



# FABRICATION, OPTICAL SYNTHESIZATION AND SYNTHESIZATION OF MANGANESE OXIDE (MnO) THIN FILMS DOPED WITH IRON (II) (Fe)

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## ABSTRACT

The fabrication, optical synthesization and synthesization of manganese oxide (MnO) thin films doped with iron (ii) (Fe) was studied using chemical bath deposition (CBD) technique. Manganese Oxide was doped with Fe (II) at different time and millage of 0.2M aqueous ammonia (NH<sub>4</sub>OH) solution. The effect of deposition time on complexed and non-complexed of iron doping on structure of the films were investigated. Optical analysis showed that MnO have high transparency at the near infra-red (NIR) region and could be possibly be used as material for poultry roofs and walls which is more advantageous than using the conventional methods of heating.

**Keywords:** *Optical, Thin films, MnO, synthesized , CBD ,Fe, Characterization. spectrophotometer and spectrofluorometer*

## INTRODUCTION

Over the years, the improvement in the field of Nanotechnology is great. A recent development in science and technology is to synthesize new and different kinds of nanoparticles with different methodologies. A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness (Faustini, *et al.*, 2014). A familiar application of thin film is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface (Hanaor, *et al.*, 2011). Manganese oxide (MnO) is a transitional material having interesting physical and chemical properties. They can also be prepared each other by varying the temperature and atmosphere (vacuum or air, oxygen, hydrogen etc.) of the calcinations (Yu, *et al.*, 2002). Fe doped MnO are prepared in the form of thin films on glass substrate by chemical bath deposition technique and their structural and optical properties will be discussed.

Toshiro and Yoshinori, (1995), studied electrochromic properties of manganese oxide thinfilms prepared by chemical vapour deposition (CVD). The x-ray photoelectron spectroscopy (XPS) measurements showed that the atomic ratios O/Mn were 1.4 for the manganese oxide films prepared at substrate temperatures 250 and 300°C and 1.7 for the film prepared at 400°C. At +3.0 V, a decrease in optical transmittance throughout the visible wavelength spectrum is observed. This decrease in optical transmittance (30 to 50 % at 550 nm) finds a practical application as an anodic electrochromic material in combination with a cathodic electrochromic material like tungsten oxide for window applications. The x-ray diffraction patterns of the Mn<sub>3</sub>O<sub>4</sub> films deposited on a borosilicate glass substrate showed substrate temperatures of 250, 300, and 400°C respectively. The Mn<sub>3</sub>O<sub>4</sub> film deposited at 250°C is amorphous, while the peaks appeared for the films deposited at 300 and 400°C showed that the films are composed of crystallites with a predominant tetragonal structure (hausmannite).

Chi, *et al.*, (2014) reported that boron-doped manganese dioxide (MnO<sub>2</sub>) showed superior electrochemical performance as super-capacitors and the boron dopant was an effective way to improve and modify the characteristics of manganese oxide (MnO<sub>2</sub>).

Dopants have been utilized on MnO to improve cycling performance and stabilize electrochemically favorable structures (Thackeray, 2001). Dopants may be able to improve capacity retention upon cycling

if phase transformation is suppressed and volume expansion becomes isotropic and minimized upon lithium insertion (Chi, *et al.*, 2014). Potassium has been observed to act as a phase-transforming suppressant, but capacity fading and phase conversion have been found to occur at higher current rates (Zhang, *et al.*, 2000).

MnO and boron doped MnO films can be prepared by different techniques such as radiofrequency sputtering (Mayen-Hernandez, *et al.*, 2003), solvothermal synthesis (Mu, *et al.*, 2008), hydrothermal method, molecular beam epitaxy (David, *et al.*, 2003), thermal vacuum evaporation (Jahne, *et al.*, 1988), successive ionic layer adsorption and reaction (SILAR) (Pathan, *et al.*, 2007), chemical bath deposition (CBD) (Fan, *et al.*, 2003), and spray pyrolysis (Fan, *et al.*, 2003), (Sur, *et al.*, 2011). Manganese oxide (MnO) is a transitional material having interesting physical and chemical properties. It has optoelectronic applications and is often used in electrode materials (Nardi, 1985), (Sanchez, *et al.*, 1996), electro-chemical capacitors (Reddy and Reddy, 2004), (Reddy and Reddy, 2006), rechargeable batteries, sensors (Xu and Watanabe, 1998). and magneto-electronic devices (Kim and Park, 2004).

