> Na <sub>0.46</sub> Ni <sub>0.04</sub> Mn <sub>0.46</sub> O <sub>x</sub>	1.7131	1.27942	0.43368
Bi <sub>0.07</sub> Na <sub>0.40</sub> Ni <sub>0.03</sub> Mn <sub>0.51</sub> O <sub>x</sub>	1.77381	1.26059	0.51322
Bi <sub>0.05</sub> Na <sub>0.39</sub> Ni <sub>0.03</sub> Mn <sub>0.53</sub> O <sub>x</sub>	1.7875	1.20874	0.57876
Bi <sub>0.05</sub> Na <sub>0.37</sub> Ni <sub>0.04</sub> Mn <sub>0.54</sub> O <sub>x</sub>	1.66999	1.25763	0.41236
Bi <sub>0.04</sub> Na <sub>0.39</sub> Ni <sub>0.05</sub> Mn <sub>0.53</sub> O <sub>x</sub>	1.7408	1.26463	0.47617
Bi <sub>0.04</sub> Na <sub>0.37</sub> Ni <sub>0.06</sub> Mn <sub>0.53</sub> O <sub>x</sub>	1.72959	1.26411	0.46548
Bi <sub>0.09</sub> Na <sub>0.29</sub> Ni <sub>0.04</sub> Mn <sub>0.58</sub> O <sub>x</sub>	1.79196	1.25556	0.5364
Bi <sub>0.04</sub> Na <sub>0.30</sub> Ni <sub>0.09</sub> Mn <sub>0.57</sub> O <sub>x</sub>	1.72166	1.26862	0.45304
Bi <sub>0.07</sub> Na <sub>0.28</sub> Ni <sub>0.04</sub> Mn <sub>0.61</sub> O <sub>x</sub>	1.71245	1.25338	0.45907
Bi <sub>0.05</sub> Na <sub>0.27</sub> Ni <sub>0.06</sub> Mn <sub>0.61</sub> O <sub>x</sub>	1.73492	1.25797	0.47695
Bi <sub>0.04</sub> Na <sub>0.27</sub> Ni <sub>0.10</sub> Mn <sub>0.59</sub> O <sub>x</sub>	1.73232	1.25183	0.48049
Bi <sub>0.15</sub> Na <sub>0.18</sub> Ni <sub>0.04</sub> Mn <sub>0.62</sub> O <sub>x</sub>	1.84281	1.26442	0.57839
Bi <sub>0.08</sub> Na <sub>0.23</sub> Ni <sub>0.06</sub> Mn <sub>0.63</sub> O <sub>x</sub>	1.73434	1.25227	0.48207
Bi <sub>0.06</sub> Na <sub>0.24</sub> Ni <sub>0.08</sub> Mn <sub>0.62</sub> O <sub>x</sub>	1.77157	1.26958	0.50199
Bi <sub>0.05</sub> Na <sub>0.26</sub> Ni <sub>0.11</sub> Mn <sub>0.59</sub> O <sub>x</sub>	1.71163	1.27081	0.44082
Bi <sub>0.04</sub> Na <sub>0.19</sub> Ni <sub>0.15</sub> Mn <sub>0.61</sub> O <sub>x</sub>	1.70922	1.27089	0.43833

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### 4.3.4 Galvanostatic Charge/Discharge Performance

Voltage profile during charging and discharging varied quite significantly from sample to sample. Some samples did not have a plateau at all. Figure 4.21 gives an example which refers to  $\text{Bi}_{0.04}\text{Na}_{0.44}\text{Ni}_{0.03}\text{Mn}_{0.49}\text{O}_x$  where charge and discharge profiles are sampled up to 50<sup>th</sup> cycle.

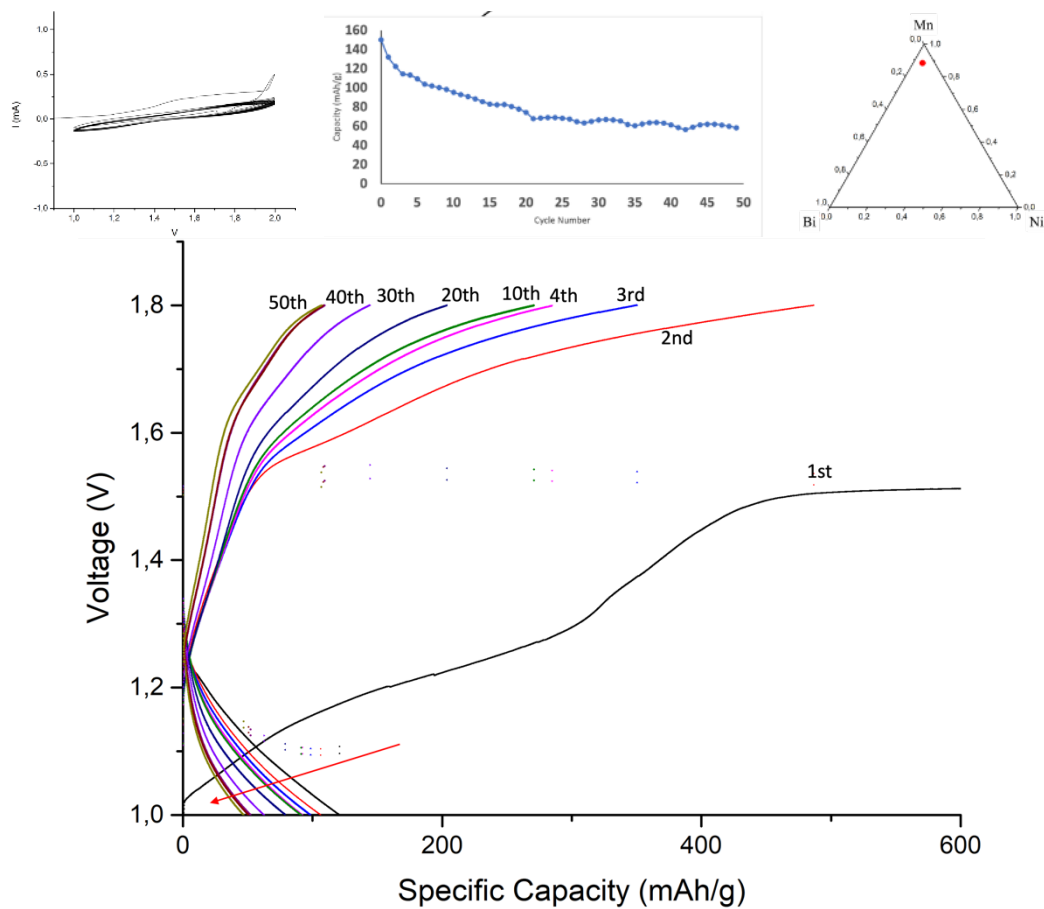


Figure 4.21 Charge-discharge profiles of  $\text{Bi}_{0.04}\text{Na}_{0.44}\text{Ni}_{0.03}\text{Mn}_{0.49}\text{O}_x$ . Note that there is no plateau formation in the profiles

Figure 4.22 refers to  $\text{Bi}_{0.08}\text{Na}_{0.39}\text{Ni}_{0.07}\text{Mn}_{0.46}\text{O}_x$  where defined plateau both in charge and in discharge can be seen in the initial cycles. There seems to be two plateau like regions in the discharge curve with turning points at 1.43 and 1.31 V. However, after 10<sup>th</sup> cycle all disappear and charge and discharge curves are without plateau.

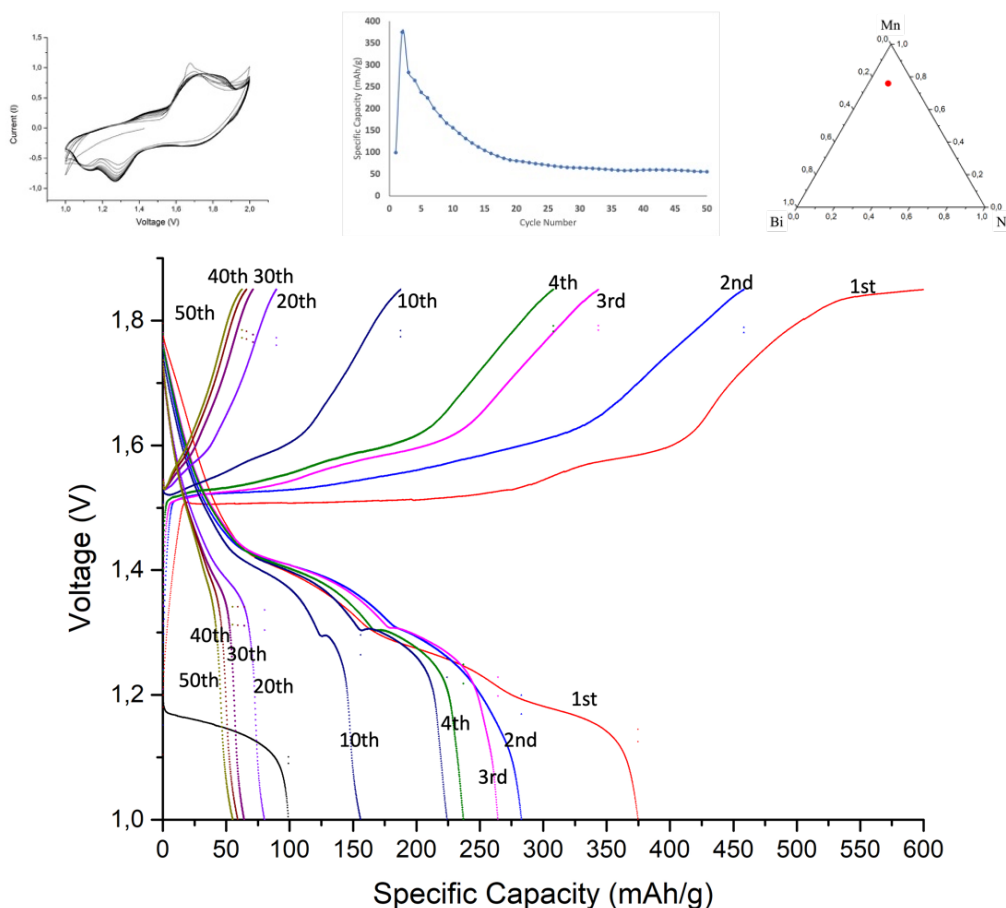


Figure 4.22 Charge-discharge profiles of  $\text{Bi}_{0.08}\text{Na}_{0.39}\text{Ni}_{0.07}\text{Mn}_{0.46}\text{O}_x$ . Note that there is a plateau formation with a turning point at 1.3 V in the profiles.

Figure 4.23 is an example where there are three plateau like regions in the discharge curve. These curves refer to  $\text{Bi}_{0.05}\text{Na}_{0.39}\text{Ni}_{0.12}\text{Mn}_{0.44}\text{O}_x$ . Transition occurs at 1.39, 1.24 and 1.10 V. After 5<sup>th</sup> cycle third turning point disappears as a result there are two plateaus. This is reduced to a single plateau after 20<sup>th</sup> cycle.

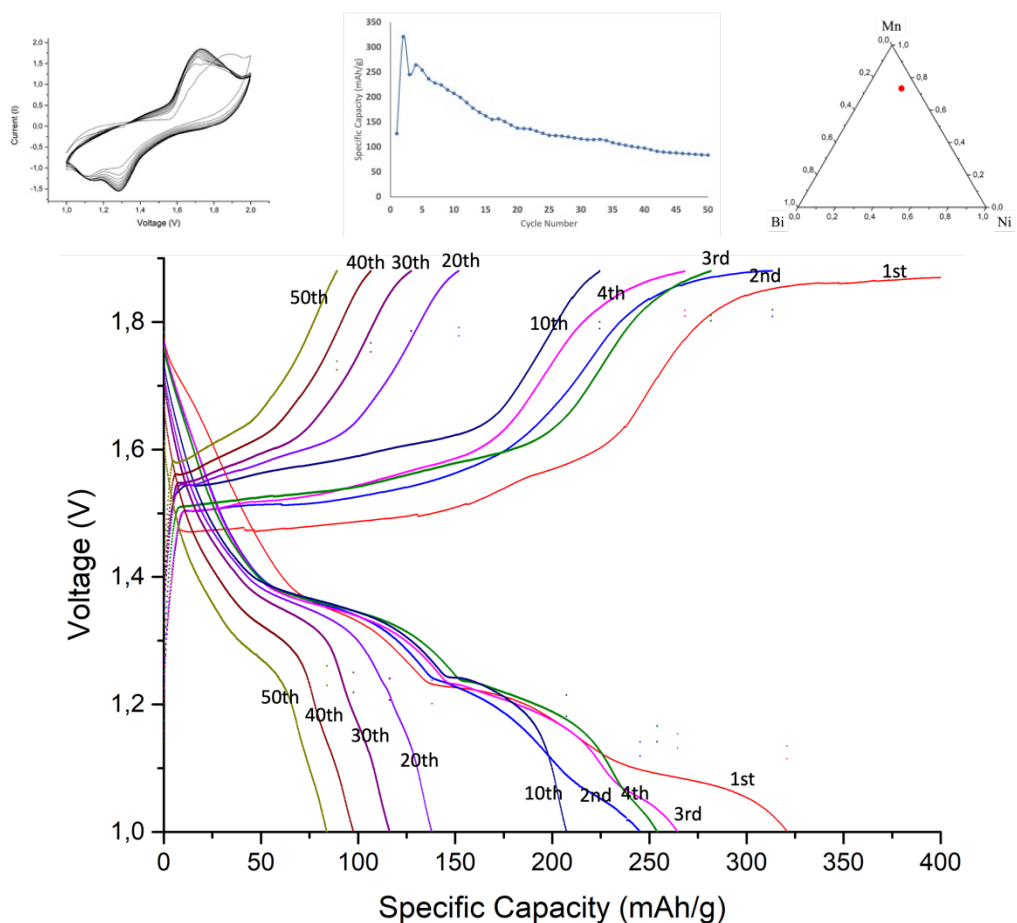


Figure 4.23 Charge-discharge profiles of  $\text{Bi}_{0.05}\text{Na}_{0.39}\text{Ni}_{0.12}\text{Mn}_{0.44}\text{O}_x$ . Note that there is a plateau formation with a turning point at 1.3 and 1.1 V in the profiles



Discharge capacities varied from cathode to cathode quite significantly. In some cathodes the capacity increased with cycling. An example for this is given Figure 4.24. The capacity which was 99 mAh/g in the first cycle then increased to 136 mAh/g and then to 152 mAh/g in 20<sup>th</sup> and 50<sup>th</sup> cycles respectively.

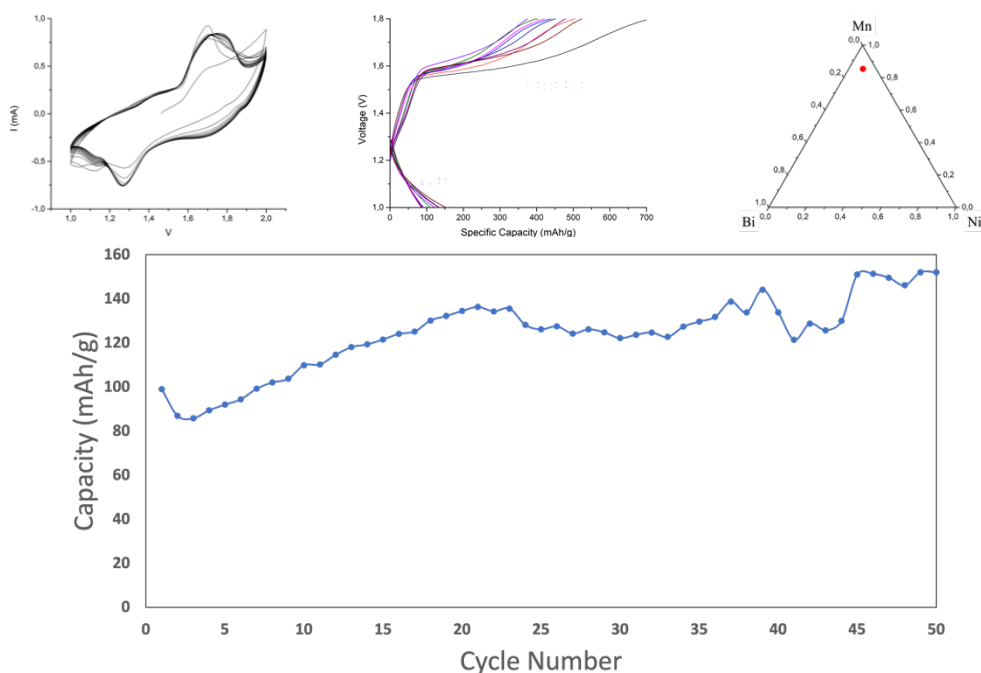


Figure 4.24 Discharge capacity versus cycle number for  $\text{Bi}_{0.03}\text{Na}_{0.54}\text{Ni}_{0.03}\text{Mn}_{0.40}\text{O}_x$ . Note that the capacity increases with increase cycle number

Figure 4.25 refers to  $\text{Bi}_{0.04}\text{Na}_{0.33}\text{Ni}_{0.22}\text{Mn}_{0.40}\text{O}_x$  cathode. Here the capacity initially is quite high but reduces with cycling. Here the value of initial capacity which was calculated more than 1400 mAh/g need to be confirmed, but the value after 50 cycle is 294 mAh/g.

Figure 4.26 refers to an example where the capacity remains almost the same with cycling. The figure refers to  $\text{Bi}_{0.23}\text{Na}_{0.21}\text{Ni}_{0.06}\text{Mn}_{0.50}\text{O}_x$ . The capacity in the first cycle is 106 mAh/g and the capacity in the 50<sup>th</sup> cycle is slightly more with a value of 126 mAh/g.

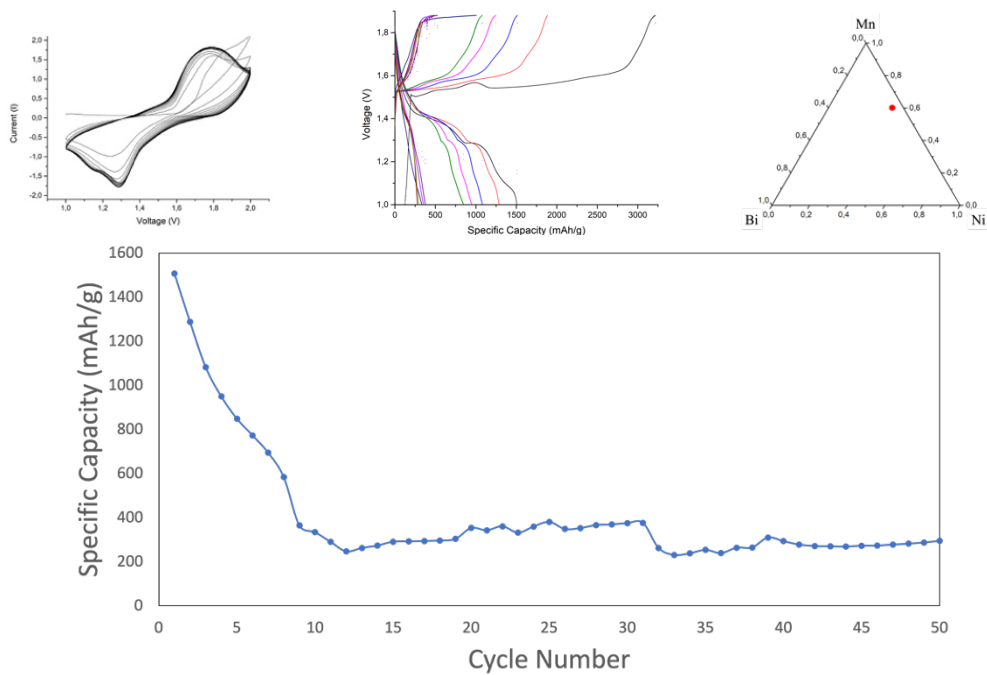


Figure 4.25 Discharge capacity versus cycle number for  $\text{Bi}_{0.04}\text{Na}_{0.33}\text{Ni}_{0.22}\text{Mn}_{0.40}\text{O}_x$ . The capacity stabilizes at 200 mAh/g after 10<sup>th</sup> cycle

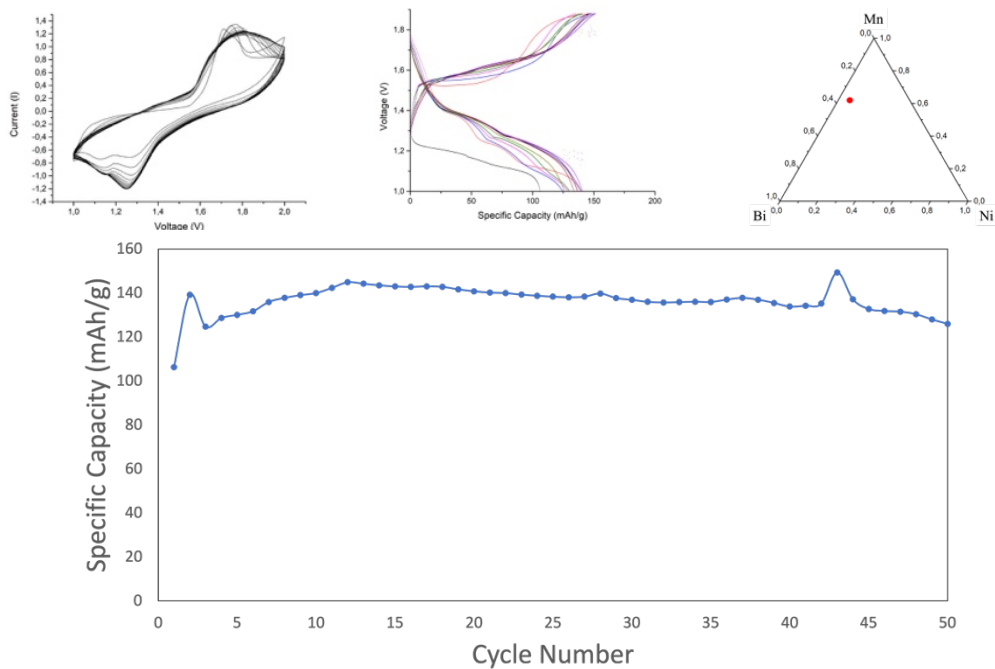


Figure 4.26 Discharge capacity versus cycle number in  $\text{Bi}_{0.23}\text{Na}_{0.21}\text{Ni}_{0.06}\text{Mn}_{0.50}\text{O}_x$  which has a stable specific capacity at 130 mAh/g for 50 cycles

It may be pointed out that in some cells the capacity was reduced drastically with no prior sign in discharge curve. Figure 4.27 is an example for this. Here the cell  $\text{Bi}_{0.11}\text{Na}_{0.31}\text{Ni}_{0.31}\text{Mn}_{0.28}\text{O}_x$  with capacities in the order of 500 mAh/g drops suddenly to 300 mAh/g at 11<sup>th</sup> cycle. This is probably due to contact problems in the cell as in the previous cycle there are irregularities in the charge curve.

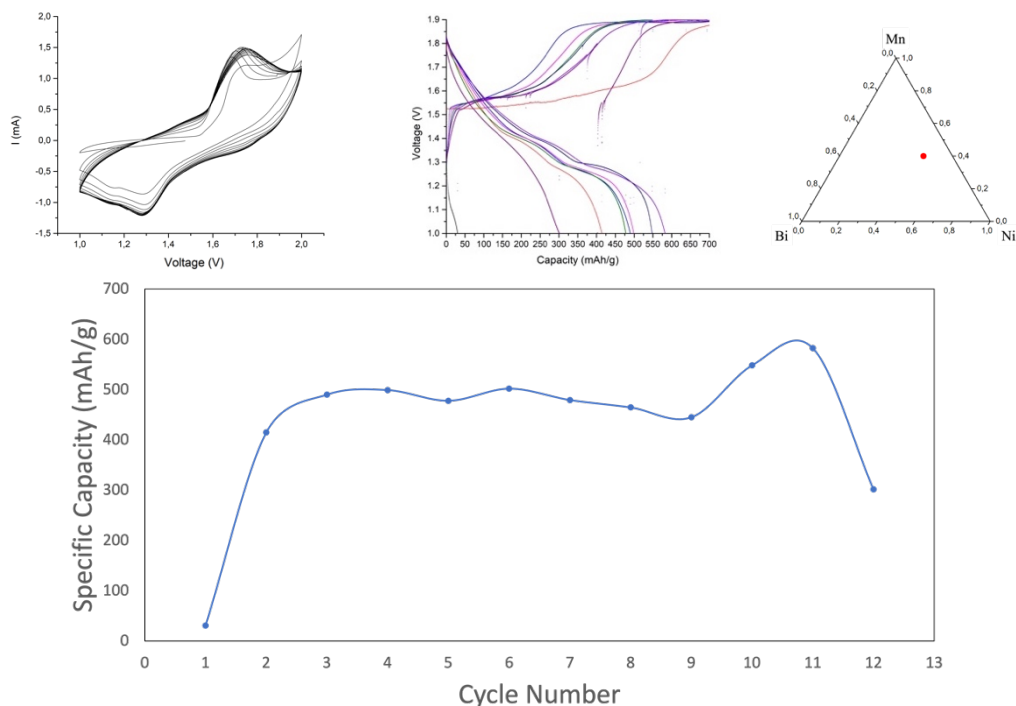


Figure 4.27 Discharge capacity versus cycle number for  $\text{Bi}_{0.11}\text{Na}_{0.31}\text{Ni}_{0.31}\text{Mn}_{0.28}\text{O}_x$  which has a sudden drop in capacity after 11<sup>th</sup> cycle

### 4.3.5 Selection of candidate cathode compositions

Results reported above indicates that capacities are quite high in Mn rich compositions. For this reason, cathodes rich in Mn content was examined in more detail. All cells were thoroughly examined and data concerning discharge capacity of initial, maximum, average, and the final are determined. These values which covers total of 57 cathodes are tabulated in Table 4.4. It should be noted that the ternary diagram just covers the Mn rich corner of the complete ternary given in Figure 4.28. It covers Mn content from 0.65 up to 0.90.

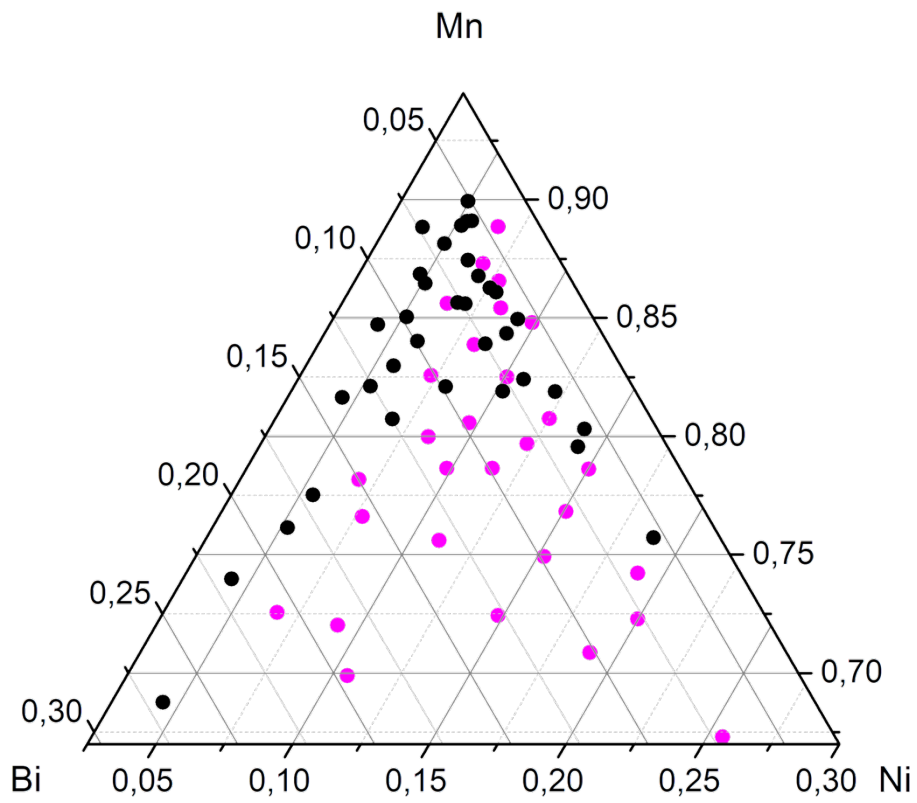


Figure 4.28 Mn-rich cathodes on Bi-Mn-Ni space

Table 4.4 Discharge capacities of the cathodes in (Bi,Na,Ni,Mn)O<sub>x</sub>

<b>Cathode Compositions</b>	<b>Initial Discharge Capacity (mAh/g)</b>	<b>Maximum Discharge Capacity (mAh/g)</b>	<b>Average Discharge Capacity (mAh/g)</b>	<b>Final Discharge Capacity (mAh/g)</b>
Bi <sub>0.01</sub> Na <sub>0.78</sub> Ni <sub>0.01</sub> Mn <sub>0.20</sub> O <sub>x</sub>	151	151	113	137
Bi <sub>0.01</sub> Na <sub>0.75</sub> Ni <sub>0.02</sub> Mn <sub>0.22</sub> O <sub>x</sub>	101	182	111	102
Bi <sub>0.01</sub> Na <sub>0.76</sub> Ni <sub>0.02</sub> Mn <sub>0.21</sub> O <sub>x</sub>	53	272	98	80
Bi <sub>0.02</sub> Na <sub>0.71</sub> Ni <sub>0.02</sub> Mn <sub>0.24</sub> O <sub>x</sub>	39	382	153	137
Bi <sub>0.02</sub> Na <sub>0.72</sub> Ni <sub>0.02</sub> Mn <sub>0.24</sub> O <sub>x</sub>	222	222	103	77
Bi <sub>0.01</sub> Na <sub>0.72</sub> Ni <sub>0.03</sub> Mn <sub>0.24</sub> O <sub>x</sub>	235	238	144	165
Bi <sub>0.04</sub> Na <sub>0.64</sub> Ni <sub>0.03</sub> Mn <sub>0.29</sub> O <sub>x</sub>	765	765	259	201
Bi <sub>0.03</sub> Na <sub>0.63</sub> Ni <sub>0.03</sub> Mn <sub>0.31</sub> O <sub>x</sub>	335	341	180	132
Bi <sub>0.03</sub> Na <sub>0.62</sub> Ni <sub>0.04</sub> Mn <sub>0.31</sub> O <sub>x</sub>	222	222	123	92
Bi <sub>0.03</sub> Na <sub>0.63</sub> Ni <sub>0.05</sub> Mn <sub>0.30</sub> O <sub>x</sub>	734	734	199	159
Bi <sub>0.04</sub> Na <sub>0.55</sub> Ni <sub>0.04</sub> Mn <sub>0.36</sub> O <sub>x</sub>	571	571	393	429
Bi <sub>0.04</sub> Na <sub>0.56</sub> Ni <sub>0.05</sub> Mn <sub>0.35</sub> O <sub>x</sub>	361	361	189	201
Bi <sub>0.12</sub> Na <sub>0.43</sub> Ni <sub>0.04</sub> Mn <sub>0.42</sub> O <sub>x</sub>	374	374	110	68
Bi <sub>0.09</sub> Na <sub>0.45</sub> Ni <sub>0.04</sub> Mn <sub>0.42</sub> O <sub>x</sub>	329	329	177	118
Bi <sub>0.04</sub> Na <sub>0.49</sub> Ni <sub>0.08</sub> Mn <sub>0.39</sub> O <sub>x</sub>	47	47	23	17
Bi <sub>0.12</sub> Na <sub>0.35</sub> Ni <sub>0.06</sub> Mn <sub>0.47</sub> O <sub>x</sub>	968	968	381	230
Bi <sub>0.08</sub> Na <sub>0.39</sub> Ni <sub>0.07</sub> Mn <sub>0.46</sub> O <sub>x</sub>	374	374	102	55
Bi <sub>0.06</sub> Na <sub>0.40</sub> Ni <sub>0.09</sub> Mn <sub>0.45</sub> O <sub>x</sub>	16	16	7	4
Bi <sub>0.05</sub> Na <sub>0.39</sub> Ni <sub>0.12</sub> Mn <sub>0.44</sub> O <sub>x</sub>	320	320	143	83
Bi <sub>0.04</sub> Na <sub>0.38</sub> Ni <sub>0.16</sub> Mn <sub>0.41</sub> O <sub>x</sub>	446	455	234	141
Bi <sub>0.14</sub> Na <sub>0.30</sub> Ni <sub>0.07</sub> Mn <sub>0.49</sub> O <sub>x</sub>	615	618	260	162
Bi <sub>0.07</sub> Na <sub>0.36</sub> Ni <sub>0.12</sub> Mn <sub>0.45</sub> O <sub>x</sub>	239	239	156	108
Bi <sub>0.06</sub> Na <sub>0.34</sub> Ni <sub>0.17</sub> Mn <sub>0.44</sub> O <sub>x</sub>	244	244	126	66
Bi <sub>0.01</sub> Na <sub>0.71</sub> Ni <sub>0.01</sub> Mn <sub>0.26</sub> O <sub>x</sub>	180	228	151	164
Bi <sub>0.02</sub> Na <sub>0.64</sub> Ni <sub>0.02</sub> Mn <sub>0.32</sub> O <sub>x</sub>	40	40	7	0.2
Bi <sub>0.02</sub> Na <sub>0.63</sub> Ni <sub>0.02</sub> Mn <sub>0.33</sub> O <sub>x</sub>	396	763	538	750
Bi <sub>0.03</sub> Na <sub>0.56</sub> Ni <sub>0.02</sub> Mn <sub>0.39</sub> O <sub>x</sub>	423	507	284	507
Bi <sub>0.03</sub> Na <sub>0.54</sub> Ni <sub>0.03</sub> Mn <sub>0.40</sub> O <sub>x</sub>	99	151	124	151
Bi <sub>0.02</sub> Na <sub>0.56</sub> Ni <sub>0.02</sub> Mn <sub>0.40</sub> O <sub>x</sub>	51	58	43	33
Bi <sub>0.04</sub> Na <sub>0.44</sub> Ni <sub>0.03</sub> Mn <sub>0.49</sub> O <sub>x</sub>	120	120	78	46
Bi <sub>0.03</sub> Na <sub>0.45</sub> Ni <sub>0.04</sub> Mn <sub>0.47</sub> O <sub>x</sub>	195	195	72	18

**Table 4.4 (cont'd)**

$\text{Bi}_{0.03}\text{Na}_{0.46}\text{Ni}_{0.04}\text{Mn}_{0.46}\text{O}_x$	88	172	134	119
$\text{Bi}_{0.07}\text{Na}_{0.40}\text{Ni}_{0.03}\text{Mn}_{0.51}\text{O}_x$	54	101	79	102
$\text{Bi}_{0.05}\text{Na}_{0.39}\text{Ni}_{0.03}\text{Mn}_{0.53}\text{O}_x$	398	398	29	97
$\text{Bi}_{0.05}\text{Na}_{0.37}\text{Ni}_{0.04}\text{Mn}_{0.54}\text{O}_x$	528	528	195	161
$\text{Bi}_{0.04}\text{Na}_{0.39}\text{Ni}_{0.05}\text{Mn}_{0.53}\text{O}_x$	442	442	151	114
$\text{Bi}_{0.04}\text{Na}_{0.37}\text{Ni}_{0.06}\text{Mn}_{0.53}\text{O}_x$	282	1282	574	661
$\text{Bi}_{0.10}\text{Na}_{0.30}\text{Ni}_{0.03}\text{Mn}_{0.57}\text{O}_x$	196	196	41	7
$\text{Bi}_{0.09}\text{Na}_{0.29}\text{Ni}_{0.04}\text{Mn}_{0.58}\text{O}_x$	403	403	129	81
$\text{Bi}_{0.06}\text{Na}_{0.36}\text{Ni}_{0.03}\text{Mn}_{0.54}\text{O}_x$	62	62	36	35
$\text{Bi}_{0.05}\text{Na}_{0.32}\text{Ni}_{0.05}\text{Mn}_{0.58}\text{O}_x$	37	37	25	17
$\text{Bi}_{0.04}\text{Na}_{0.34}\text{Ni}_{0.06}\text{Mn}_{0.56}\text{O}_x$	39	64	55	64
$\text{Bi}_{0.04}\text{Na}_{0.30}\text{Ni}_{0.09}\text{Mn}_{0.57}\text{O}_x$	359	359	142	103
$\text{Bi}_{0.18}\text{Na}_{0.18}\text{Ni}_{0.04}\text{Mn}_{0.61}\text{O}_x$	23	23	6	5
$\text{Bi}_{0.13}\text{Na}_{0.21}\text{Ni}_{0.04}\text{Mn}_{0.61}\text{O}_x$	32	32	11	9
$\text{Bi}_{0.09}\text{Na}_{0.25}\text{Ni}_{0.04}\text{Mn}_{0.63}\text{O}_x$	526	526	210	167
$\text{Bi}_{0.07}\text{Na}_{0.28}\text{Ni}_{0.04}\text{Mn}_{0.61}\text{O}_x$	259	259	104	58
$\text{Bi}_{0.05}\text{Na}_{0.27}\text{Ni}_{0.06}\text{Mn}_{0.61}\text{O}_x$	89	89	46	34
$\text{Bi}_{0.05}\text{Na}_{0.25}\text{Ni}_{0.08}\text{Mn}_{0.62}\text{O}_x$	124	188	137	103
$\text{Bi}_{0.04}\text{Na}_{0.27}\text{Ni}_{0.10}\text{Mn}_{0.59}\text{O}_x$	204	367	236	247
$\text{Bi}_{0.24}\text{Na}_{0.12}\text{Ni}_{0.04}\text{Mn}_{0.61}\text{O}_x$	157	157	73	37
$\text{Bi}_{0.15}\text{Na}_{0.18}\text{Ni}_{0.04}\text{Mn}_{0.62}\text{O}_x$	220	220	90	32
$\text{Bi}_{0.10}\text{Na}_{0.20}\text{Ni}_{0.05}\text{Mn}_{0.65}\text{O}_x$	67	155	75	30
$\text{Bi}_{0.08}\text{Na}_{0.23}\text{Ni}_{0.06}\text{Mn}_{0.63}\text{O}_x$	99	185	131	164
$\text{Bi}_{0.06}\text{Na}_{0.24}\text{Ni}_{0.08}\text{Mn}_{0.62}\text{O}_x$	270	270	84	44
$\text{Bi}_{0.05}\text{Na}_{0.26}\text{Ni}_{0.11}\text{Mn}_{0.59}\text{O}_x$	51	51	40	45
$\text{Bi}_{0.04}\text{Na}_{0.19}\text{Ni}_{0.15}\text{Mn}_{0.61}\text{O}_x$	283	283	105	73

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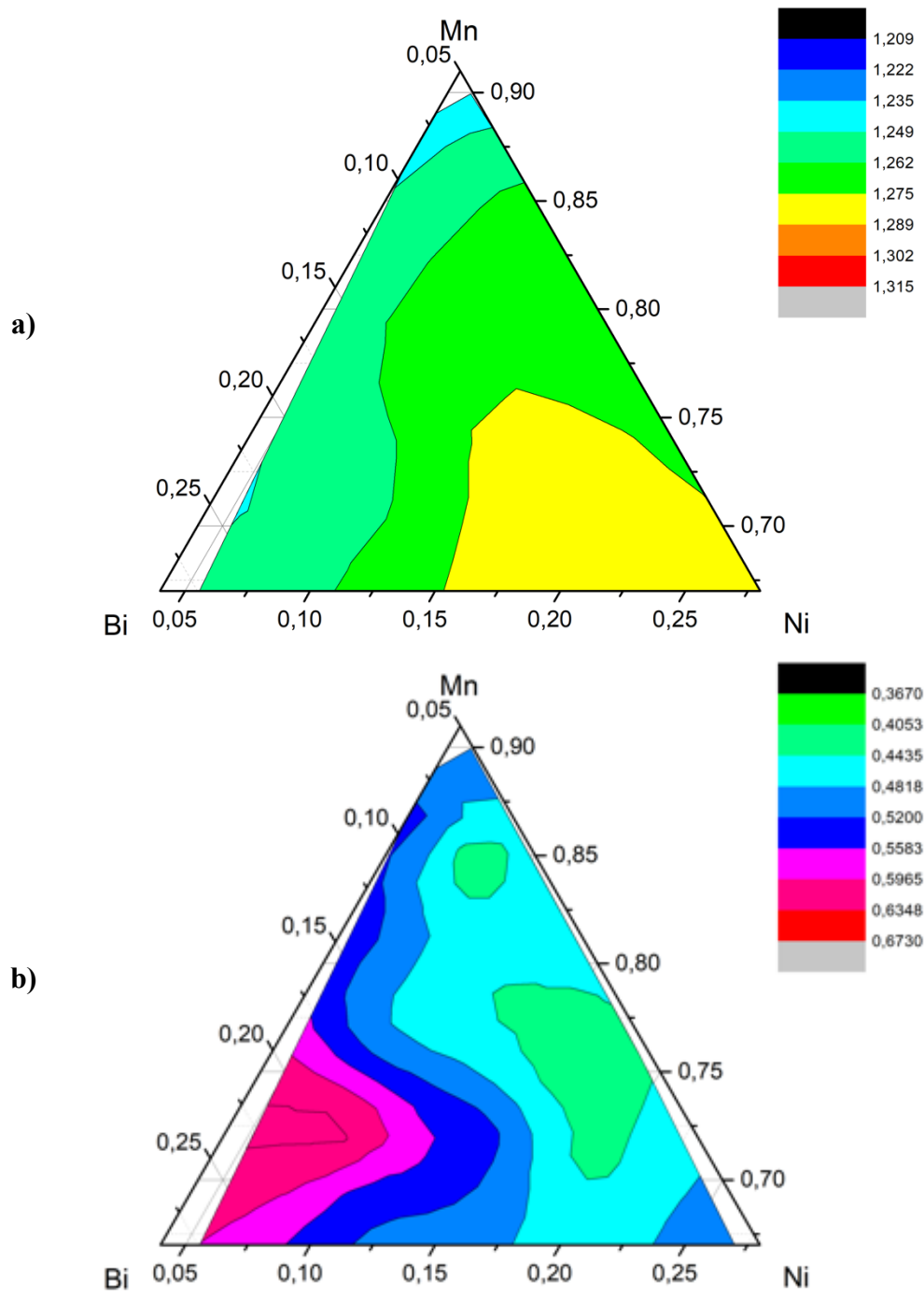


Figure 4.29 Sample distribution on Bi-Mn-Ni ternary diagram; **a)** discharge voltages, **b)** redox potential difference

Figure 4.29 shows maps two maps. The first one refers to discharge voltages as determined from CV (10<sup>th</sup> cycle), Figure 4.29 (a). The value of this potential is

important in terms of the cell power. Figure 4.29 (b) refers to voltage difference between oxidation and reduction peaks in CV again at the 10<sup>th</sup> cycle, which is a measure of the ease of rechargeability.

Figure 4.30 (a) shows a map of initial discharge capacity for Mn rich cathodes. It should be noted that the initial capacity is highest in  $\text{Bi}_{0.12}\text{Na}_{0.35}\text{Ni}_{0.06}\text{Mn}_{0.47}\text{O}_x$  and  $\text{Bi}_{0.14}\text{Na}_{0.30}\text{Ni}_{0.07}\text{Mn}_{0.36}\text{O}_x$  cathodes marked with yellow and orange contours. This position was marked with “L” in Figure 4.30 (a) The position of their battery performance plotted in Figure 4.32.

Figure 4.30 (b) shows a map of maximum discharge capacity in the cathodes. It is seen that it is in the same region as that in Figure 4.30 (a) where the maximum capacity was observed. Therefore, this position was also marked with L. Highest capacity observed was 968 mAh/g. However, this high capacity decreased with cycle number and stabilized at around 175 mAh/g after 50 cycles.

In terms of galvanostatic performance of cathodes, perhaps most representative map is that of average capacity, i.e., capacity averaged over 50 cycles. Figure 4.31 (a). It is seen that there are three maxima along the line where  $\text{Ni} \approx 0.10$ . The highest average capacity is obtained in the same position as that marked with L in the maps given above. This cathode has  $\text{Mn} \approx 0.72$ . The next positions are two yellow area where Mn content is  $\text{Mn} \approx 0.80$  and  $0.85$  respectively. These marked with M and H1.

Figure 4.31 (b) is most instructive map which gives the final capacities of the cathode. Here the position M which was already marked above shows up very clearly as it is the area with highest final capacity. Here the value is 700 mAh/g. The map also shows up a region in the upper left corner of the ternary diagram. This region is marked with H2.