The electrode reaction of manganese oxide has been studied during the last two decades for their application in alkaline batteries (Boden, *et al.*, 1967), (McBreen, 1975). Recently, electrochromic properties of manganese oxide thin film have been observed by several authors (Burke and Murphy, 1980), (Lopez de Mishima, *et al.*, 1988), it has been reported that MnO<sub>2</sub> is an anodic electrochromic material like hydrated nickel oxide (Maruyama and Arai, 1993), and that the bleaching is based on the reduction of MnO<sub>2</sub> to MnOOH (Lopez de Mishima, *et al.*, 1988), (Yoshino, *et al.*, 1989), (Garnich, *et al.*, 1990), (Cordoba de Torresi and Gorenstein, 1992). In the meantime, (Seike and Nagai, 1991) prepared MnO<sub>x</sub> (Mn<sub>3</sub>O<sub>4</sub> or  $\gamma$ -Mn<sub>2</sub>O<sub>3</sub>) films by electron-beam evaporation. They reported electrochromic properties of the films polarized in 1.0M LiClO<sub>4</sub>  $\gamma$ -butyrolactone solution. Their objective is to clarify the electrochromism of Mn<sub>3</sub>O<sub>4</sub> thin films prepared by chemical vapor deposition (CVD) from manganese (III) acetylacetonate. Preparation conditions and structure of Mn<sub>3</sub>O<sub>4</sub> thin films were discussed on the basis of the measurements of the films which were deposited at different substrate temperatures. The optical properties were studied using in situ electrochemical polarization in a spectrophotometer cell.

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manganese dioxide (MnO<sub>2</sub>) showed superior electrochemical performance as super-capacitors and the boron dopant was an effective way to improve and modify the characteristics of manganese oxide (MnO<sub>2</sub>). Dopants have been utilized on MnO to improve cycling performance and stabilize electrochemically favorable structures (Thackeray, 2001). Dopants may be able to improve capacity retention upon cycling if phase transformation is suppressed and volume expansion becomes isotropic and minimized upon lithium insertion (Chi, *et al.*, 2014). Potassium has been observed to act as a phase-transforming suppressant, but capacity fading and phase conversion have been found to occur at higher current rates (Zhang, *et al.*, 2000). Vanadium-doping on MnO has also been studied recently for a potential pillaring effect in crystalline structures (Charles and Jun, 2003). Most Vanadium-doped compounds for battery applications have been synthesized using hydrothermal and sol-gel techniques (Charles and Jun, 2003).

Cobalt oxide is another excellent material for super-capacitor electrode, whereby addition of cobalt ions to MnO<sub>2</sub> shows a reasonable improvement in pseudo-capacitive performances (Liu, *et al.*, 1999), (Venkat and Weidner, 2002). Sharma *et al.*, (1999), reported the doping of Cobalt (Co) ions into the layered alkali MnO<sub>2</sub> that showed a considerable improvement in the conductivity of the electrodes, and following this work a series of reports have been published on Co-MnO<sub>2</sub> showing it to be a promising super-capacitor electrode material (Chang, *et al.*, 2004), (Chang, *et al.*, 2008).

Toshiro and Yoshinori, 1995 studied electrochromic properties of manganese oxide thin films prepared by chemical vapour deposition (CVD). The x-ray photoelectron spectroscopy (XPS) measurements showed that the atomic ratios O/Mn were 1.4 for the manganese oxide films prepared at substrate temperatures 250 and 300°C and 1.7 for the film prepared at 400°C. At +3.0 V, a decrease in optical transmittance throughout the visible wavelength spectrum is observed. This decrease in optical transmittance (30 to 50 % at 550 nm) finds a practical application as an anodic electrochromic material in combination with a cathodic electrochromic material like tungsten oxide for window applications. The present work report Optical Characterisation and synthesization of manganese Oxide (MnO) thin films doped with iron (11) (Fe)

## MATERIALS AND METHODS

The glass substrates (micro slide-25.4 mm wide × 76.2 mm lengths and thickness 1mm-1.2mm) will be washed in detergent rinsed with distilled water and soaked in concentrated hydrochloric (HCl) acid (to degrease the substrates from any possible stains) for 72 hours. Thereafter, they were removed from the concentrated hydrochloric (HCl) acid, rinsed with distilled water and cleaned with cotton wool, dipped with acetone to make it more electropositive.