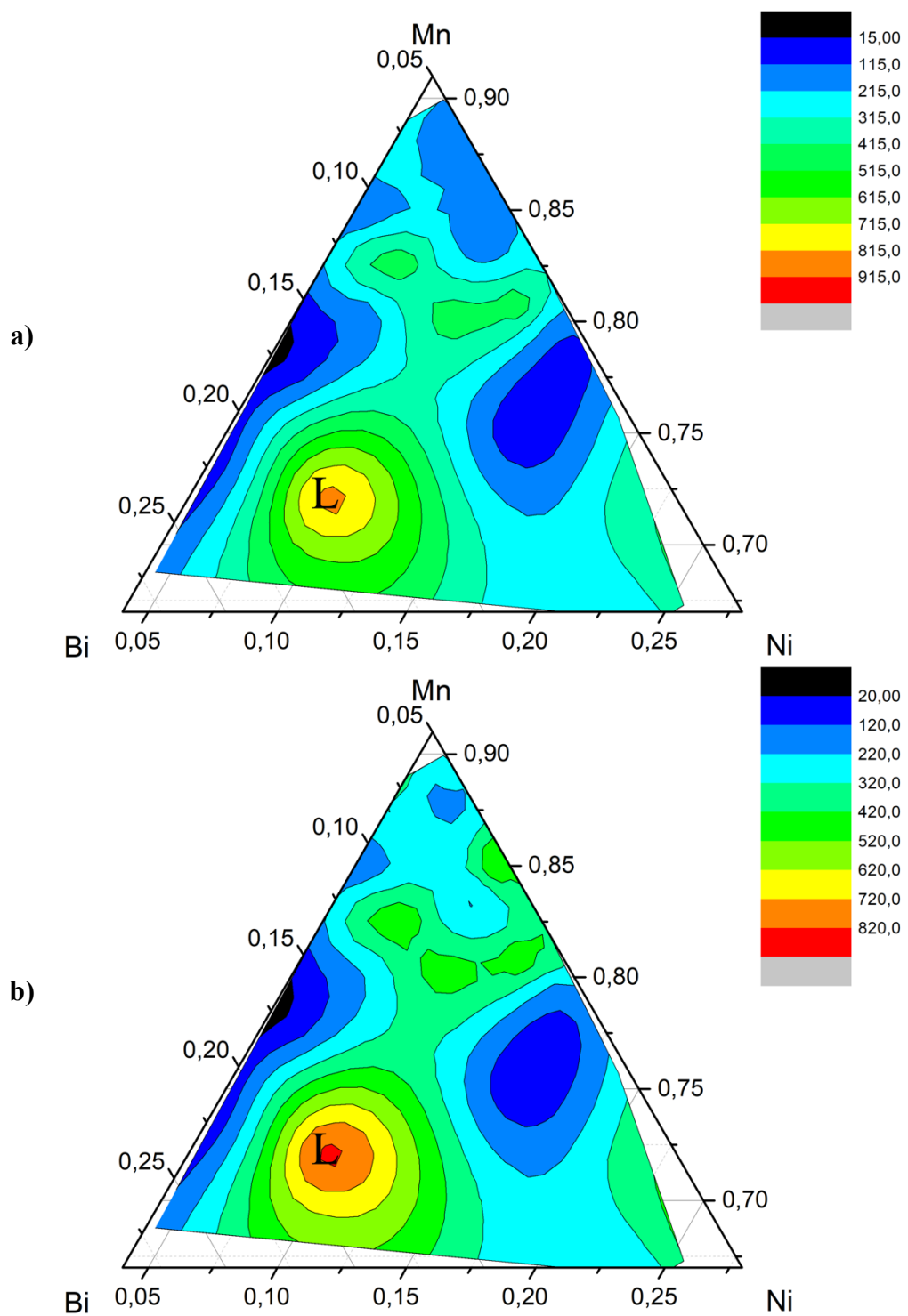


Figure 4.30 Discharge capacities of cathodes; **a)** initial capacity, **b)** maximum capacity. Note that red, orange, and yellow color codes indicate higher capacity

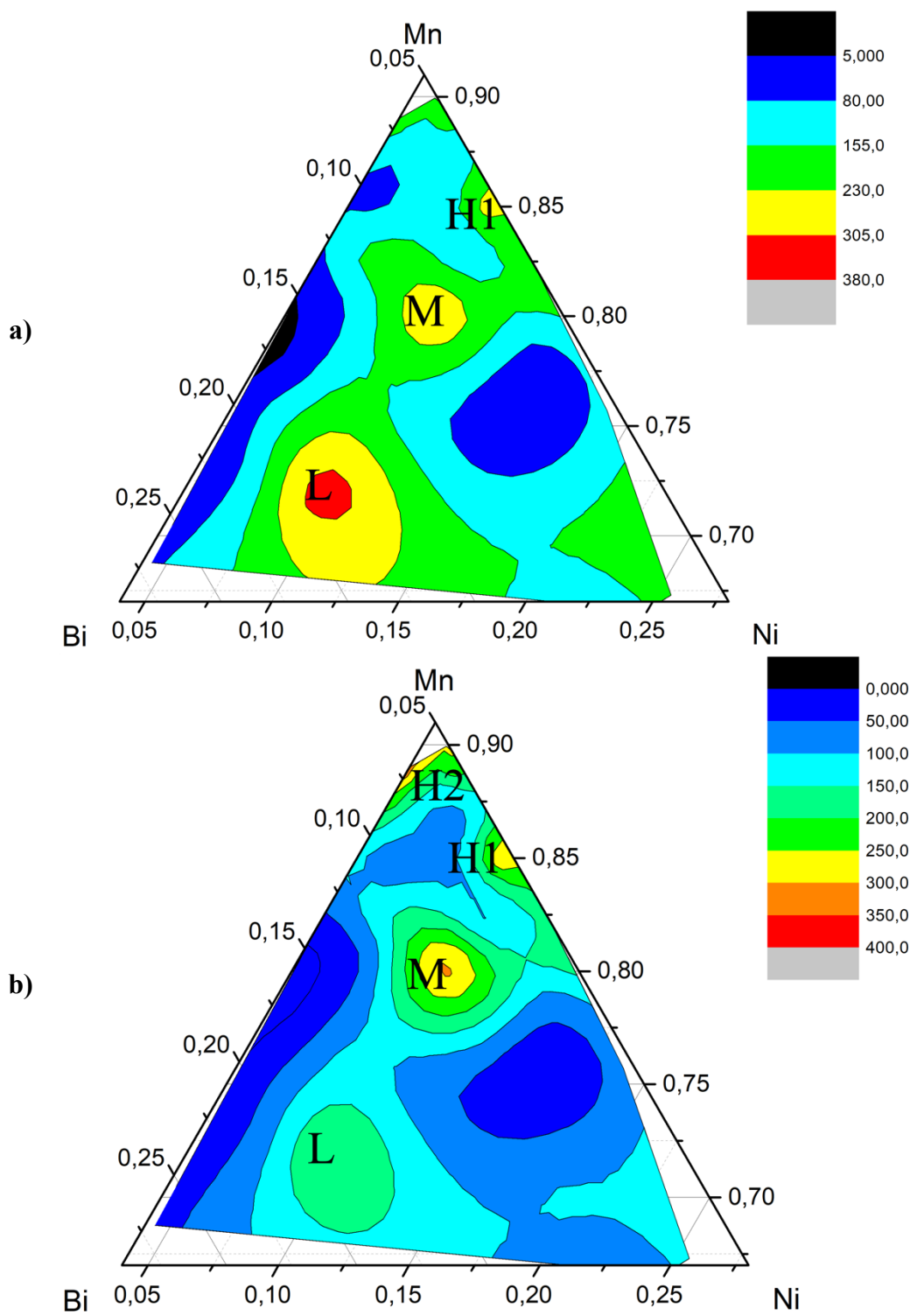


Figure 4.31 Discharge capacities of cathodes; **a)** average capacity, **b)** final capacity. Note that red, orange, and yellow color codes indicate higher capacity

Candidate compositions therefore fall into four regions in the ternary diagram. These are examined in detail below.

Figure 4.32 refers to a representative sample in region L. It is seen that the voltammogram appears to have a single oxidation and two reduction peaks, which with cycling become quite stable. Charge-discharge profile changes quite significantly with cycling with loss of plateaus. The capacity is reduced with cycling and goes down to quite a low value of 162 mAh/g. XRD pattern of the cathode before and after cycling is given in Figure 4.33 where it is seen that the cathode remains amorphous with no sign of crystallization.

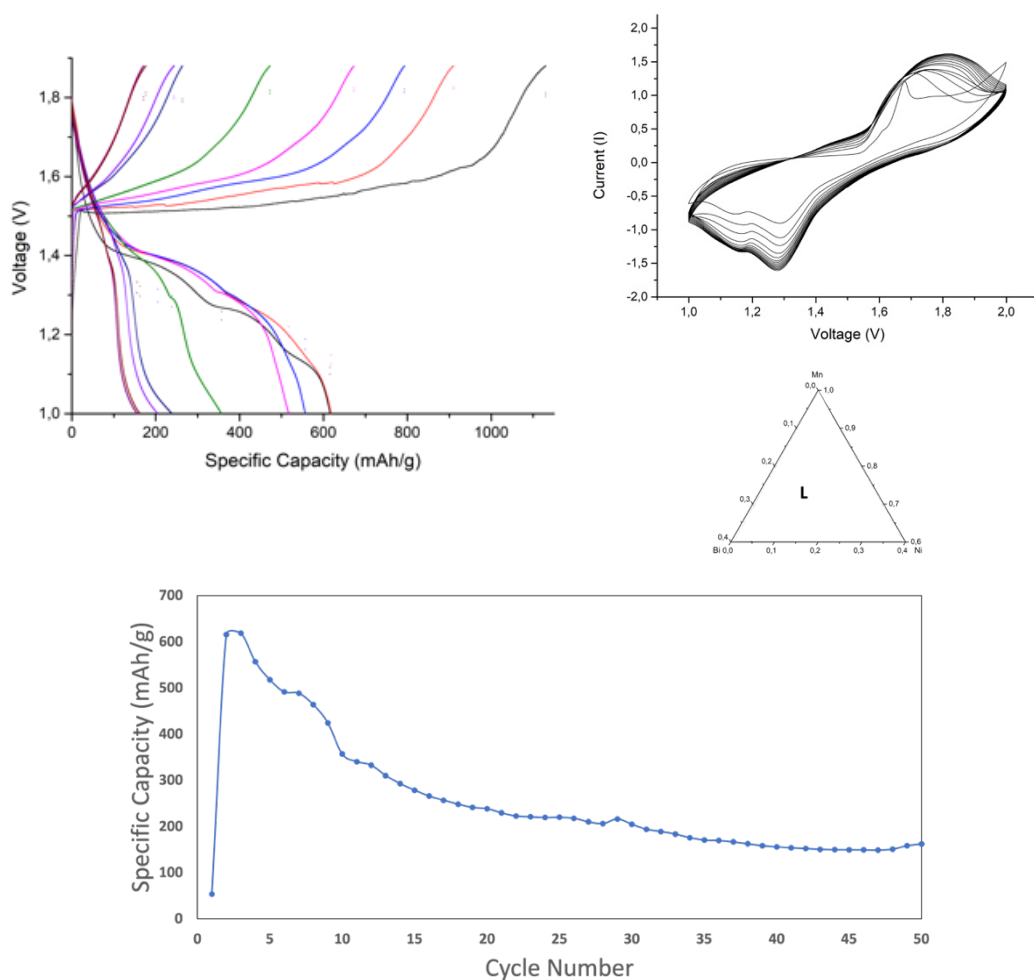


Figure 4.32 Battery performance of the cathode composition of **L**  
 $\text{Bi}_{0.14}\text{Na}_{0.30}\text{Ni}_{0.07}\text{Mn}_{0.36}\text{O}_x / \text{Bi}_{0.20}\text{Na}_{0.43}\text{Ni}_{0.11}\text{Mn}_{0.70}\text{O}_x$

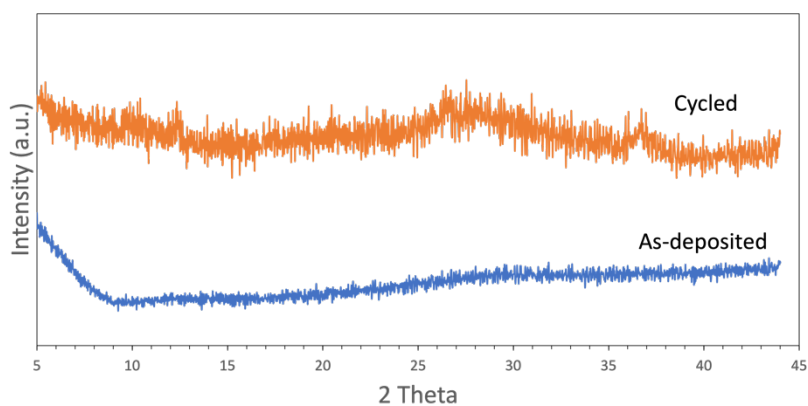


Figure 4.33 XRD pattern of the representative sample from the region L, having composition of  $\text{Bi}_{0.14}\text{Na}_{0.30}\text{Ni}_{0.07}\text{Mn}_{0.36}\text{O}_x/\text{Bi}_{0.20}\text{Na}_{0.43}\text{Ni}_{0.11}\text{Mn}_{0.70}\text{O}_x$

Unlike region L, the region M display structural change upon cycling. XRD patterns of a representative sample from this region is given in Figure 4.34 The cathode was amorphous in the as-deposited case but it is crystalline after cycling with peak positions matching  $\delta\text{-MnO}_2$ . The voltammogram is similar to that reported above implying that charge discharge reactions are similar in both region L and M. In terms of capacity, the initial value close 600 mAh/g shows a decrease but stabilizes at an immersive value of 400 mAh/g and remain the same from 15<sup>th</sup> cycle onwards Figure 4.35.

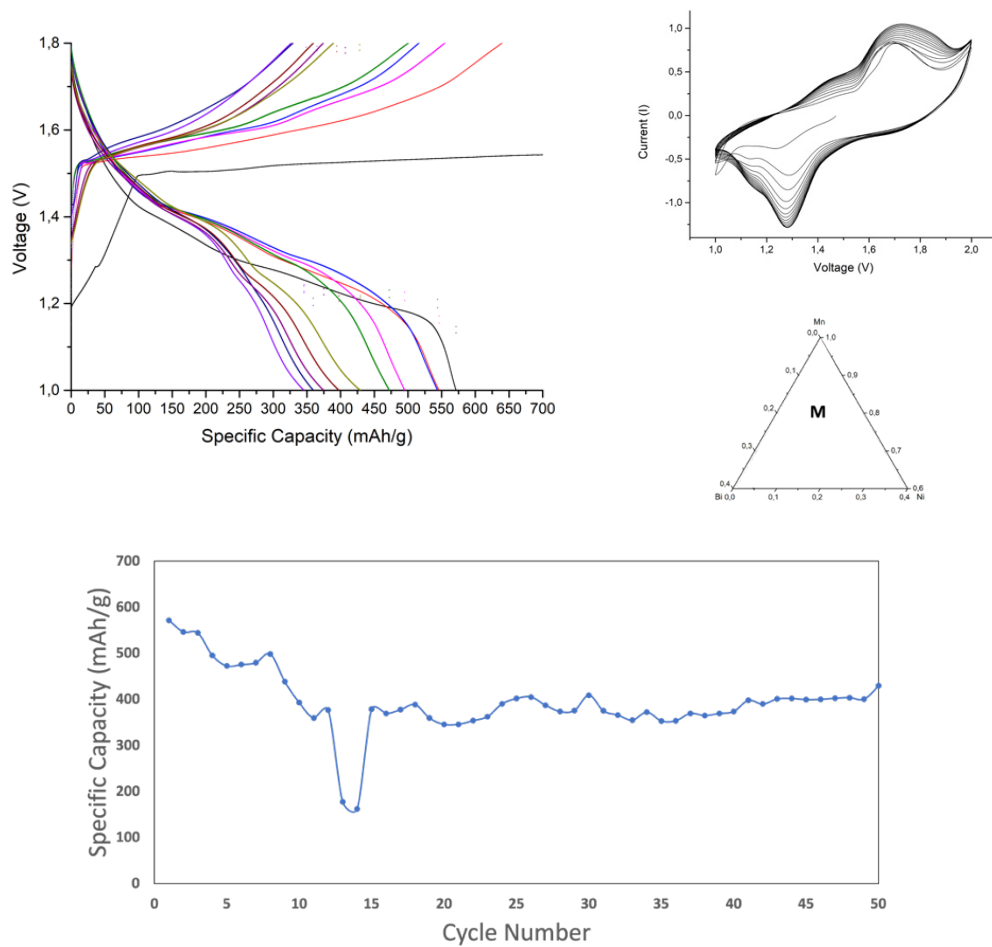


Figure 4.34 Representative battery performance of the **M** region cathodes with the composition of  $\text{Bi}_{0.04}\text{Na}_{0.55}\text{Ni}_{0.04}\text{Mn}_{0.36}\text{O}_x/\text{Bi}_{0.10}\text{Na}_{1.22}\text{Ni}_{0.10}\text{Mn}_{0.81}\text{O}_x$

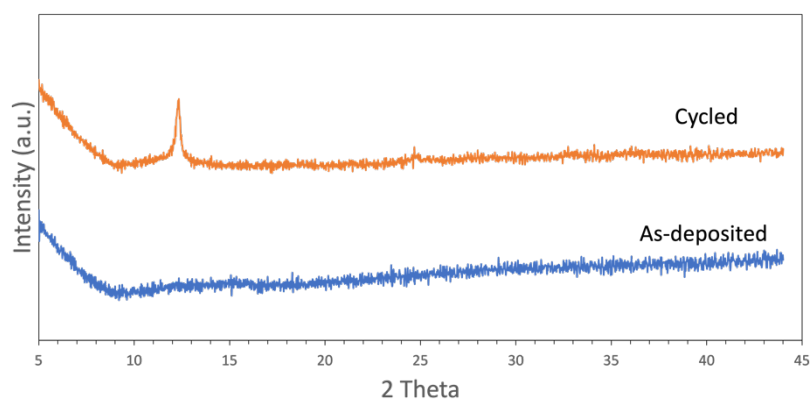
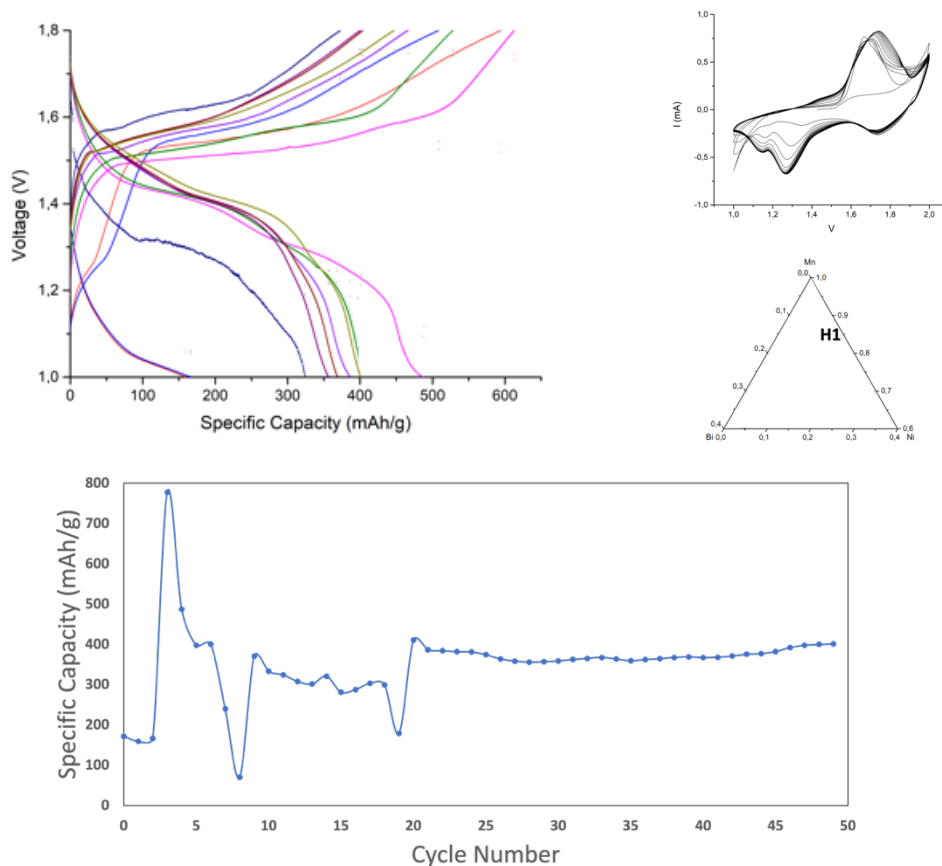


Figure 4.35 XRD pattern of the representative sample from the region **M**, having composition of  $\text{Bi}_{0.04}\text{Na}_{0.55}\text{Ni}_{0.04}\text{Mn}_{0.36}\text{O}_x/\text{Bi}_{0.10}\text{Na}_{1.22}\text{Ni}_{0.10}\text{Mn}_{0.81}\text{O}_x$

The region H1 have features which are quite similar to those of region M, Figure 4.36. The amorphous cathode crystallizes into layered structure of delta  $\text{MnO}_2$ , but here the peaks are not as sharp as those in region M implying that the cathode is nanocrystalline, Figure 4.37. In capacity versus cycle number curve, there are temporary falls in the capacity which recovers later on, similar sudden drop was also observed in region M. Rate capability of the H1 was impressive which is the discharge capacity is between 400 and 300 mAh/g as increasing the current from 61.6 mA/g to 616 mA/g.



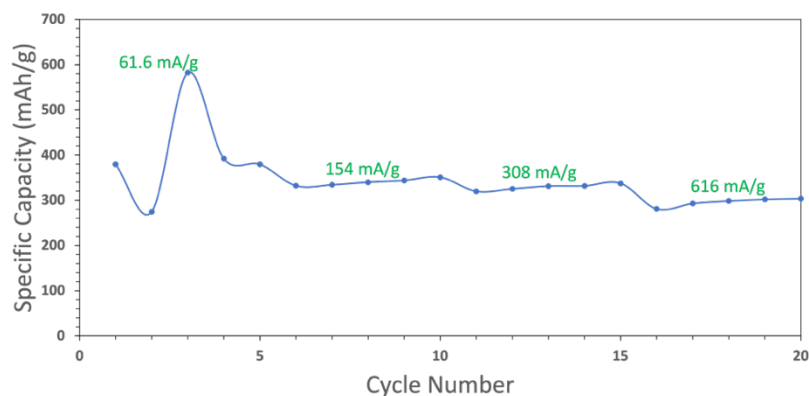


Figure 4.36 Representative battery performance of the **H1** region cathodes with the composition of  $\text{Bi}_{0.04}\text{Na}_{0.37}\text{Ni}_{0.06}\text{Mn}_{0.53}\text{O}_x/\text{Bi}_{0.06}\text{Na}_{0.60}\text{Ni}_{0.09}\text{Mn}_{0.85}\text{O}_x$

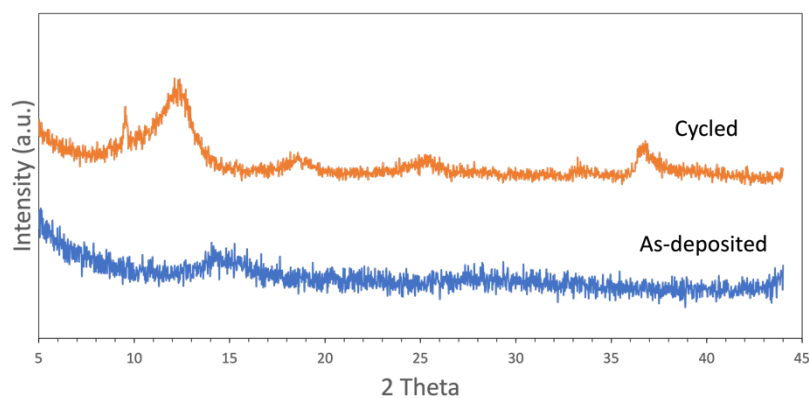


Figure 4.37 XRD pattern of the representative sample from the region **H1**, having composition of  $\text{Bi}_{0.04}\text{Na}_{0.37}\text{Ni}_{0.06}\text{Mn}_{0.53}\text{O}_x/\text{Bi}_{0.06}\text{Na}_{0.60}\text{Ni}_{0.09}\text{Mn}_{0.85}\text{O}_x$

The region H2 display quite different features, Figure 4.38. Here the most striking feature is that the capacity increases with cycling. Initially high capacity drops to 270 mAh/g, but then rises steadily and after 30<sup>th</sup> cycle yields a capacity close to 700 mAh/g. Voltammogram of this cathode have also different features. Shoulders close to the main oxidation and reduction peaks on their left side are almost non-existent. XRD pattern of this sample before and after cycling is given in Figure 4.39. Here the cathode was nanocrystalline in the as-deposited state and upon cycling the peaks are broadened more implying that the structure was refined upon cycling. Rate capability of the H2 was impressive which is the discharge capacity is between 300 and 150 mAh/g as increasing the current from 61.6 mA/g to 616 mA/g.

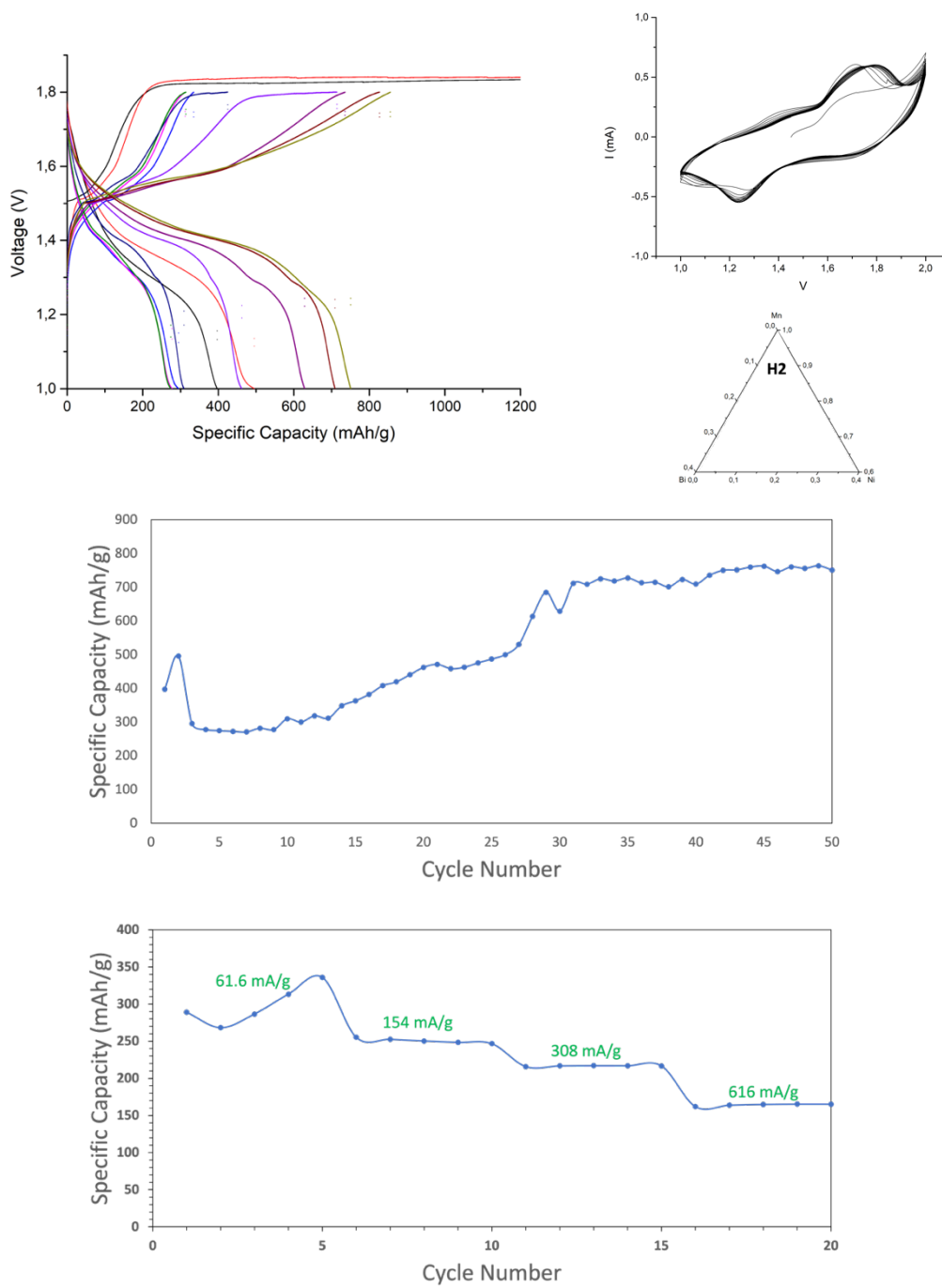


Figure 4.38 Representative battery performance of the **H2** region cathodes with composition of  $\text{Bi}_{0.02}\text{Na}_{0.63}\text{Ni}_{0.02}\text{Mn}_{0.33}\text{O}_x$ / $\text{Bi}_{0.05}\text{Na}_{1.71}\text{Ni}_{0.06}\text{Mn}_{0.89}\text{O}_x$



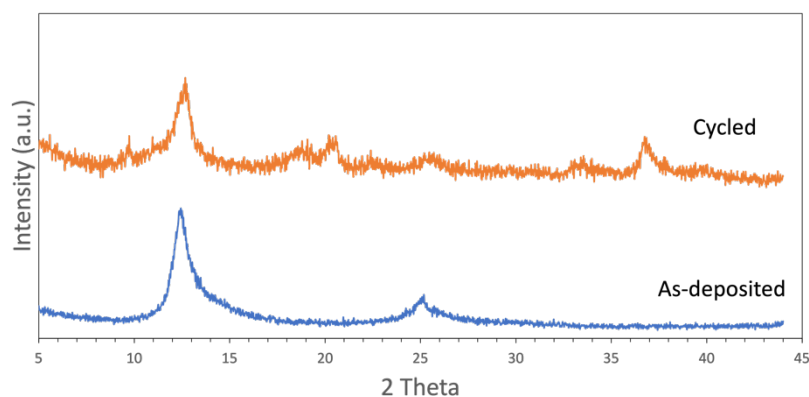


Figure 4.39 XRD pattern of the representative sample from the region **H2**, having composition of  $\text{Bi}_{0.02}\text{Na}_{0.63}\text{Ni}_{0.02}\text{Mn}_{0.33}\text{O}_x/\text{Bi}_{0.05}\text{Na}_{1.71}\text{Ni}_{0.06}\text{Mn}_{0.89}\text{O}_x$

Having selected the candidate compositions, it would be useful to examine Bi content less than 10% contributes to the improvement of redox potential via decreasing the difference between the charge and discharge potential. Meanwhile, region L, M and H1 are on the 10% Ni line in the ternary diagram.

As a result, three different locations were selected namely, M, H1 and H2 having representative compositions of  $\text{Bi}_{0.04}\text{Na}_{0.55}\text{Ni}_{0.04}\text{Mn}_{0.36}\text{O}_x$ ,  $\text{Bi}_{0.04}\text{Na}_{0.37}\text{Ni}_{0.06}\text{Mn}_{0.53}\text{O}_x$ , and  $\text{Bi}_{0.02}\text{Na}_{0.63}\text{Ni}_{0.02}\text{Mn}_{0.33}\text{O}_x$ , respectively. They are tabulated in Table 4.5. Na content in the ternary phase field is shown plotted in Figure 4.40 It is seen that the selected compositions M, H1 and H2 fall in Na rich region.

Table 4.5 Specific discharge capacities (mAh/g) of selected compositions

Composition	Region	First	Last	Max.	Min.	Avg.	1st discharge OCV (V)
$\text{Bi}_{0.04}\text{Na}_{0.55}\text{Ni}_{0.04}\text{Mn}_{0.36}\text{O}_x$	M	571	429	571	162	393	1.79
$\text{Bi}_{0.04}\text{Na}_{0.37}\text{Ni}_{0.06}\text{Mn}_{0.53}\text{O}_x$	H1	171	401	777	70	348	1.49
$\text{Bi}_{0.02}\text{Na}_{0.63}\text{Ni}_{0.02}\text{Mn}_{0.33}\text{O}_x$	H2	396	750	763	270	538	1.77

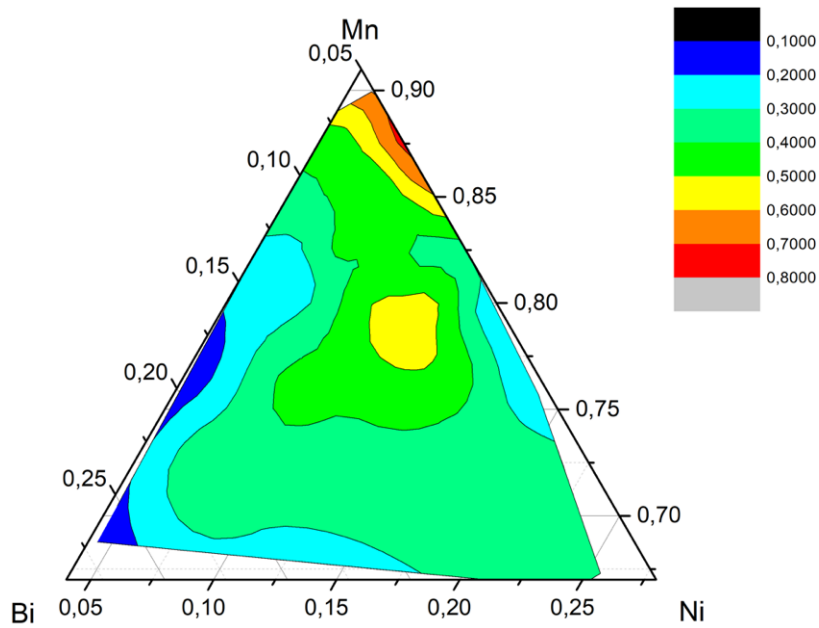


Figure 4.40 Na distribution on Bi-Mn-Ni ternary diagram

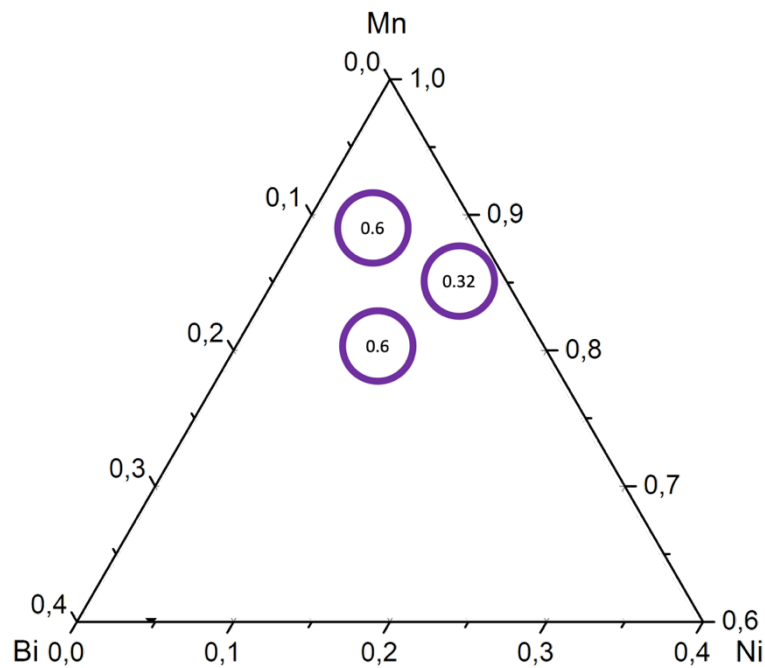


Figure 4.41 Selected regions from the Mn-rich cathodes. Note that their Na content written in the circles

Some of the capacities reported in this study is quite high, higher than that obtained with two electron exchanges of  $\text{MnO}_2$  (616 mAh/g). These cathodes are quite rich both in Na and Mn. A preliminary study was made as to the source of these additional capacity. An experiment was therefore carried using nickel foil without any active

material on it, anode was zinc foil. Two cells were made one with 2M ZnSO<sub>4</sub> and the other 2M ZnSO<sub>4</sub>+0.1M MnSO<sub>4</sub> aqueous electrolyte. Cells were cycled with 20  $\mu$ A between 1.0 V and 1.8 V. Voltammograms were recorded from 1.0 to 1.8 V with a sweep rate of 2 mV/sec.

Voltage profile and the CV profile of those two cells were plotted in Figure 4.42. The capacity was 0.0015 mAh for the cell with 2M ZnSO<sub>4</sub> electrolyte while with 2M ZnSO<sub>4</sub>+0.1M MnSO<sub>4</sub> the capacity was six times higher with 0.009 mAh. CV profiles confirm these results as with 2M ZnSO<sub>4</sub>+0.1M MnSO<sub>4</sub> electrolyte has a well-defined oxidation and reduction peaks at around 1.7 V and 1.35 V respectively.

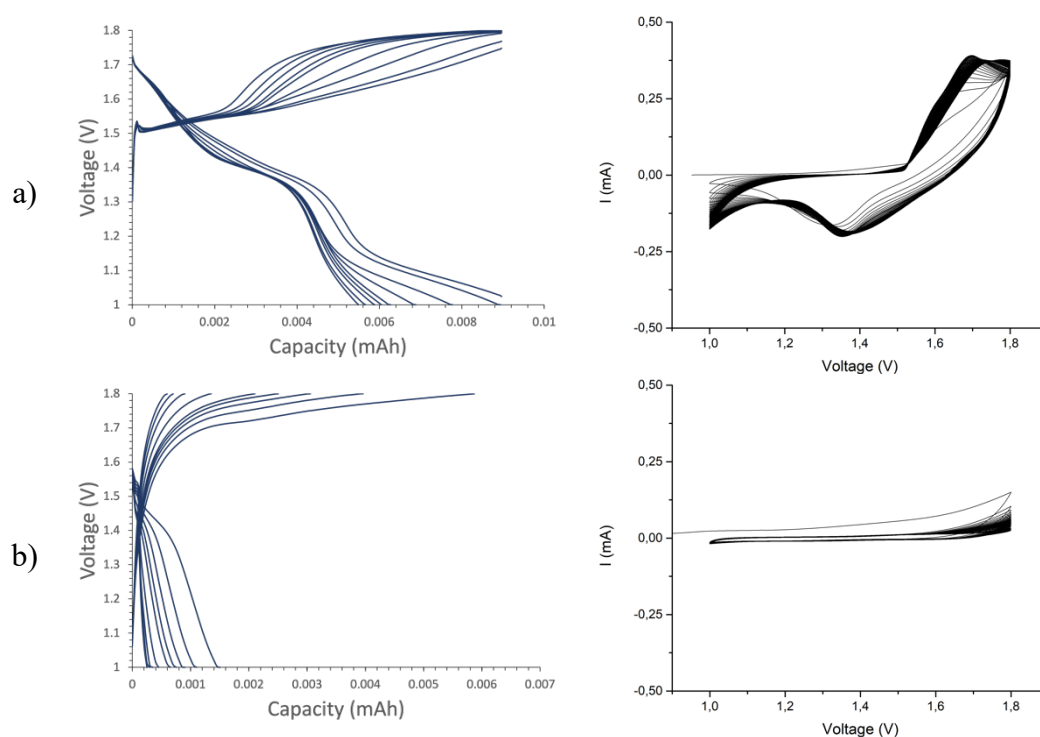


Figure 4.42 Voltage and CV profile of Ni-Zn cell in electrolyte of **a)** 2M ZnSO<sub>4</sub>+0.1M MnSO<sub>4</sub> and **b)** 2M ZnSO<sub>4</sub>

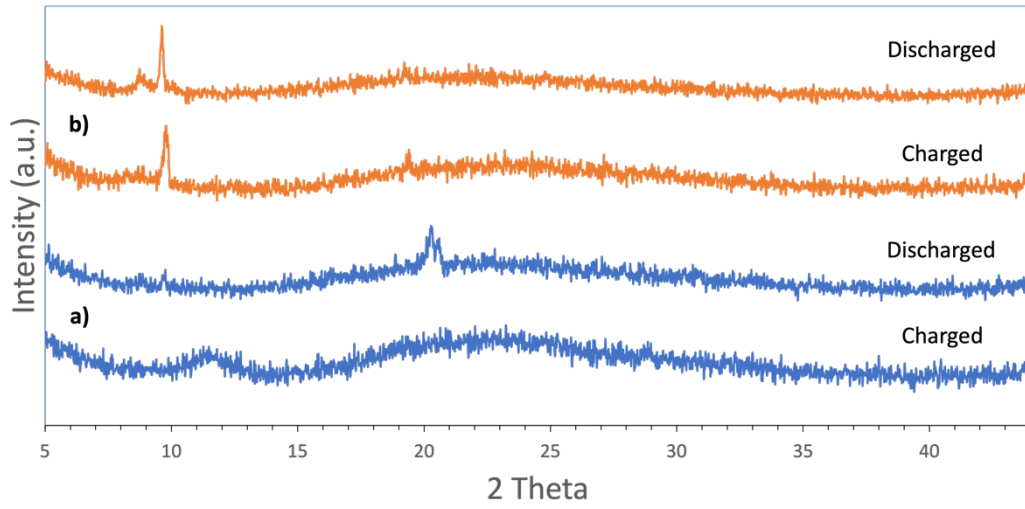


Figure 4.43 XRD pattern of Ni cathodes at charged/discharged state in electrolyte of **a)** 2M ZnSO<sub>4</sub>+0.1M MnSO<sub>4</sub> and **b)** 2M ZnSO<sub>4</sub>

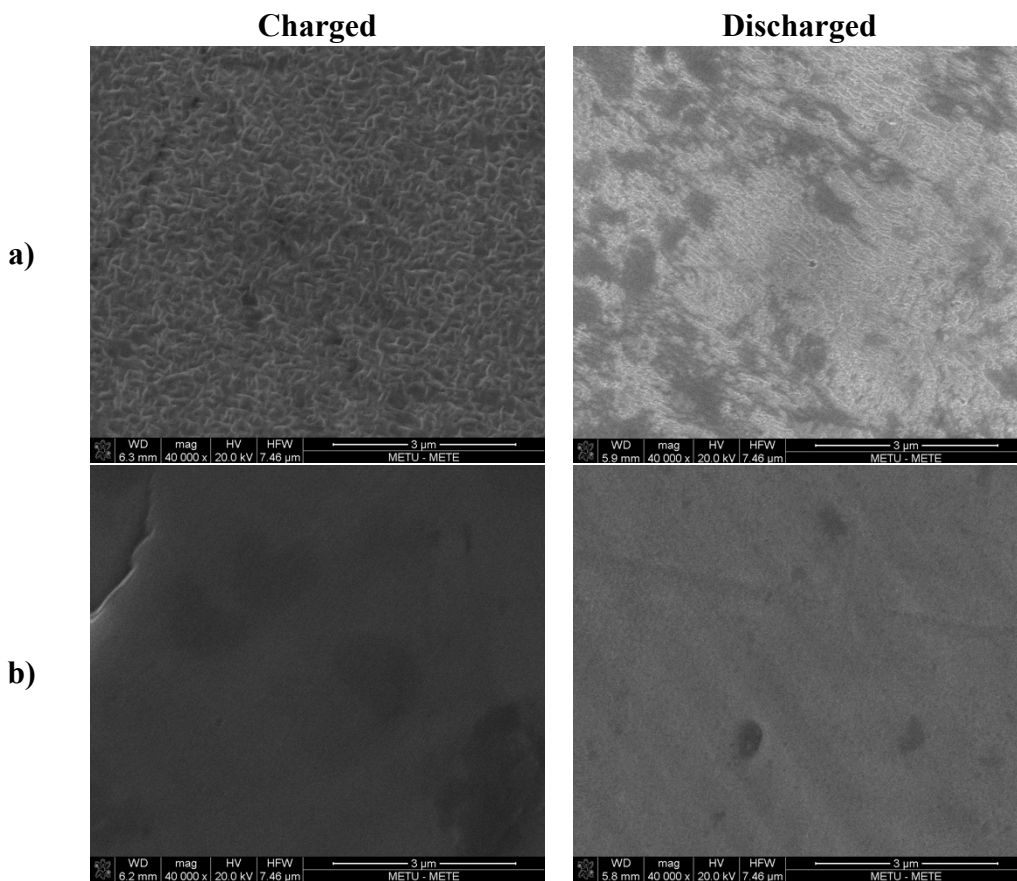


Figure 4.44 SEM image of Ni cathodes surface after 50 cycles in electrolyte of **a)** 2M ZnSO<sub>4</sub>+0.1M MnSO<sub>4</sub> and **b)** 2M ZnSO<sub>4</sub>

XRD pattern of these cathodes in charged and discharged states are given in Figure 4.43. The patterns appear to differ from each other in the case of 2M ZnSO<sub>4</sub>+0.1M MnSO<sub>4</sub> electrolyte from charged and discharge state, whereas with 2M ZnSO<sub>4</sub> electrolyte there is not much difference. SEM micrographs were also similar, Figure 4.44. Without MnSO<sub>4</sub> the “cathode” surface is featureless whereas with 2M ZnSO<sub>4</sub>+0.1M MnSO<sub>4</sub> there are quite distinct changes in the surface. In the charged state, there are platelet structure which is similar to those commonly observed in δ-MnO<sub>2</sub>. All these point out to the possibility that the active compound may deposit onto cathode reversibly which might be responsible for a fraction of the observed capacity.

#### 4.3.6 Conclusion

Thick film cathodes were successfully deposited in combinatorial geometry on (Bi, Na, Ni, Mn)O<sub>x</sub> quaternary compositional space. A total of 108 thick film cathode were tested in terms of CV, charge, and discharge profiles as well as in terms of capacity versus cycle number. A Mn rich space was mapped in terms of discharge voltage, redox potential difference, initial, maximum, average, and final capacities. The study has shown three compositions where the capacity was 400 mAh/g or above. These were Bi<sub>0.04</sub>Na<sub>0.55</sub>Ni<sub>0.04</sub>Mn<sub>0.36</sub>O<sub>x</sub>, Bi<sub>0.04</sub>Na<sub>0.37</sub>Ni<sub>0.06</sub>Mn<sub>0.53</sub>O<sub>x</sub>, and Bi<sub>0.02</sub>Na<sub>0.63</sub>Ni<sub>0.02</sub>Mn<sub>0.33</sub>O<sub>x</sub>.



## CHAPTER 5

### GENERAL CONCLUSION

This thesis focuses on finding a new MnO<sub>2</sub>-based cathode composition(s) for Zn-ion batteries. For this purpose combinatorial approach was employed using thick film cathodes deposited via magnetron sputtering. The system under study was MnO<sub>2</sub> alloyed with NaMnO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, NiO. Accordingly, four sputter targets were prepared; MnO<sub>2</sub> target was in 3-inch diameter placed in the center and the other oxides were 2-inch in diameter placed 120° to one another forming a triangle. Substrates were 12.7 mm in diameter placed in a substrate magazine with a triangular geometry mimicking the targets underneath. A total of 36 cathode were deposited in a single sputtering experiment each with a different composition.

A total of six experiments were carried yielding 216 cathodes. Cathodes were deposited on Ni foil used as a current collector. They were typically 3 μm thick with a mass varying from 0.23 to 2.38 mg. Cells used was of Swagelok type, anode was 300 μm thick Zn foil electrolyte was 2M ZnSO<sub>4</sub> + 0.1 M MnSO<sub>4</sub> aqueous solution.

The preliminary results indicated favorable results in Mn rich cathodes. As a result, out of six sets three set of cathodes were selected for detailed study.

Cyclic voltammetry as well as galvanostatic tests were carried for each cathode. Mn rich corner of the Bi-Mn-Ni ternary diagram where Na varied from 11 to 78% were mapped in terms of capacities, cyclic stability, and discharge plateau potential. Based on maps, three candidate compositions were selected with discharge capacities above 400 mAh/g. These are Bi<sub>0.04</sub>Na<sub>0.55</sub>Ni<sub>0.04</sub>Mn<sub>0.36</sub>O<sub>x</sub>, Bi<sub>0.04</sub>Na<sub>0.37</sub>Ni<sub>0.06</sub>Mn<sub>0.53</sub>O<sub>x</sub> and Bi<sub>0.02</sub>Na<sub>0.63</sub>Ni<sub>0.02</sub>Mn<sub>0.33</sub>O<sub>x</sub>.

The findings reported above, and the compositions reported refer to a rather special case of cathodes which were in the form coating no more than 3  $\mu\text{m}$  thick which is fully adhered to the nickel current collector. Although with cycling the coatings may break-off in some cases, this geometry is rather special making full use of the cathode material. This is unlike the case in cathodes prepared with slurry method where it is well known that  $\text{MnO}_2$  has severe conductivity problems. Therefore, further work is needed to check the full potential of the selected cathodes with slurry method and establish what fraction of capacity obtained in this work is reproducible with slurry method. An optimization study would therefore be needed, with regard to the preparation of slurry in terms of the choice of conductivity agent and the binder. Another aspect is that the current cathodes being in the form of films has large specific surface area, this advantage will no longer be applicable with slurry method. Mass load of the cathodes can be optimized, and cathode performance can be compared in terms of areal current density.