Before the deposition technique, mass of zinc of Determined: using the formula:

$$m = \frac{M \text{ of } (MnCl_2.4H_2O) \times Mol. \text{ of } (MnCl_2.4H_2O) \times V \text{ of water}}{1000} \dots (1)$$

Where m is the mass of manganese, M is the molar mass of MnCl<sub>2</sub>.4H<sub>2</sub>O, Mol. is the molarity of MnCl<sub>2</sub>.4H<sub>2</sub>O and V is the volume of water.

Molar mass of (MnCl<sub>2</sub>.4H<sub>2</sub>O) = 197.91 g/mol, Molarity of (MnCl<sub>2</sub>.4H<sub>2</sub>O) = 0.4M and volume of water is 100ml. From calculation using the above figures, the mass of manganese is 7.92g. 0.2M of aqueous ammonia (NH<sub>4</sub>OH) at 2ml solution, were prepared.

Aqueous ammonia was gently added to form a white precipitate of manganese (II) hydroxide [Mn(OH)<sub>2</sub>] precursor solution. The aqueous ammonia were used as a complexing agent in some undoped films, doped films were non complexed while the remaining film were undoped and non complexed. All these samples will be deposited in 48 and 72 hours intervals respectively.

Iron (Fe) doped manganese solution, have formula as

$$m = \frac{\% \text{ dopant} \times M \times Mol \times V \text{ of water}}{1000} \dots (2)$$

The percentages of dopant used will be 1% and 2% respectively.

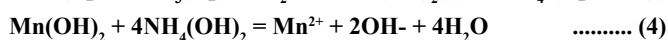
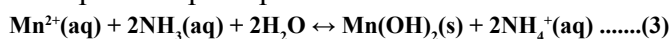
Pure and Iron (Fe) doped manganese oxide (MnO) thin films were grown on glass substrates. The deposition solutions were formed by first dissolving weighed amounts of manganese (II) chloride tetra-hydrate (MnCl<sub>2</sub>.4H<sub>2</sub>O) in water to the volume of 100ml with molar concentration of 0.4M.

The growth of MnO thin films, 48 and 72 hourly deposition times were carried out in complexed films, non complexed films and non complexed doped films respectively.

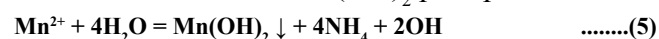
In case of Fe doped MnO thin films, a measured amount of Iron (II) tetraoxo sulphate (VI) heptahydrate (FeSO<sub>4</sub>.7H<sub>2</sub>O) was added to the initial solution. MnO thin films were complexed 0.2M NH<sub>4</sub>OH, non-complexed, and non-complexed doped

at 1% and 2% at 48 and 72 hours respectively are presented in Equations (3) - (7) and they illustrate the chemical reaction related to both undoped complexed and non-complexed doped process:

Undoped complex process:



During the reaction process, complex  $\text{Mn}^{2+}$  decomposes with the final formation of  $\text{Mn}(\text{OH})_2$  precipitation:

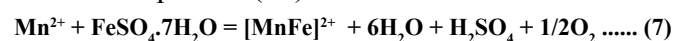


Reaction process,  $\text{Mn}(\text{OH})_2$  produced in equation (5) will transformed into manganese (II) oxide as shown in equation (6): Therefore



Non-complexed doped process:

When the  $\text{Mn}^{2+}$ , is doped with iron (II) tetraoxosulphate (VI) heptahydrate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , a configuration of manganese (II), iron (II) ion,  $[\text{MnFe}]^{2+}$  is formed as shown in equation (18):



The crystal structure and orientation of the MnO films were investigated. The optical characterization of the MnO thin films were carried out by ultraviolet-visible-near-infrared (UV-vis-NIR) spectrophotometer and spectrofluorometer.