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## APPENDICES

### A. Fabrication And Testing of Slurry Based Zn-MnO<sub>2</sub> Battery

#### A.1 Introduction

A study conducted on (Bi,Na,Ni)MnO<sub>2</sub> system using thick film approach has yielded two compositions with high discharge capacity; Bi<sub>0.04</sub>Na<sub>0.37</sub>Ni<sub>0.06</sub>Mn<sub>0.53</sub>O<sub>x</sub>, and Bi<sub>0.02</sub>Na<sub>0.63</sub>Ni<sub>0.02</sub>Mn<sub>0.33</sub>O<sub>x</sub>. Following the selection of these candidate compositions, attempts were made to manufacture conventional battery using the slurry method. The cell is that of Swagelok, but instead of using thick film cathode deposited on Ni foil, here, the cathode was prepared using conventional slurry method on nickel foam.

#### A.2 Experimental Procedure

Structural characterization was carried using Rigaku DMAX2200 or Bruker D8 Advance X-ray diffractometer using with Cu-K $\alpha$  radiation ( $\lambda=1.5406\text{\AA}$ ) at 30 kV at 40 mA current. The scanning rate was 1 $^\circ$ /min with step size of 0.02 $^\circ$ . Material characterization also included scanning electron microscopy. For this purpose, FEI Nova NanoSEM was used. Where necessary the samples were investigated with EDS analysis.

Active material for cathode was prepared by two methods; mixing and milling the oxide ingredients of the selected proportions or via calcination of the mixture prepared from ingredients of selected proportions at elevated temperature. Having prepared the active materials, the cathode slurry was prepared by mixing the active ingredients with carbon black and binder of selected proportions in DI water-ethanol (60:40) solution using. First, the binder (Teflon or CMC) was dissolved in the solution for 15 min and then carbon black was added and mixed for 30 min. Finally, active material was added and mixed for 60 minutes. All mixings were carried out using magnetic stirrer. Ni foam was used as the current collector. The slurry was coated onto Ni foams by dipping it into the solution. Then nickel foam was dried

overnight in an oven at 60°C. Before and after coating, the foam was weighed (Sartorius CPA225D -0.01 mg sensitivity) from which the quantity of the cathode was determined. Ni foam loaded with cathode material was then pressed under 20 MPa to increase the compaction of the whole assembly.

Cells used for electrochemical characterization was of Swagelok type. Conventionally prepared MnO<sub>2</sub> based cathodes were loaded on Ni foams of 12.7 mm in diameter. Anode was Zn foil 300 μm thick (99.8% pure). Separator was Freudenberg FS 2226. Electrolyte was 2M ZnSO<sub>4</sub>+0.1M MnSO<sub>4</sub> in DI water. Current collectors in the Swagelok cell were 12.9 mm diameter stainless steel rods. The Cell had a spring between the anode and the stainless-steel current collector which presses the cell assembly against the current collector on the cathode side. Spring was made of 1 mm stainless steel wire wound to a diameter of 12.4 mm with the length of 10.5 mm.

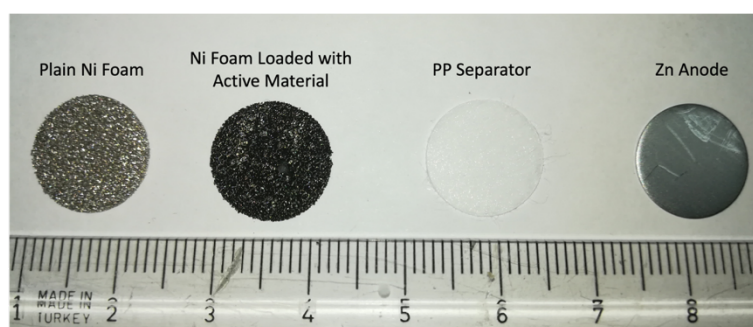


Figure A. 1 The components of the battery

Components of the cell are shown in Figure A. 1. Cells were assembled first by inserting the current collector and fixing the position of it using the conical insert. Then the cathode was placed against the current collector. This was followed by placing the separator on the cathode. Then 0.5 ml electrolyte were applied by drops which was absorbed by separator. Finally, Zn anode were placed over the separator. Then the cell was closed by placing a short stainless-steel rod followed by the spring and the current collector which was lightly pressed and fixed in position by a conical insert.

Electrochemical measurements were made with BioLogic MPG2 multichannel battery testing system.

### **A.3 Results and discussion**

#### **A.3.1 Separator (Polypropylene)**

First, we investigated the separator. For this purpose, active material used was  $\beta$ -MnO<sub>2</sub> in powder form (Alfa Aesar, 98% pure). It was ball milled (Retsch PM 400 Ma-Type) at 400 rpm for 10 hours. XRD pattern of the milled powder is given in Figure A. 2. After ball milling, the powder had a mixture of phases, namely  $\beta$ -MnO<sub>2</sub> and Mn<sub>2</sub>O<sub>3</sub>. Active material, binder (Teflon) and conductive agent (carbon black) in mass proportions of 75:5:20 were mixed in DI water-ethanol as explained above.

Three cells were prepared where the number of separators used was changed. The capacity versus cycle number determined for the cell prepared with single separator is shown in blue in Figure A. 2 (a). The maximum capacity is around 80 mAh/g, but more importantly, the capacity drops to zero unexpectedly at 18<sup>th</sup> cycle. Upon examining the cell, it was observed that there was a short circuit between the anode and cathode as a result of dendritic growth of zinc which perforated the separator. So as to prevent the short circuit, multiple separators were used. The performance of the cell with 3 separator was included in Figure A. 3 (yellow). The cycle life was slightly longer and reached 24 cycles before it has failed.

Figure A. 3 also comprise data with cell incorporating 5 separators. The cell continued to function well even after 100 cycles. Fig 5.4 shows photograph of both the electrodes and the separators in sequence. It is seen that the first separator in contact with zinc was blackened quite markedly probably containing fragments of zinc dendrites. The second, third and fourth separators are affected less and less. Based on these observations it was concluded for cycle numbers of near 100 or so, a total of 5 separators yielding a total thickness of 900 micron would be necessary so as to prevent shorting of the electrodes.

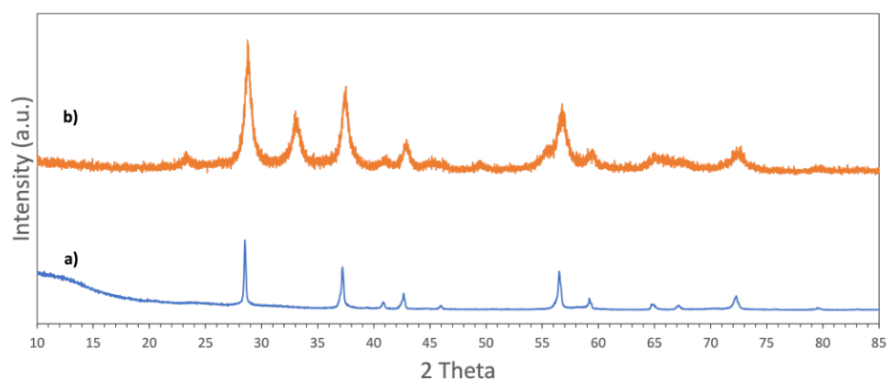


Figure A. 2 XRD pattern of **a)**  $\beta$ -MnO<sub>2</sub> and **b)** ball milled MnO<sub>2</sub>

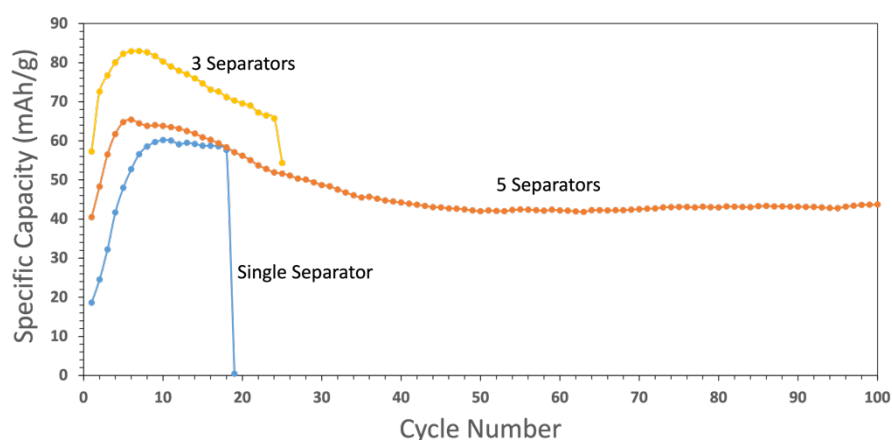


Figure A. 3 Cycling performance of ball milled MnO<sub>2</sub> with 20% carbon black. Note that increasing the number of the separator, increases the cycle life

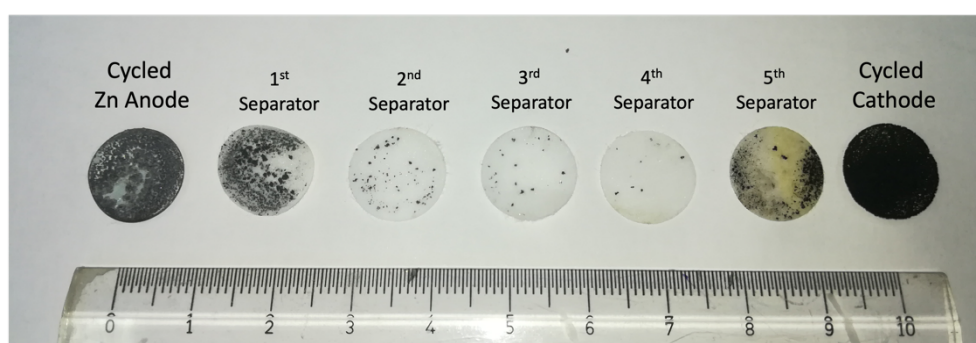


Figure A. 4 Disassembled battery with five separators

### A.3.2 Conductive Agent (Carbon Black)

Four experiments were conducted to see the effect of conductive agent (carbon black) addition. For this purpose, slurries were prepared mixing active material (ball milled MnO<sub>2</sub> or as-synthesized Na<sub>0.7</sub>MnO<sub>2</sub>, binder (Teflon) and carbon black in mass

proportions of 85:5:10 and 75:5:20. For ball milled  $\text{MnO}_2$ , the capacity versus cycle number for both carbon black additions are shown in Figure A. 5. It is seen that 10% carbon black addition for which two experiments were carried out yielded better performance. The initial capacity with 10% CB was higher in excess of 60 mAh/g. The capacity after 100 cycle was around 50 mAh/g which was slightly better than that with 20% CB.

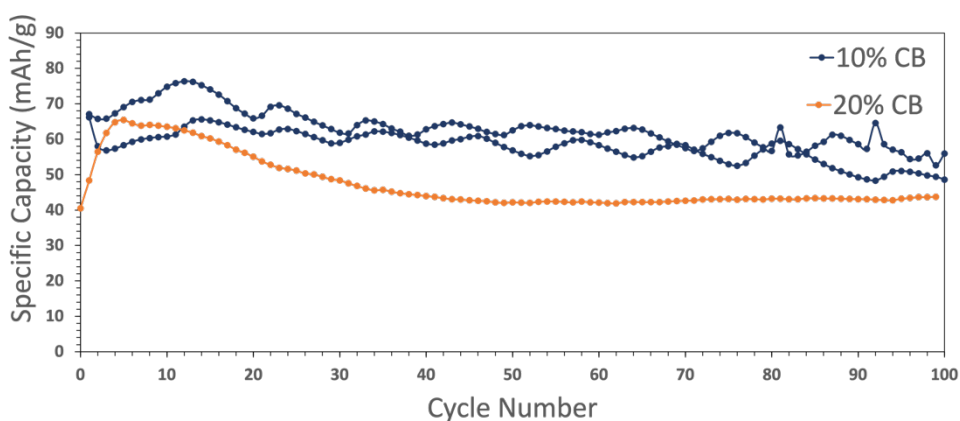


Figure A. 5 Cycling performance of ball milled  $\text{MnO}_2$  with 10% and 20% carbon black

For as-synthesized  $\text{Na}_{0.7}\text{MnO}_2$ , the capacity versus cycle number was plotted in Figure A. 6. As seen in the figure, the initial capacity with 10% CB was low but increased with cycling reaching a capacity of around 60 mAh/g. The capacity after 100 cycles were similar in both samples.

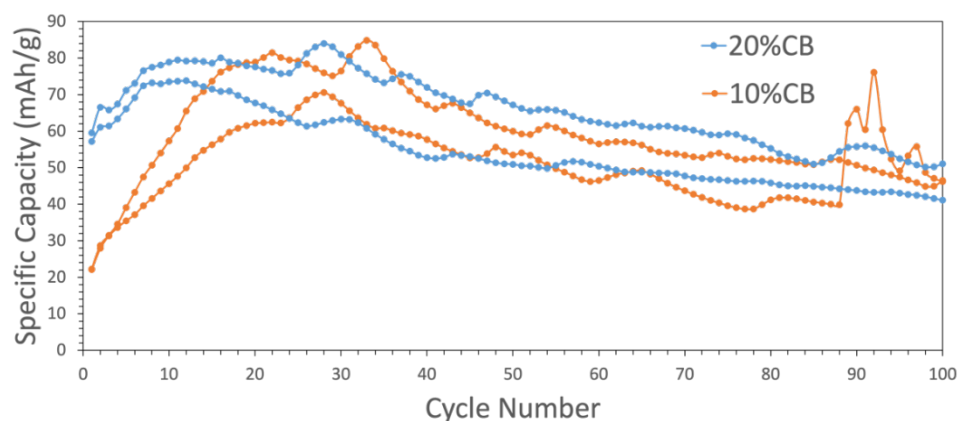


Figure A. 6 Cycling performance of as-synthesized  $\text{Na}_{0.7}\text{MnO}_2$  with 10% and 20% carbon black

In conclusion, there was no significant difference between 10% and 20% carbon black additions and both additions may be preferred, though 10% CB has its advantage as it would maximize the active ingredient of the cathode.

### A.3.3 Particle Size Reduction (Ball Milling)

Experiment reported above with  $\text{Na}_{0.7}\text{MnO}_2$  was carried out by hand grinding of as-synthesized powder in mortar. So as to see the effect of ball milling, a separate experiment was also carried out where the as-synthesized powder was milled at 180 rpm for 6 hours.

For electrochemical measurements, slurry was prepared mixing the ball milled powder, Teflon (binder) and carbon black (conductive agent) in mass proportions of 75:5:20. Capacities versus cycle number are plotted in Figure A. 7. It is seen that the electrode with ball milled powder is already active yielding significantly higher capacity at around 140 mAh/g. However, the capacity decays quite rapidly with cycling and after 10 cycles or so there is very little difference between ground and milled samples.

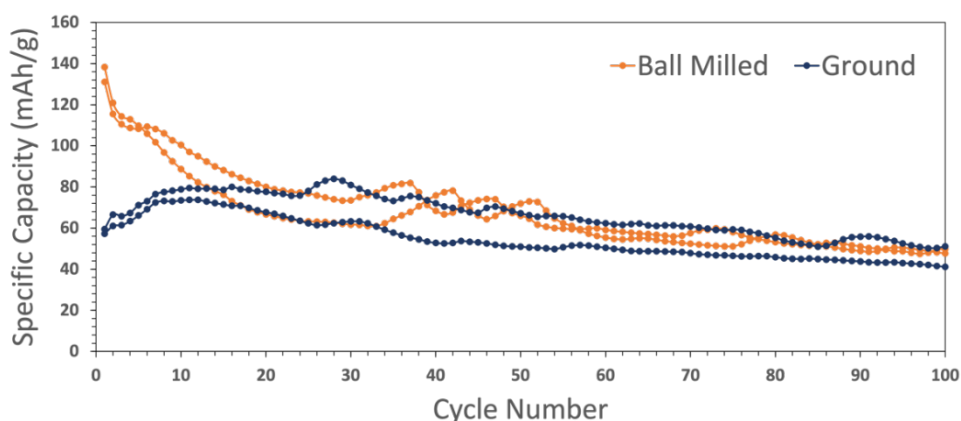


Figure A. 7 Cycling performance of ball milled  $\text{Na}_{0.7}\text{MnO}_2$  and non-ball milled  $\text{Na}_{0.7}\text{MnO}_2$

### A.3.4 Binder ( $\text{Na}_{0.7}\text{MnO}_2$ )

Several binders were used to evaluate their effect on the cell performance. The active material was ball milled  $\text{Na}_{0.7}\text{MnO}_2$ , the conductive agent was carbon black. The



binder used were Teflon, PVDF, PVA, PVB and CMC. An electrode without binder was also included in the study, Table A. 1. Capacities versus cycle number are given in Figure A. 8.

Table A. 1 List of slurry compositions with different type of binders

Active Material (A)	Binder (B)	Conductive Agent (C)	Weight Ratio A:B:C
Na <sub>0.7</sub> MnO <sub>2</sub> (Ball milled)	Teflon	Carbon Black	75:5:20
	PVDF	Carbon Black	70:10:20
	PVA	Carbon Black	70:10:20
	PVB	Carbon Black	70:10:20
	CMC	Carbon Black	70:10:20
	-	Carbon Black	80:0:20

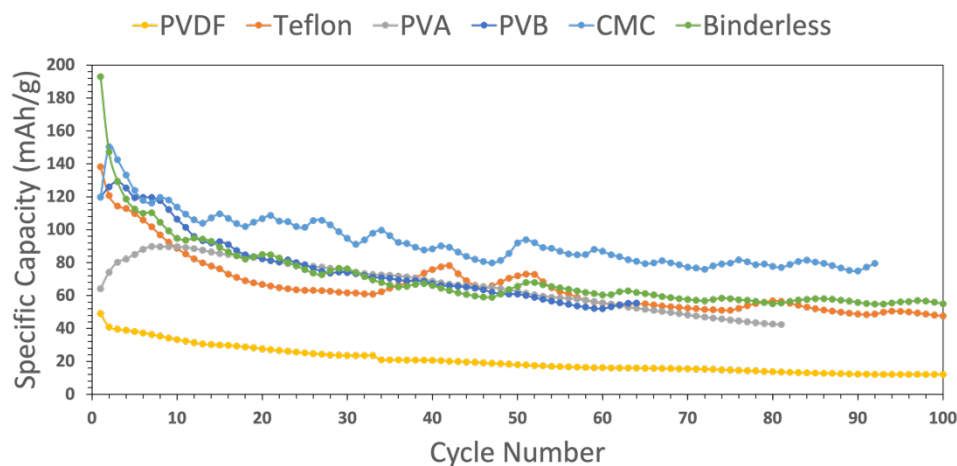


Figure A. 8 Cycling performance of Na<sub>0.7</sub>MnO<sub>2</sub> with different binders and without a binder. Note that batteries tested with using 5 separators

As seen in Figure A. 8, the cathode without binder delivered highest initial capacity. All binders display similar performances except for PVDF with which the capacity is quite low. CMC as binder yield better performance where the capacity is around 80 mAh/g.

### A.3.4 Cells with (Bi,Na,Ni,Mn)O<sub>x</sub> Cathodes

Cathodes were prepared with conventional slurry making. The locations of the cathode compositions in ternary Bi-Mn-Ni oxides diagram are shown in Figure A. 9 and tabulated in Table A. 2.

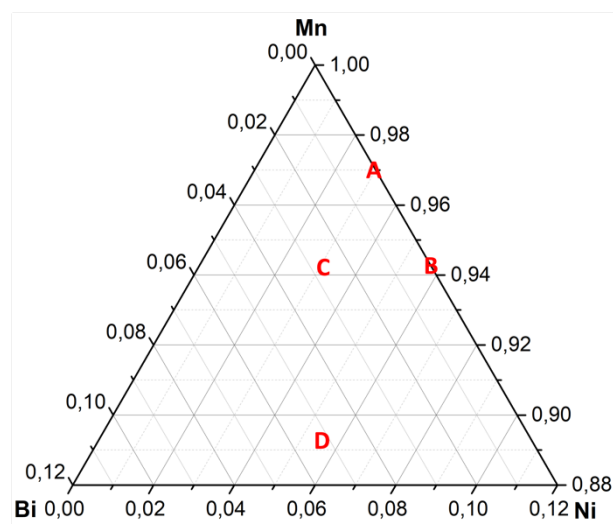


Figure A. 9 Synthesized compositions on Bi-Mn-Ni ternary diagram

Table A. 2 Cathodes prepared with slurry method

Code	Active Material (A)	Binder (B)	Conductive Agent (C)	Weight Ratio A:B:C
A	Na <sub>0.49</sub> Ni <sub>0.03</sub> Mn <sub>0.49</sub> O <sub>x</sub> (Calcined&ground)	Teflon:CMC	Carbon Black	84:5:1:10
B	Na <sub>0.49</sub> Ni <sub>0.01</sub> Mn <sub>0.49</sub> O <sub>x</sub> (Calcined&ground)	Teflon:CMC	Carbon Black	84:5:1:10
C	Bi <sub>0.01</sub> Na <sub>0.49</sub> Ni <sub>0.01</sub> Mn <sub>0.49</sub> O <sub>x</sub> (Calcined&ground)	Teflon:CMC	Carbon Black	84:5:1:10
D	Bi <sub>0.03</sub> Na <sub>0.47</sub> Ni <sub>0.03</sub> Mn <sub>0.47</sub> O <sub>x</sub> (Calcined&ground)	Teflon:CMC	Carbon Black	84:5:1:10
D	Bi <sub>0.05</sub> Na <sub>0.08</sub> Ni <sub>0.05</sub> Mn <sub>0.82</sub> O <sub>x</sub> (Calcined&ground)	Teflon:CMC	Carbon Black	84:5:1:10
D	Bi <sub>0.05</sub> Na <sub>0.08</sub> Ni <sub>0.05</sub> Mn <sub>0.82</sub> O <sub>x</sub> (Ball milled)	Teflon:CMC	Carbon Black	84:5:1:10
D	Bi <sub>0.04</sub> Na <sub>0.25</sub> Ni <sub>0.04</sub> Mn <sub>0.67</sub> O <sub>x</sub> (Ball milled)	Teflon:CMC	Carbon Black	84:5:1:10

The cathodes were in two groups. One group comprising two cathodes were without bismuth, i.e.,  $\text{Na}_{0.49}\text{Ni}_{0.03}\text{Mn}_{0.49}\text{O}_x$  and  $\text{Na}_{0.49}\text{Ni}_{0.01}\text{Mn}_{0.49}\text{O}_x$ . These were prepared using stoichiometric proportions of  $\text{Na}_2\text{CO}_3$ ,  $\text{MnO}_2$ , and  $\text{NiO}$  which were mixed and calcined at  $850^\circ\text{C}$  for 15 hours. XRD pattern of the samples without Bi are shown in Figure A. 10. Here the cathode is crystalline containing more than one phase.

Slurries were prepared in the ratio of 84:10:1:5 active material, carbon black, CMC and Teflon. Capacities versus cycle number are given in Figure A. 11. It is seen that the capacity which was above 100 mAh/g decreases rapidly down to 50 mAh/g with cycling. The voltage profiles of the cells are given in Figure A. 12.

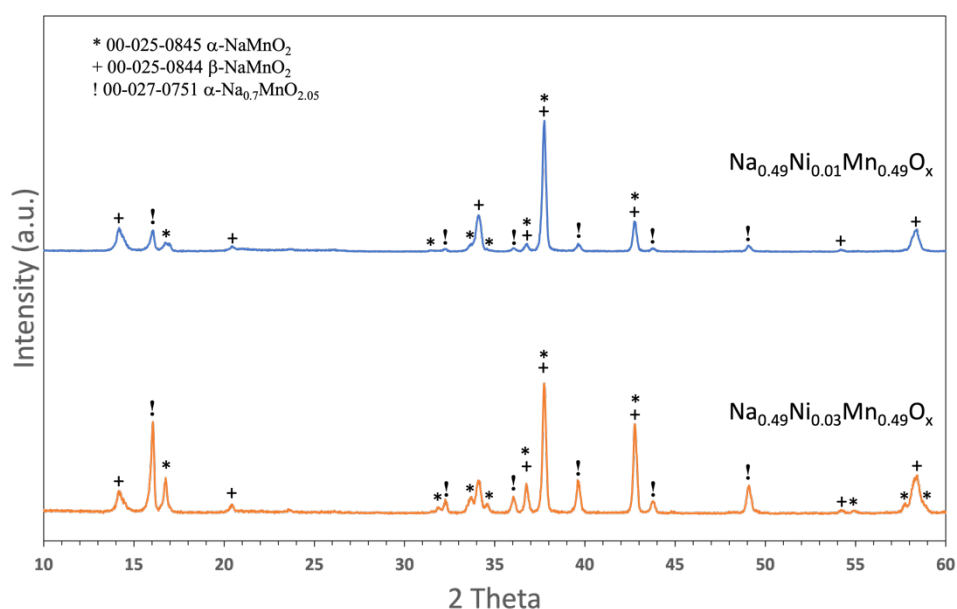


Figure A. 10 XRD patterns of solid state synthesized  $(\text{Na},\text{Ni},\text{Mn})\text{O}_x$  cathodes

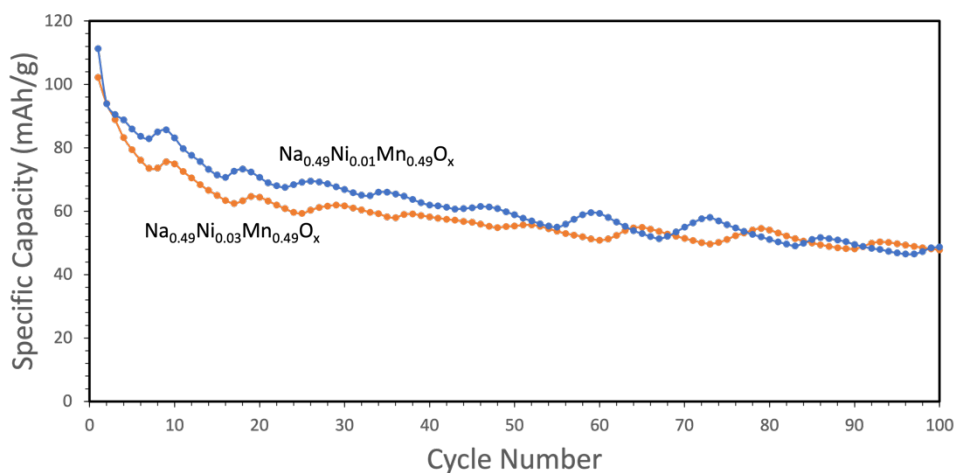


Figure A. 11 Capacity versus cycle number of cells with solid state synthesized (Na,Ni,Mn) $O_x$  cathodes

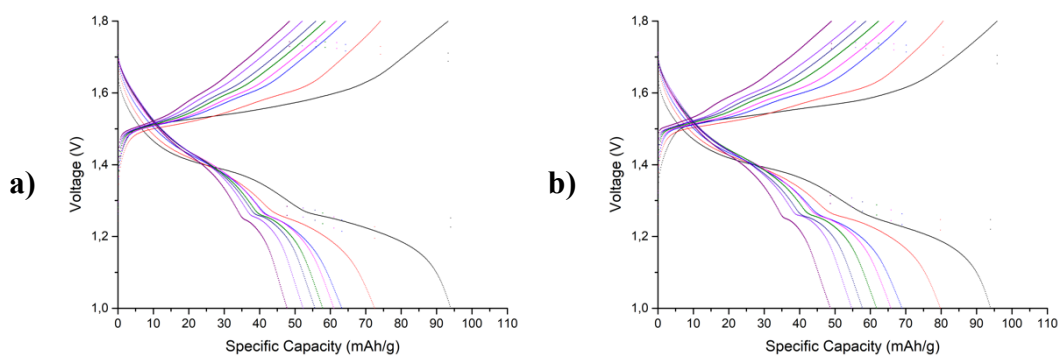


Figure A. 12 Voltage profiles of **a)**  $Na_{0.49}Ni_{0.03}Mn_{0.49}O_x$ , **b)**  $Na_{0.49}Ni_{0.01}Mn_{0.49}O_x$

The other group of samples which contained bismuth were prepared in similar way using  $Na_2CO_3$ ,  $MnO_2$ ,  $Bi_2O_3$  and  $NiO$ . XRD Pattern of the synthesized powders are given in Figure A. 13. The structure as before contained mixture of phases. In addition, there was unidentified phases due to Bi addition.

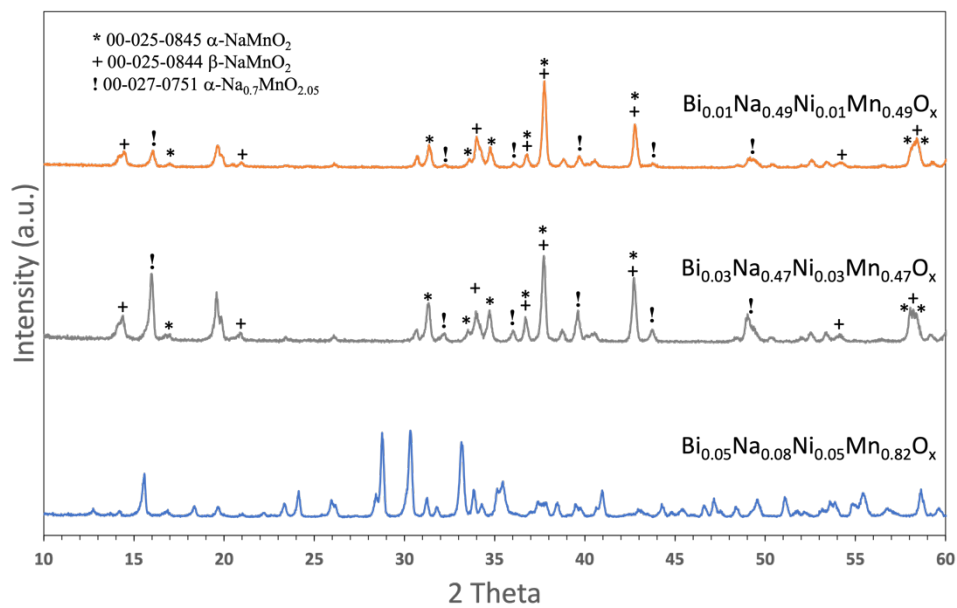


Figure A. 13 XRD patterns of solid state synthesized (Bi,Na,Ni,Mn)O<sub>x</sub> cathodes

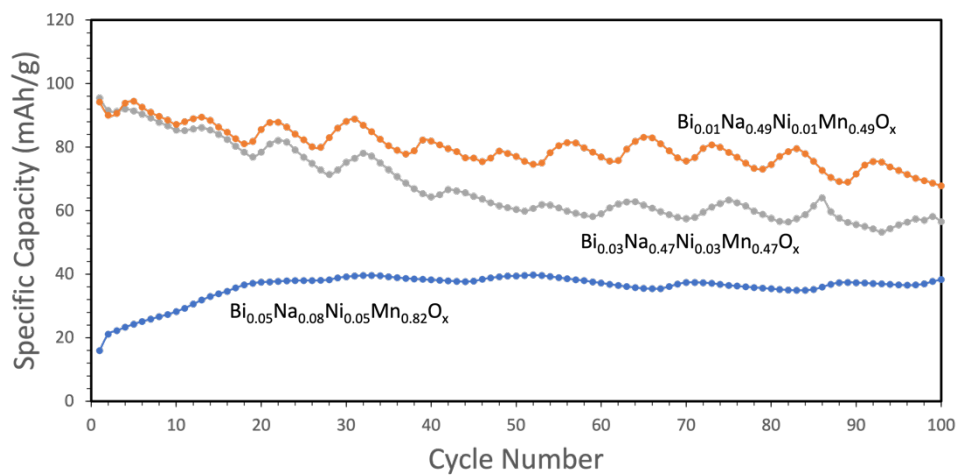


Figure A. 14 Capacity versus cycle number of cells with solid state synthesized (Bi,Na,Ni,Mn)O<sub>x</sub> cathodes

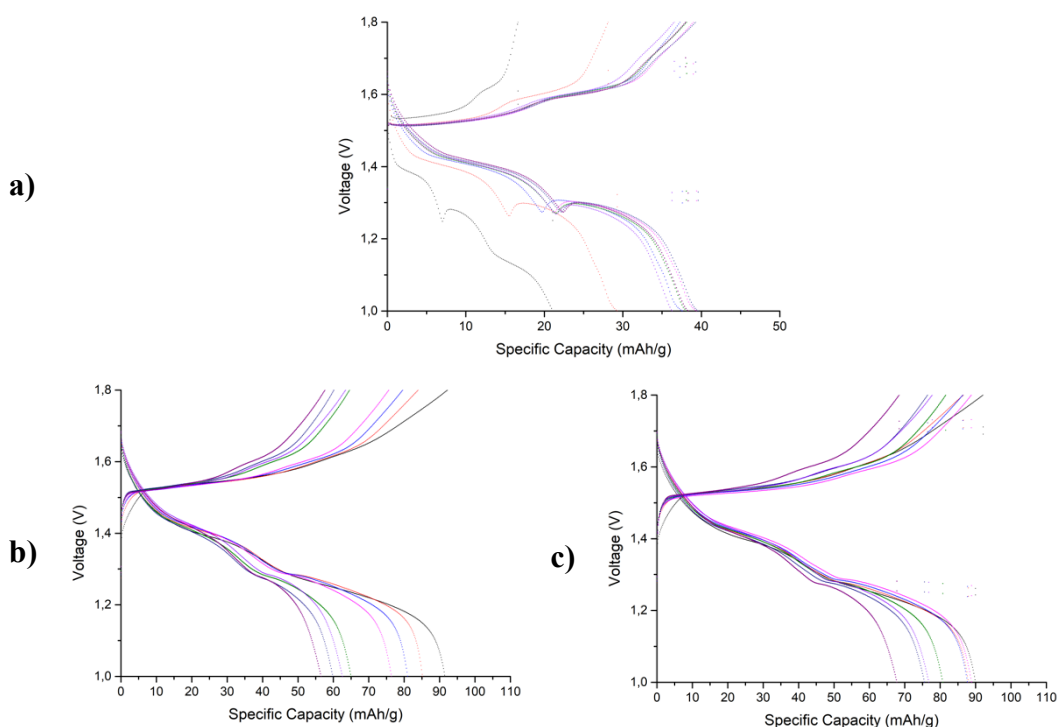


Figure A. 15 Voltage profiles of cells with Bi containing solid state synthesized (Bi, Na,Ni,Mn) $O_x$  cathodes; **a)**  $Bi_{0.05}Na_{0.08}Ni_{0.05}Mn_{0.82}O_x$ , **b)**  $Bi_{0.03}Na_{0.47}Ni_{0.03}Mn_{0.47}O_x$ , **c)**  $Bi_{0.01}Na_{0.49}Ni_{0.01}Mn_{0.49}O_x$

Capacity versus cycle number of Bi containing cathodes is given in Figure A. 14. It is seen that the capacity varies depending on the composition, but one property which are common to all composition the cells have better cyclic performance. The best cathode is  $Bi_{0.03}Na_{0.47}Ni_{0.03}Mn_{0.47}O_x$  which had an initial capacity close to 100 mAh/g. The capacity is quite high with a value close to 70 mAh/g even after 100 cycles. Voltage profile of the cells with Bi containing cathodes are given in Figure A. 15.

So as to prepare a nanocrystalline/amorphous cathode, a separate experiment was carried out using ball milling. As shown in Table A. 2. Two cathodes were prepared which had the compositions of  $Bi_{0.05}Na_{0.08}Ni_{0.05}Mn_{0.82}O_2$  and  $Bi_{0.04}Na_{0.25}Ni_{0.04}Mn_{0.67}O_2$ . These were prepared by mixing  $Bi_2O_3$ ,  $NiO$   $MnO_2$  and  $Na_{0.7}MnO_2$  in stoichiometric proportions and milled for 10 hours.

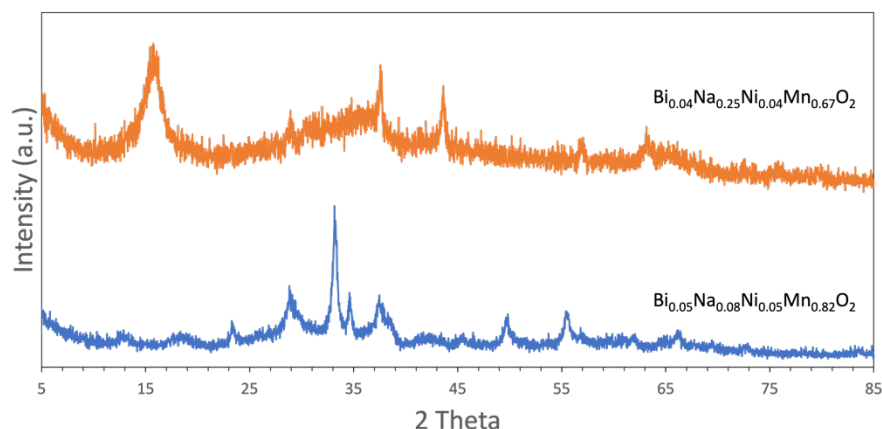


Figure A. 16 XRD pattern of (Bi,Na,Ni,Mn)O<sub>x</sub> cathode prepared by ball milling

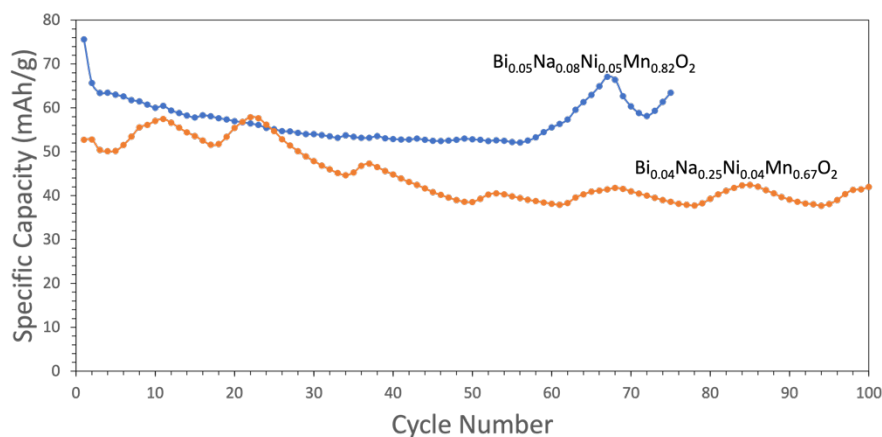


Figure A. 17 Capacity versus cycle number of (Bi,Na,Ni,Mn)O<sub>x</sub> cathodes synthesized via ball milling

XRD pattern of the resulting powder, Figure A. 16 were nanocrystalline with broad peaks. Slurries were prepared in ratio of 84:10: 1:5 for active material, carbon black, CMC and Teflon. Capacity versus cycle number of the cells with ball milled cathode are given in Figure A. 17. The capacity retention is quite good but overall level of capacity is not high enough.

#### A.4. Summary

A study was carried out on (Bi,Na,Ni,Mn)O<sub>x</sub> cathodes prepared with slurry method using zinc as anode and 2M ZnSO<sub>4</sub>+0.1 MnSO<sub>4</sub> as electrolyte. The current study has shown that the use of more than one separator, preferably 5, may be needed so as to prevent the short circuit caused by dendritic growth of zinc. As for the additives in

cathode, carbon black with 10 or 20 wt.% of the electrode gives similar performance. For binder, CMC added with 10 wt.% of the electrode yielded the best performance as compared to other alternatives PVDF, Teflon, PVA and PVB. Of the compositions studied in this work, best performance was obtained with  $\text{Bi}_{0.03}\text{Ni}_{0.03}\text{NaMnO}_x$  with discharge capacity over 70 mAh/g after 100 cycles.

Further work is needed to increase the discharge capacity of the cells using the slurry method.



## B. Preparation of Sputter Targets: Fe<sub>2</sub>O<sub>3</sub>, NaFeO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, CuO, CaO, Mn<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub>,

### B.1 Powder Synthesis and Target Making

#### Fe<sub>2</sub>O<sub>3</sub>

Fe<sub>2</sub>O<sub>3</sub> was synthesized from iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>, Merck 99%). For this purpose, iron nitrate powders were placed in a crucible and calcined at 725°C for 5 hours in air. In Figure B. 1., XRD pattern shows final powder has both Fe<sub>2</sub>O<sub>3</sub> (pdf card no. 01-077-9926, rhombohedral) and Fe<sub>3</sub>O<sub>4</sub> (pdf card no. 01-079-0416) phases. Therefore, temperature was increased to eliminate Fe<sub>3</sub>O<sub>4</sub> phase. Calcination at 750°C yielded a single phase of Fe<sub>2</sub>O<sub>3</sub>.

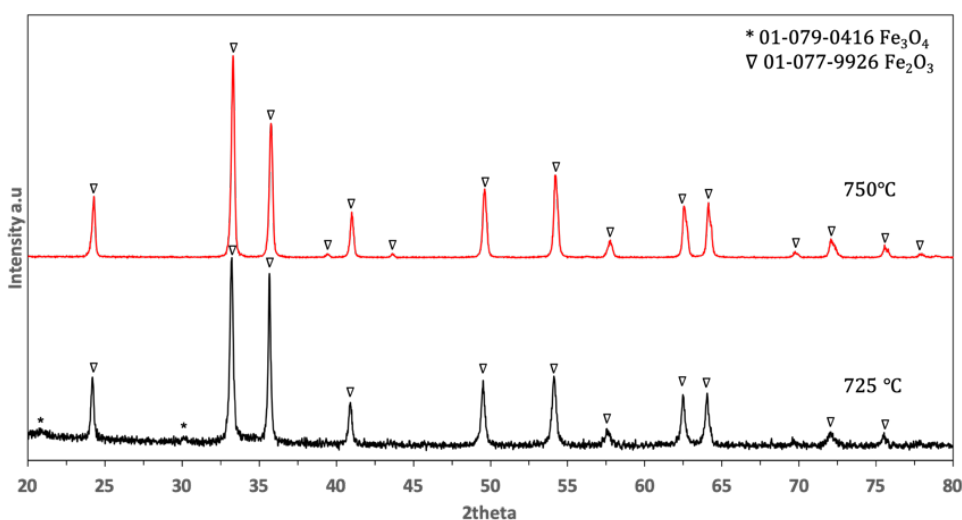


Figure B. 1 XRD pattern of Fe<sub>2</sub>O<sub>3</sub> at 725°C and 750°C

Figure B. 2 shows Rietvelt analysis and SEM image of the as-synthesized powder of Fe<sub>2</sub>O<sub>3</sub>. Analysis showed Fe<sub>2</sub>O<sub>3</sub> has cell parameters of a=5.034 Å, c=13.738 Å. SEM images showed that final powder has particle size of few micrometers.

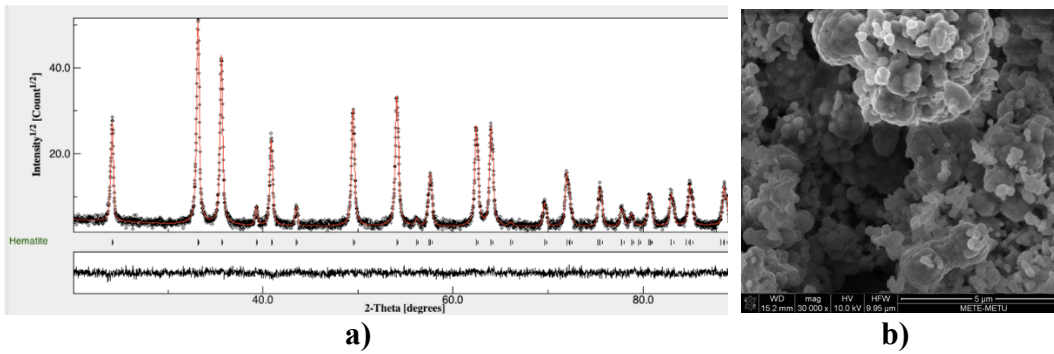


Figure B. 2 Synthesized  $\text{Fe}_2\text{O}_3$  powder at  $750^\circ\text{C}$  for 5 hours **a)** Rietvelt analysis of the powder **b)** SEM image.

As-synthesized  $\text{Fe}_2\text{O}_3$  powders were pressed in the 20 mm Teflon rings. Green bodies were sintered at  $1250^\circ\text{C}$  for 5 and 15 hours in air. In Figure B. 3 (a) and (b) show the SEM images of sintered samples. There were small pores through the sample, therefore another sintering was made at  $1350^\circ\text{C}$  for 15 hours in air, Figure B. 3 (c). At higher temperature, pores were smaller and as a result the target were prepared with these parameters.

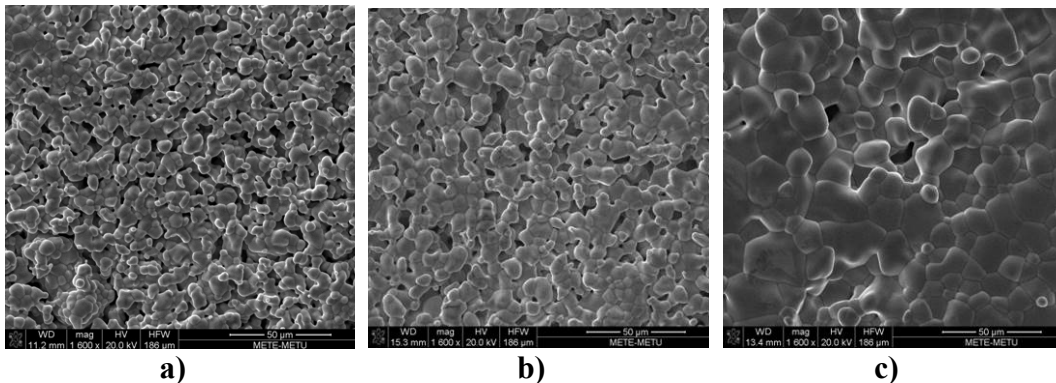
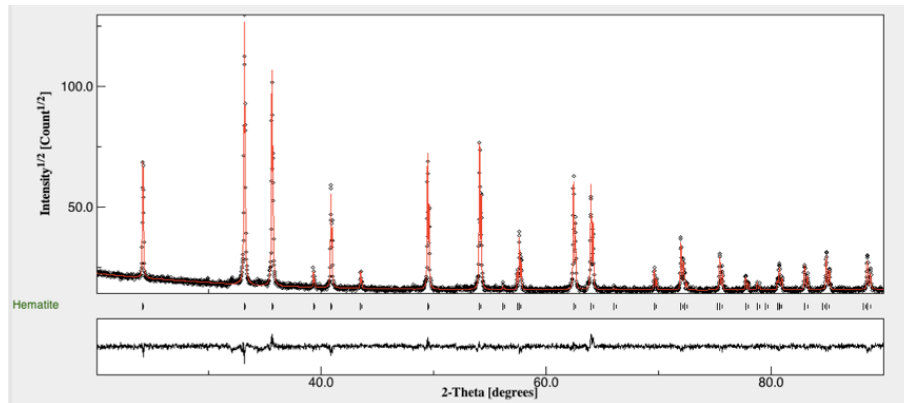
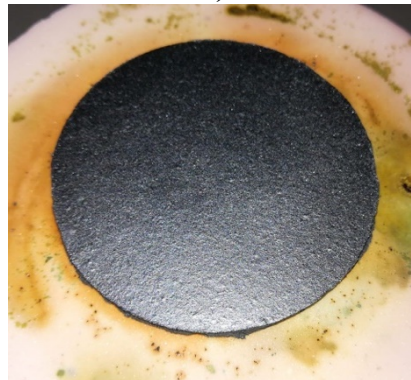


Figure B. 3 SEM images of pressed at 100 MPa and sintered  $\text{Fe}_2\text{O}_3$  (20 mm pellets) at **a)**  $1250^\circ\text{C}$  5 hours, **b)**  $1250^\circ\text{C}$  for 15 hours and **c)**  $1350^\circ\text{C}$  for 15 hours

Rietvelt refined XRD pattern of sintered sputter target is given in Figure B. 4. Rietveld refinement yielded cell parameters are  $a=5.034 \text{ \AA}$  ,  $c=13.738 \text{ \AA}$ . Photograph of the target is given in Figure 3.4.14



a)



b)

Figure B. 4 Sintered  $\text{Fe}_2\text{O}_3$  target a) Rietvelt refined XRD pattern and b) the target  $\text{NaFeO}_2$

$\text{NaFeO}_2$  was synthesized using stoichiometric mixture of 0.02 mol  $\text{Fe}_2\text{O}_3$  and 0.02 mol  $\text{Na}_2\text{CO}_3$ . In addition, two more experiments were conducted with 10% and 20% excess  $\text{Na}_2\text{CO}_3$  to compensate for Na losses. Raw materials were ball milled at 120 rpm for 6 hours. Ball milled powders were calcined at  $950^\circ\text{C}$  for 5 hours under air., XRD pattern of the final product is given in Figure B. 5. Their pattern is consistent with  $\text{NaFeO}_2$  (pdf card no. 01-074-1351, Orthorhombic). Only the sample with 20% excess  $\text{Na}_2\text{CO}_3$  has an additional peak at  $30^\circ$  (shown with a star). SEM images of the synthesized powder is given in Figure B. 6. It is seen that the structure is made up of powders with a particle size of  $5\mu\text{m}$ . EDS analysis from as-synthesis powders have Na:Fe ratio as 70:30, 60:40 and 57:43 for stoichiometric, 10% excess and 20% excess samples respectively This implies that there was more Na loss during

sintering process. Therefore, composition with 10% excess  $\text{Na}_2\text{CO}_3$  were selected for sintering of  $\text{NaFeO}_2$  powder.

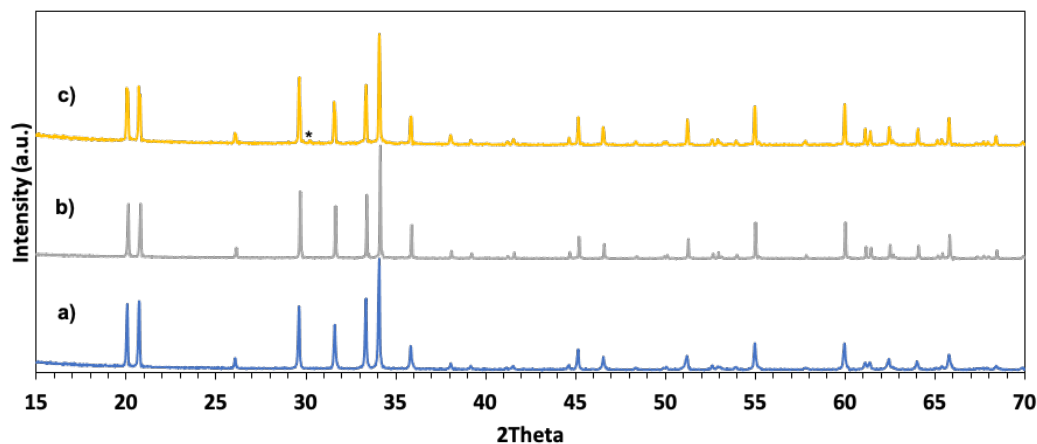


Figure B. 5 XRD pattern of synthesized powders **a)** stoichiometric, **b)** 10% excess, **c)** 20% excess

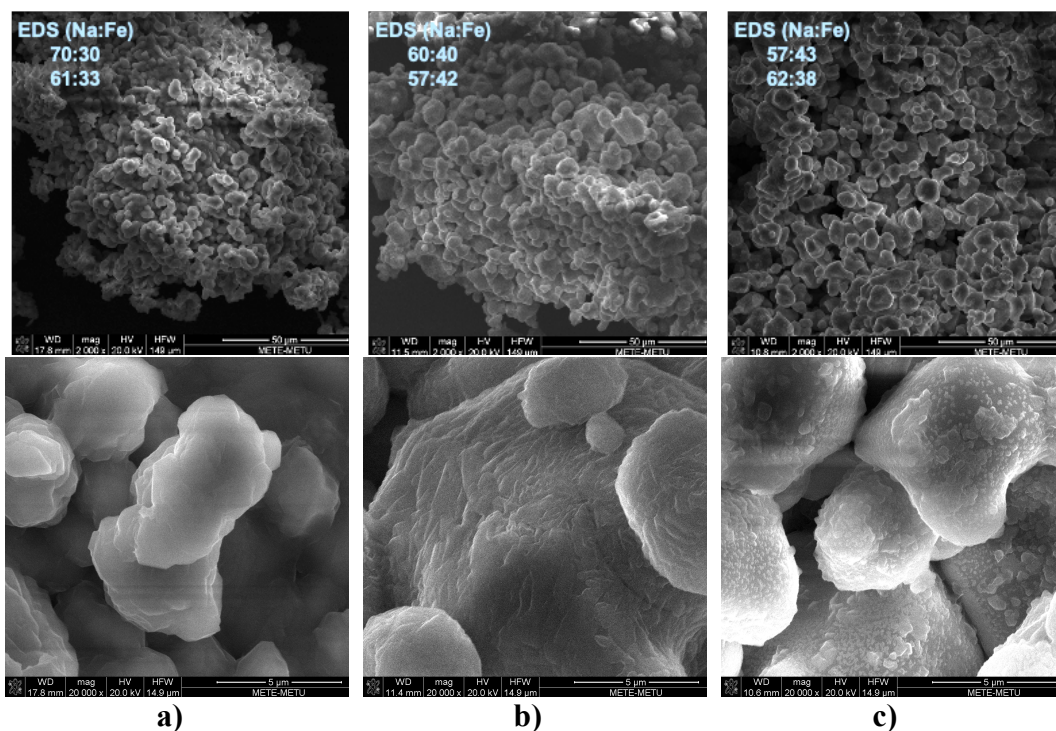


Figure B. 6 SEM images and EDS results of synthesized powders **a)** stoichiometric, **b)** 10% excess, **c)** 20% excess

So as to produce the sputter target, As-synthesized powders were mixed with DI water. Then, pressed under 100 MPa in a Teflon ring. Green bodies were first heated to 120°C with 1°/min. Then, waited at 120 for 1 hour to eliminate humidity. Finally,

sintered at 1350°C , XRD pattern of sintered NaFeO<sub>2</sub> for 5, 10, 15 hours were given in Figure B. 7. Na<sub>2</sub>FeO<sub>4</sub> was found as an impurity in the sample with 20% excess Na<sub>2</sub>CO<sub>3</sub>. Stoichiometric and 10% excess sample formed as orthorhombic NaFeO<sub>2</sub> phase., The microstructure of sintered NaFeO<sub>2</sub> was given in Figure B. 8. As Na content increased, the compaction was more efficient. Cell parameters as derived from Rietvelt refined XRD pattern are given Table B. 1.

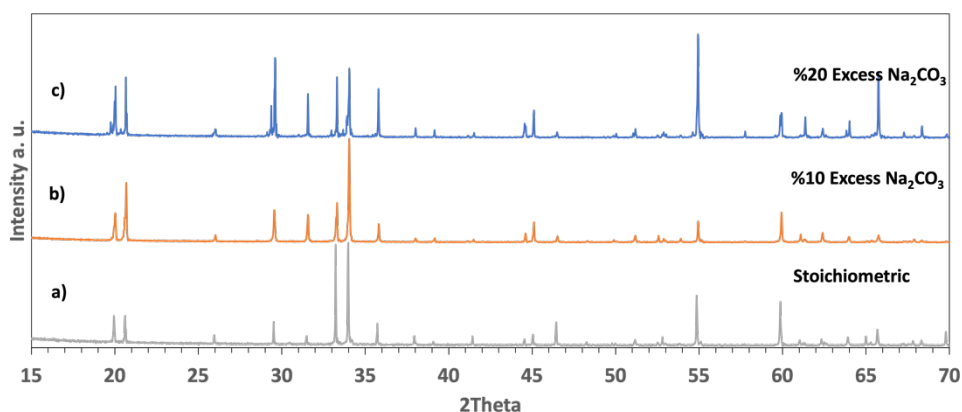


Figure B. 7 XRD pattern of sintered NaFeO<sub>2</sub> pellets at 1350°C for 5 hours

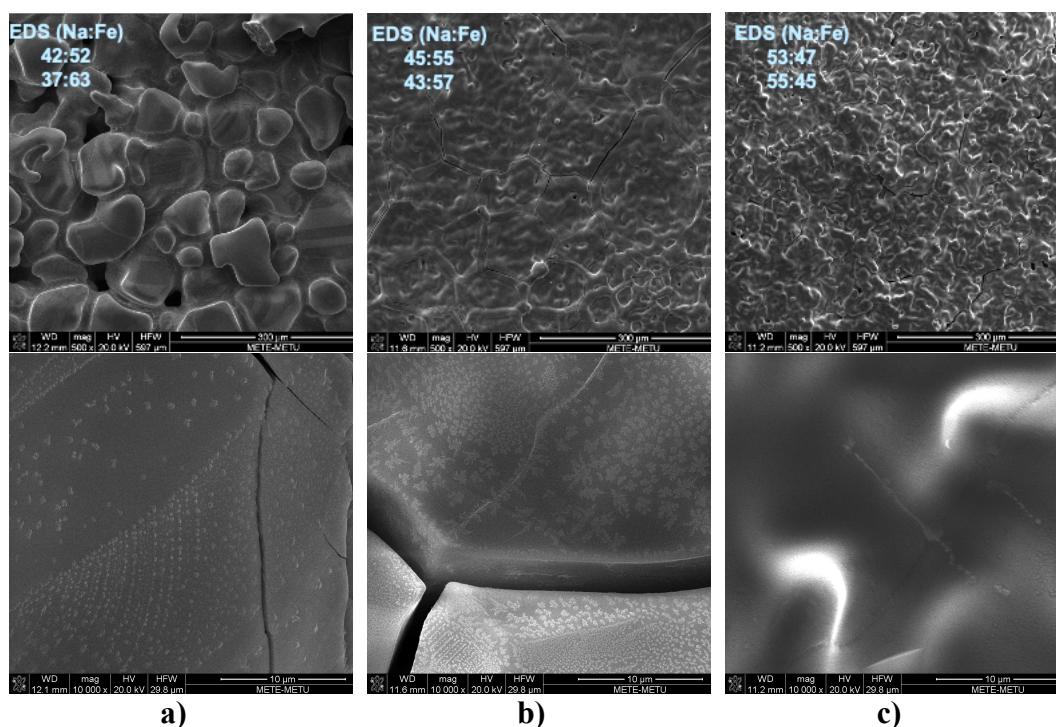


Figure B. 8 SEM images of sintered NaFeO<sub>2</sub> at 1350 for 5 hours **a)** stoichiometric, **b)** 10% excess, **c)** 20% excess

Table B. 1 Lattice parameters of NaFeO<sub>2</sub> with different Na content from Rietvelt refinement

Composition	a (Å)	b (Å)	c (Å)	Crystal Size (nm)	Rwp (%)
Stoichiometric	5.67	7.14	5.38	2576 ±29	11.24
10% Excess	5.68	7.15	5.39	2708 ±65	14.47
20% Excess	5.63	7.08	5.34	6945±66	28.11

Synthesized powders are not stable in air. Powders decomposed to NaO<sub>2</sub> (pdf card no. 00-006-0500) and Fe<sub>2</sub>O<sub>3</sub> phases. Therefore, powders and the target were stored in Ar filled glovebox to prevent from air and humidity.

### Cr<sub>2</sub>O<sub>3</sub>

Chromium (II) nitrate nonahydrate (Cr(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, Merck 98%) were used to synthesize pure Cr<sub>2</sub>O<sub>3</sub>. Chromium nitrate powders were calcined at 700°C for 4 hours in air. XRD pattern of synthesized powder is shown in Figure B. 9. It matches a single phase of Cr<sub>2</sub>O<sub>3</sub> (pdf card no. 00-038-1479).

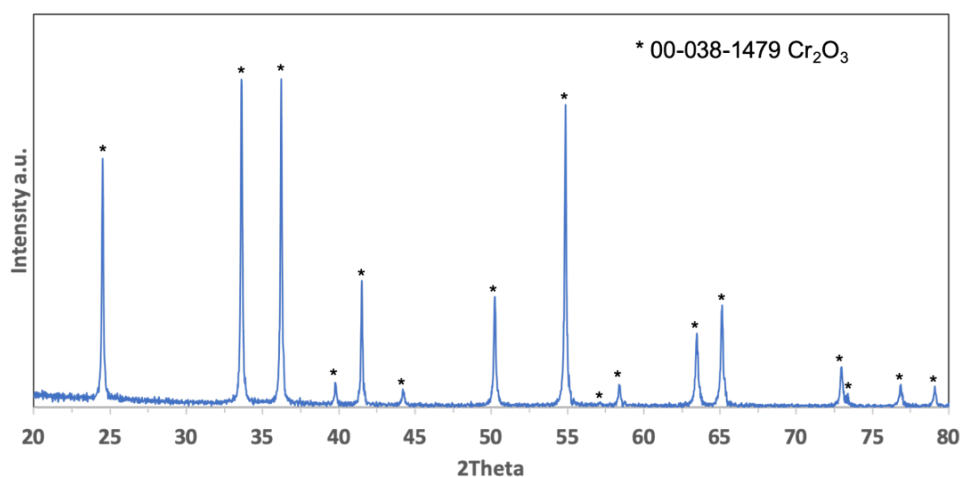
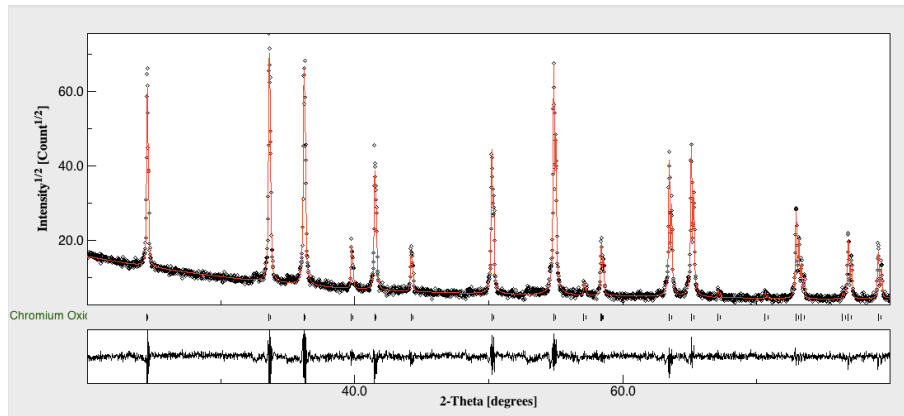
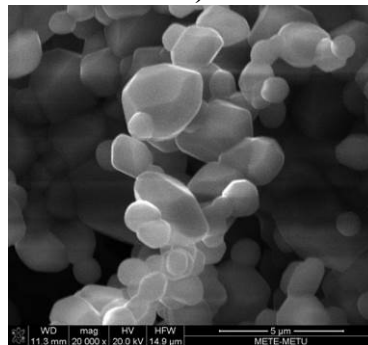


Figure B. 9 XRD pattern of Cr<sub>2</sub>O<sub>3</sub> calcined at 700°C for 4 hours.

Rietvelt refined pattern is given in Figure B. 10 (a) which yields cell parameters of a=4.968 Å, c=13.619 Å. SEM image of the as-synthesized powder is given. In Figure B. 10 (b) where particles are few micrometers in size.



**a)**



**b)**

Figure B. 10 Cr<sub>2</sub>O<sub>3</sub> powder synthesized at 700°C for 4 hours **a)** Rietveld refined XRD pattern and **b)** SEM image of the synthesized the powder

So as to fabricate sputter target, as-synthesized Cr<sub>2</sub>O<sub>3</sub> powders were mixed with few drops of DI water and pressed under 100 MPa in 20 mm Teflon ring. First, pellets were sintered at 1350°C for 5, 10 and 15 hours in air. The resulting microstructure had a bunch of large pores and thus sample was not dense enough. Therefore, new sintering process was carried out at 1450°C and 1550°C for 15 hours, see Figure B. 11. 1550°C was barely enough to yield a sputter target with acceptable properties. Rietveld refined XRD pattern, Figure B. 12, yielded  $a=4.968\text{\AA}$ ,  $c=13.619\text{\AA}$ .

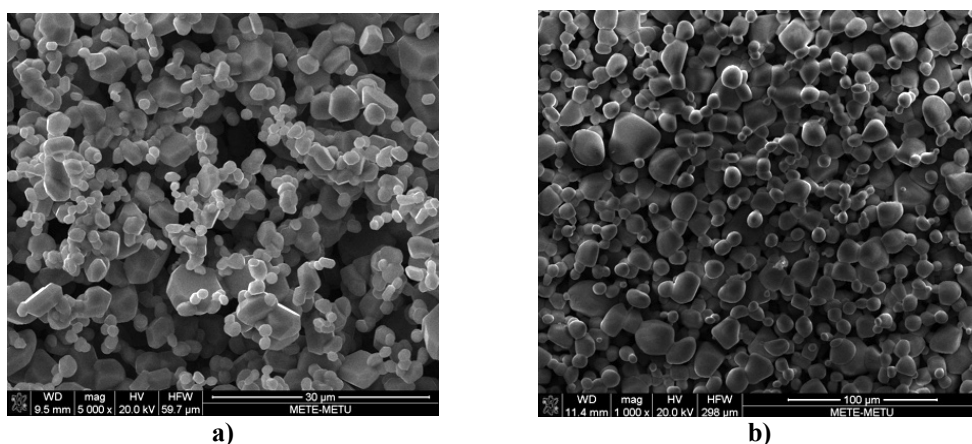


Figure B. 11 SEM image of sintered  $\text{Cr}_2\text{O}_3$  in air **a)** 1450 °C for 15 hours, **b)** 1550 °C for 15 hours

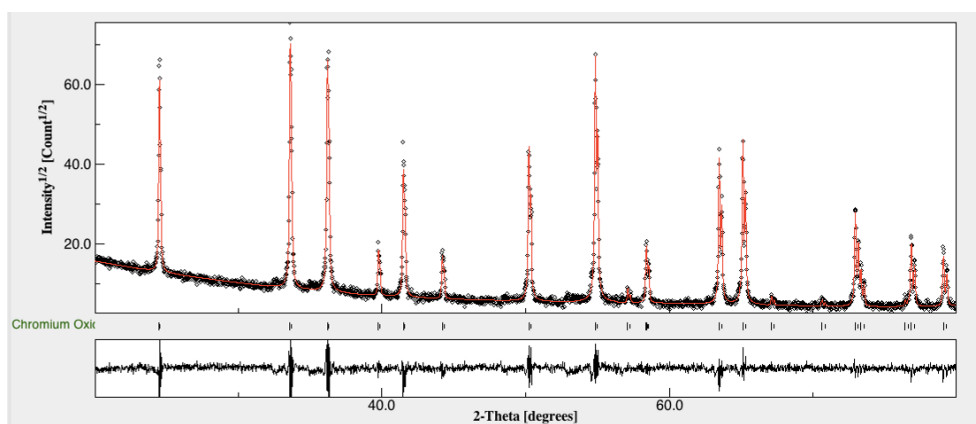


Figure B. 12 Rietveld refined XRD pattern of sintered  $\text{Cr}_2\text{O}_3$  at 1550 °C for 15 hours in air

## CuO

Copper (II) sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , Merck 99%) were used to synthesize CuO. Copper sulfate was calcined at 700°C for 5 hours in air. Figure B. 13 shows the XRD pattern of synthesized CuO. The pattern is consistent with monoclinic CuO (pdf card no. 01-073-6023).



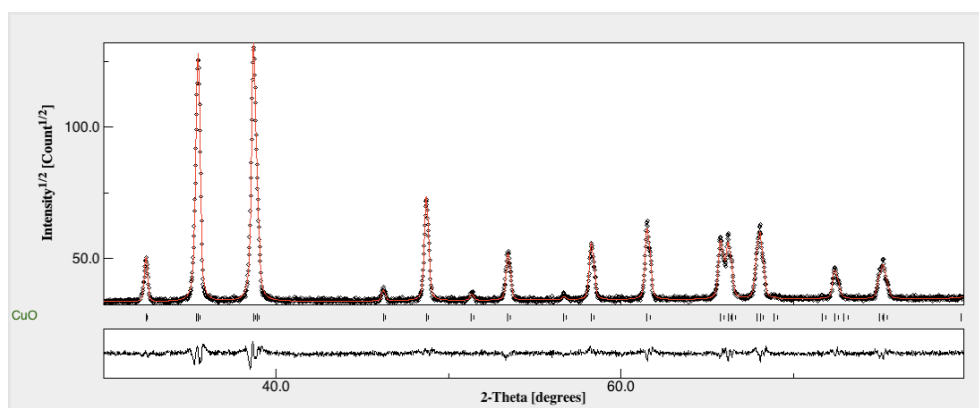


Figure B. 13 Rietvelt refined XRD pattern of as-synthesized CuO powder at 700°C for 5 hours

Rietvelt analysis of the as-synthesized powder yielded cell parameters of  $a= 4.688 \text{ \AA}$ ,  $b= 3.426 \text{ \AA}$ ,  $c=5.134 \text{ \AA}$ . SEM images showed that the powders were a few micrometers in size with agglomerates as  $10\text{-}12 \mu\text{m}$ , Figure B. 14.

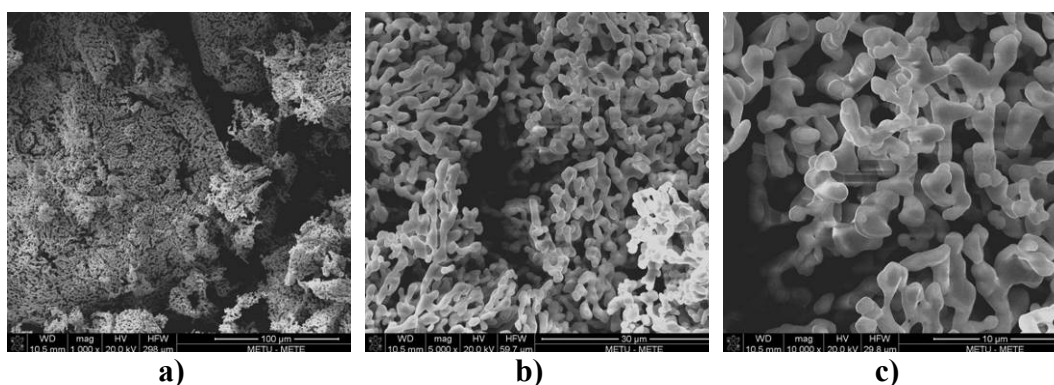


Figure B. 14 SEM image of as-synthesized CuO a) 1000x, b) 5000x, c) 10000x

To fabricate sputter target CuO powders were pressed under 100 MPa. Green bodies were sintered at 1000°C, 1100°C and 1200°C for 10 hours in air. At 1200°C was however too high which resulted in melting of the sample. XRD patterns of powders synthesized at 1000°C, 1100°C are shown in Figure B. 15. The patterns were made up of two phases  $\text{Cu}_2\text{O}$  (pdf card no. 01-071-3645) and CuO (pdf card no. 01-073-6023, monoclinic). SEM images of synthesized targets are given in Figure B. 16. Rietveld refined pattern, at 1000°C, yielded  $a=4.699 \text{ \AA}$ ,  $b=3.445 \text{ \AA}$ ,  $c=5.137 \text{ \AA}$  for the major phase CuO. It should be pointed out that the mass fraction of  $\text{Cu}_2\text{O}$  was only

0.53 wt.% in this sample. Accordingly target sintered at 1000°C may be considered as single phase CuO.

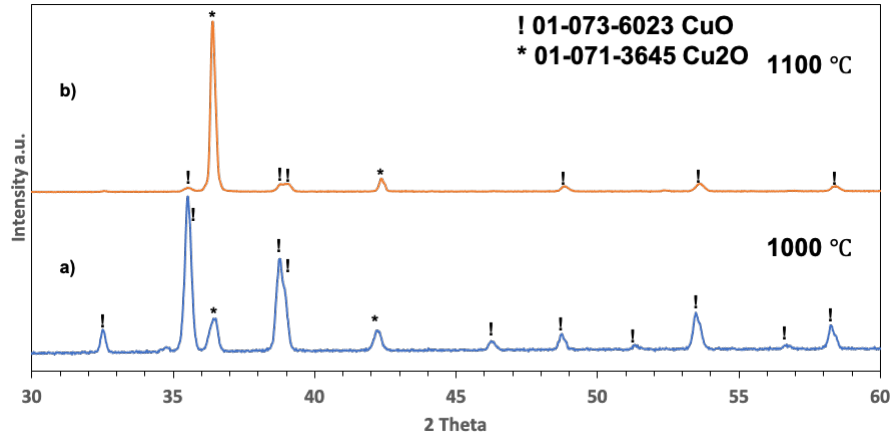


Figure B. 15 XRD pattern of sintered CuO at **a)** 1000°C, **b)** 1100°C

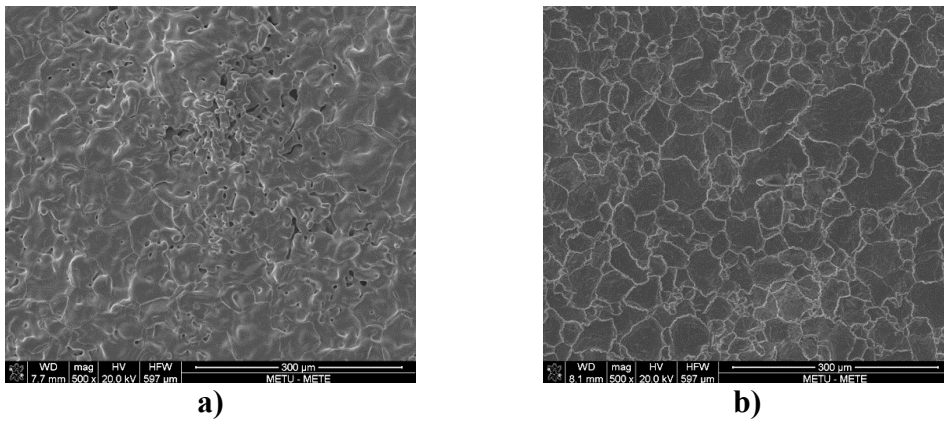
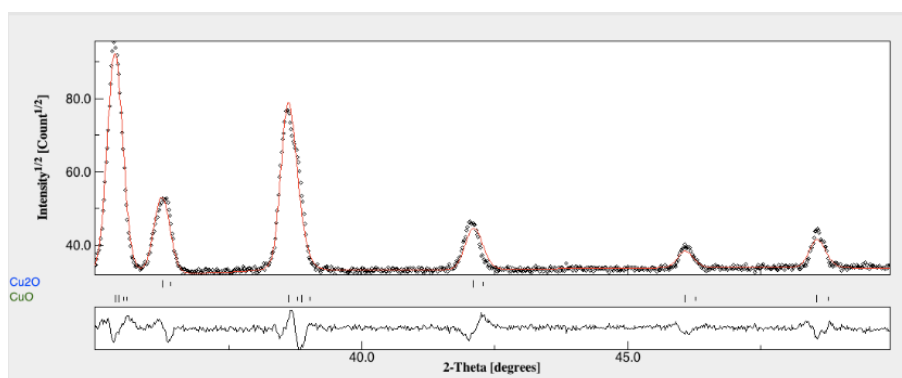
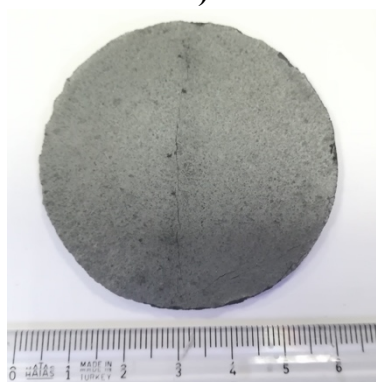


Figure B. 16 SEM images of sintered CuO at **a)** 1000°C, **b)** 1100°C



**a)**

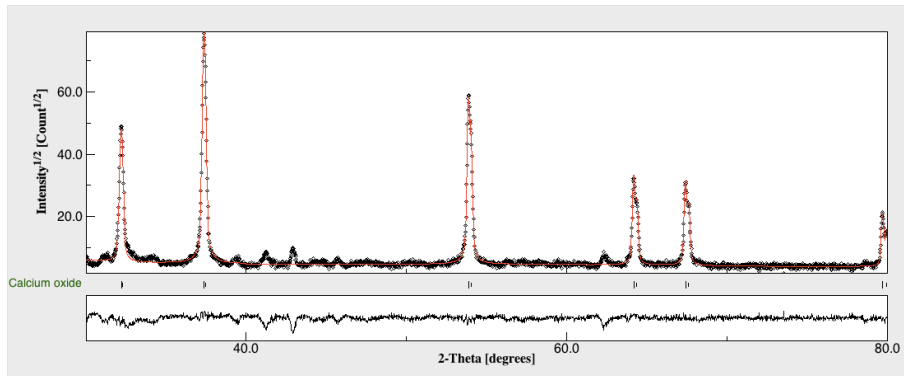


**b)**

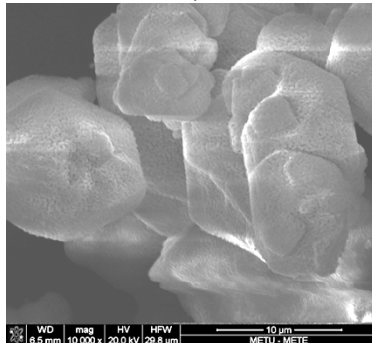
Figure B. 17 CuO target sintered at 1000°C for 10 hours **a)** Rietvelt refined XRD pattern and **b)** sintered CuO target.

## CaO

To synthesize CaO, CaCO<sub>3</sub> (Sigma-Aldrich, 98.5%) were calcined at 900°C for 5 hours in air. XRD pattern of the resulting powder, in Figure B. 18 (a), matched with cubic CaO (pdf card no. 01-070-4068). Rietvelt refined pattern yielded a cell parameter of  $a = 4.809 \text{ \AA}$ . SEM image of the synthesized powder is given in Figure B. 18 (b).



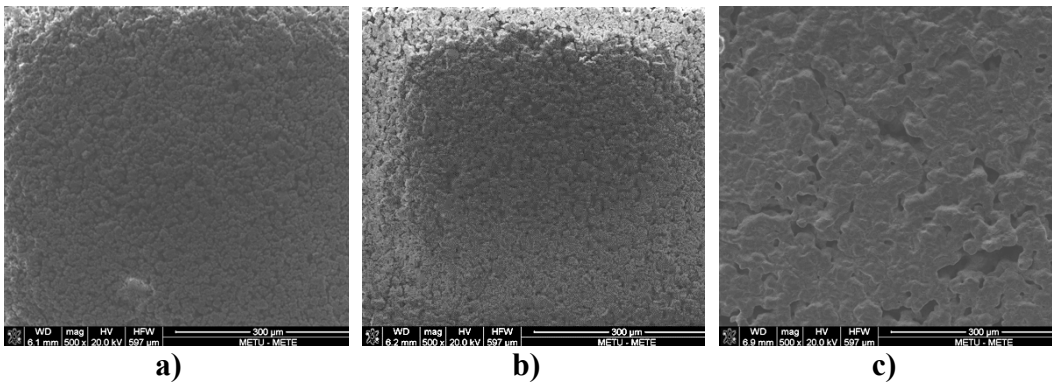
**a)**



**b)**

Figure B. 18 CaO powder synthesized at 900°C for 5 hours **a)** Rietveld refined XRD pattern and **b)** SEM image of the synthesized the powder

To fabricate sputter target as-synthesized CaO powders were pressed under 100 MPa in 20 mm Teflon rings. Green bodies were sintered at 1000°C, 1100°C and 1200°C for 10 hours in air. SEM images of the sintered pellets were given in Figure B. 19. Best densification was obtained at 1200°C. In Figure B. 20, Rietveld refined pattern at 1200°C has yielded  $a=4.809 \text{ \AA}$ . A photograph of CaO sputter target is given. Figure B. 19. (b)

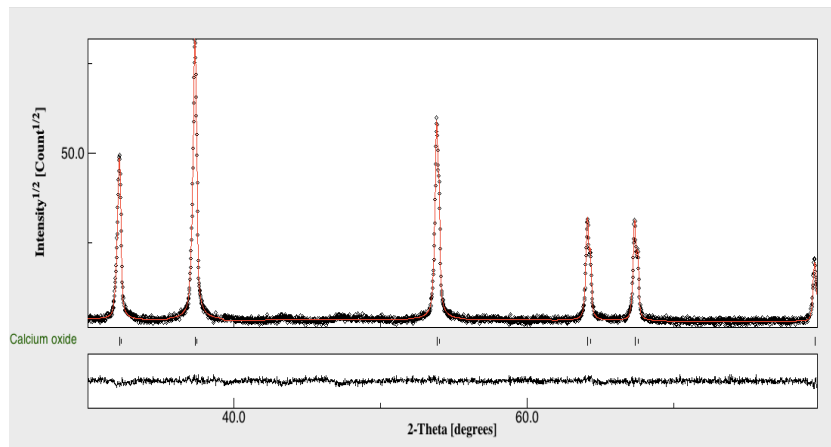


**a)**

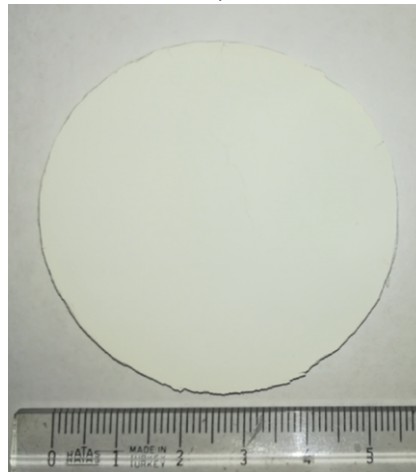
**b)**

**c)**

Figure B. 19 SEM image of sintered CaO at **a)** 1000°C, **b)** 1100°C, and **c)** 1200°C



a)



b)

Figure B. 20 Sintered at 1200°C for 10 hours CaO target a) Rietvelt refined XRD pattern and b) 2-inch CaO target

### **Mn<sub>3</sub>O<sub>4</sub>**

To fabricate Mn<sub>3</sub>O<sub>4</sub> sputter target, MnO<sub>2</sub> (Alfa Aesar, 98%) powder was used directly. They were mixed with few drops of DI water. Then the mixture was pressed in a Teflon ring with 100 MPa pressure. Green body was sintered at 1250°C for 5 hours., XRD pattern of the resulting powder is given in Figure B. 21. The pattern is consistent with Mn<sub>3</sub>O<sub>4</sub> (pdf card no. 01-080-0382). The microstructure as shown in Figure B. 21.(b), was not, however, fully dense. Still, it was sufficiently strong to be used as sputter target Figure B. 22.

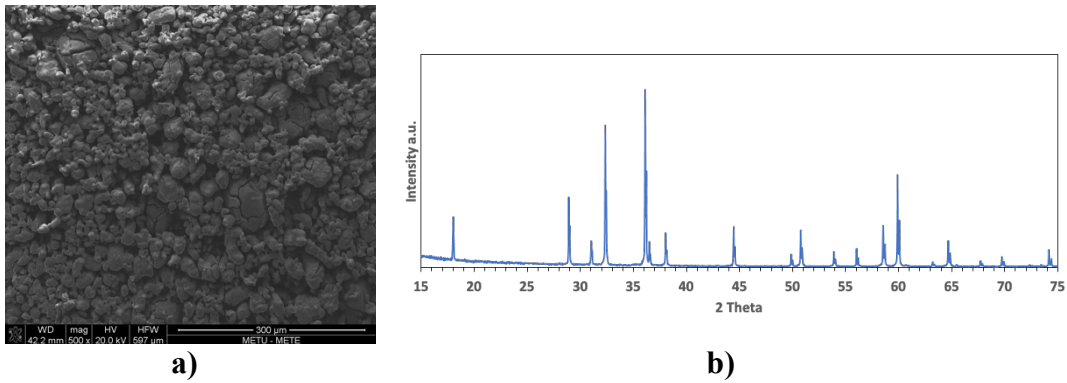
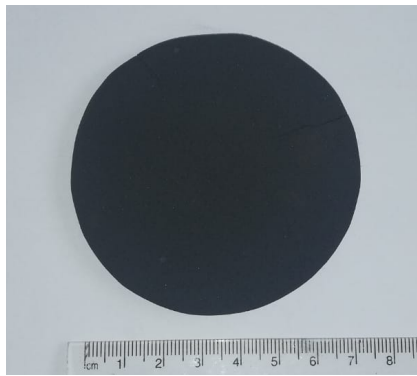


Figure B. 21 Sintered  $Mn_3O_4$  at 1250 °C for 5 hours **a)** SEM image, **b)** XRD pattern



**a)**  
Figure B. 22 Photograph of 3-inch  $Mn_3O_4$  target

### **TiO<sub>2</sub> Target**

To fabricate TiO<sub>2</sub> sputter target TiO<sub>2</sub> (Alfa Aesar, 99.8%) powder were used. The powder was pressed under 100 MPa in Teflon rings with 20 mm diameters. Then, green bodies were sintered at 1300°C, 1400°C and 1500°C for 5, 10 and 15 hours in air. However, the pressing 2-inch diameter target under 100 MPa created small cracks that has grown into larger cracks at the end of the sintering process. Therefore, pressure was decreased to 75 MPa. No phase change was seen after sintering process, (pdf card no. 03-065-0191, tetragonal), Figure B. 23. Sample sintered at 1500°C had the densest structure, Figure B. 25. Therefore, the TiO<sub>2</sub> target was fabricated by compacting 75 MPa pressure and sintering at 1500°C for 15 hours in air. Rietvelt refined XRD pattern yielded rutile TiO<sub>2</sub> has with cell parameters as TiO<sub>2</sub> a=4.589 Å, b=4.597 Å, c=2.963 Å and  $\alpha=89.886^\circ$ ,  $\beta=89.881^\circ$ ,  $\gamma=90.145^\circ$ , Figure B. 24.

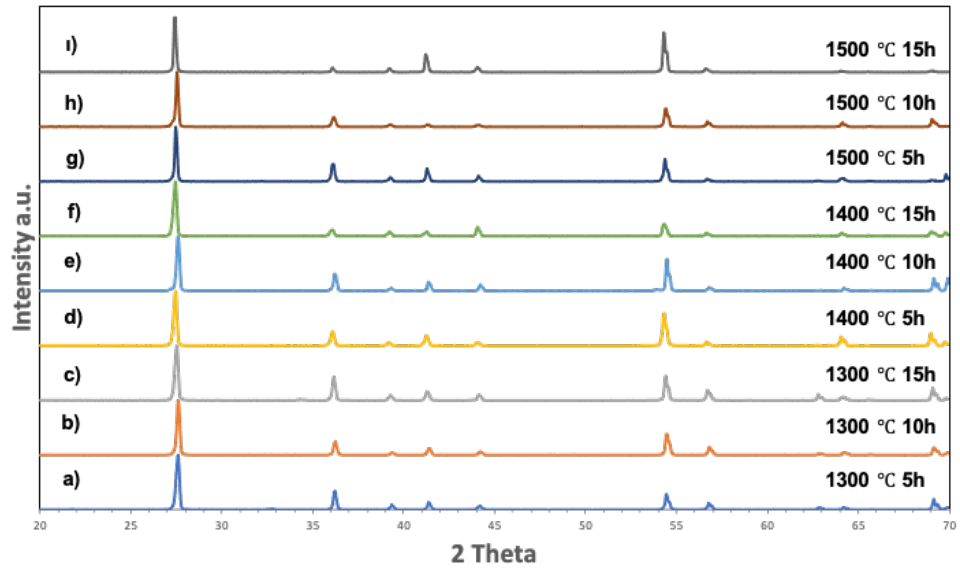
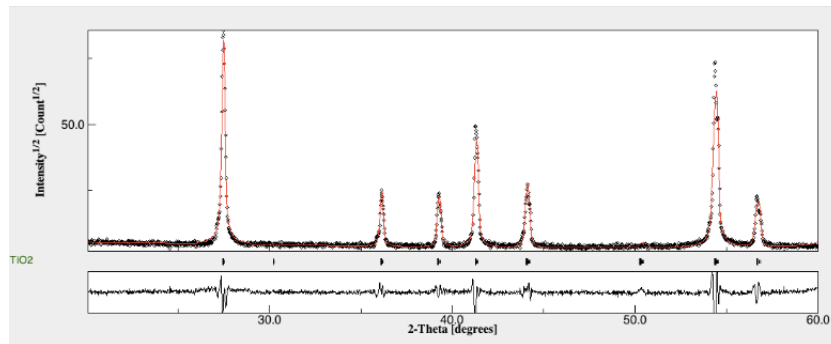
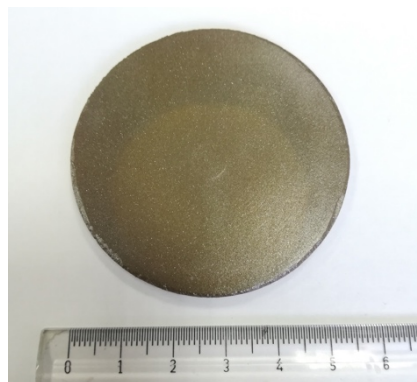


Figure B. 23 XRD pattern of sintered TiO<sub>2</sub> targets at 1300°C for a) 5h, b) 10h, c) 15h, 1400°C for d) 5h, e) 10h, f) 15h, 1500°C for g) 5h, h) 10h, i) 15h



a)



b)

Figure B. 24 TiO<sub>2</sub> target sintered at 1500°C for 15 hours a) Rietvelt refined XRD pattern and b) TiO<sub>2</sub> target

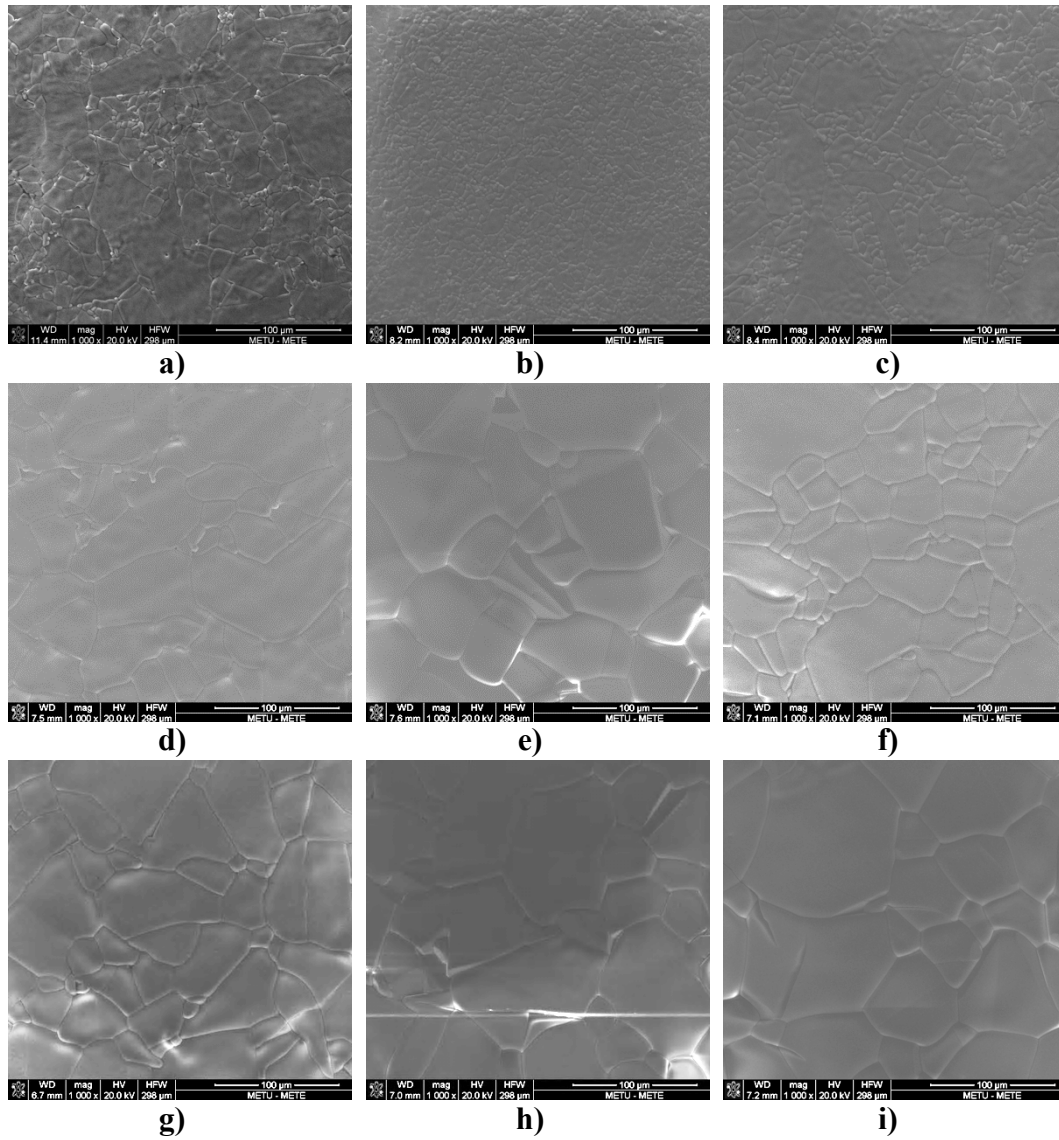


Figure B. 25 SEM images of sintered TiO<sub>2</sub> targets at 1300°C for **a)** 5h, **b)** 10h, **c)** 15h, 1400°C for **d)** 5h, **e)** 10h, **f)** 15h, 1500°C for **g)** 5h, **h)** 10h, **i)** 15h, (all with magnification of 1000x)