## RESULTS AND DISCUSSION

The structure of the pure and Fe-doped MnO were characterized and the optical absorbance was recorded by using a single beam spectrophotometer in the wavelength range 100nm-1200nm as shown in Figure 1. From the graph, it is observed that absorption spectrum of MnO thin films (i.e., both undoped and doped) increases as the wavelength increased. This shows that the optical absorbance for both undoped and doped MnO films, increased at the visible region. The absorbance values were calculated with wavelengths in the range of 200-558nm (visible region). The results show that A, B, C, D, and E have their respective absorbance at 30%, 22%, 25%, 39%, and -13% respectively. The minus absorbance could be as a result of trace slight of impurity on sample E or improper calibration of blank sample (non deposited sample) before characterization. In this case, all other samples are with higher concentrations and for this reason the absorbance is positive.

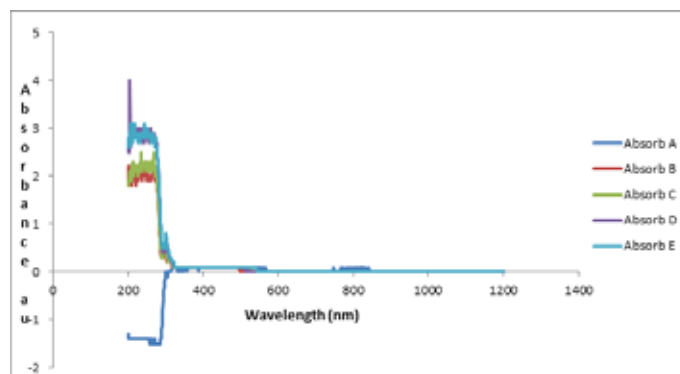


FIG. 1. Showing Absorbance as a Function Wavelength ( $\lambda$ ) MnO thin film

The optical transmittance of the thin films in the UV-vis-NIR wavelength range is presented in Figure 2. It can be seen that the films with sample E has high transparency (above 80%) at the visible region while films with samples A, B, C, and D and E have relatively very low transparency. The high transparency of sample E at the near infra-red (NIR) region could be possibly be used as material for poultry roofs and walls which is more advantageous than using the conventional methods of heating (Ezugwu, *et al.*, 2009). The minus transmittance could also be the same reason with absorbance.

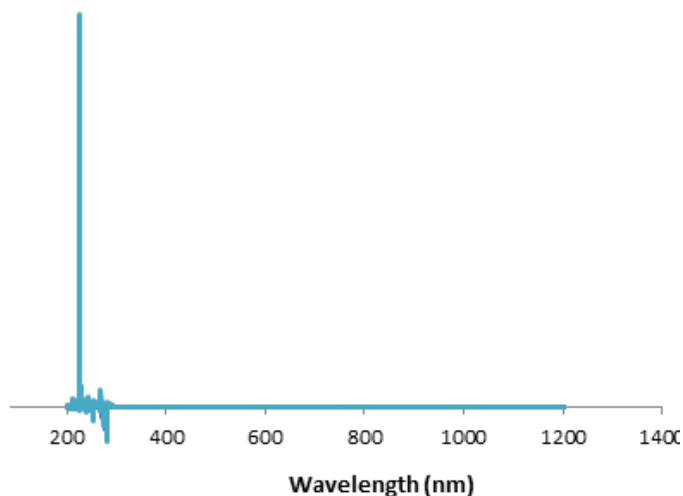


FIG. 2. Showing transmittance as a function wavelength ( $\lambda$ ) MnO thin film

Reflectance (R) of light on a given solid sample is the fraction of the incident intensity of a given wavelength that is reflected when it strikes the surface.

The typical UV-vis-NIR optical reflectance spectra of MnO thin films for the different samples are shown in figure 3. It is evident that the reflectance for all the deposited thin films is low. This low reflectance value makes MnO thin film an important material for anti-reflection coating. The negative reflectance is as a result of same reason stated in absorbance above.

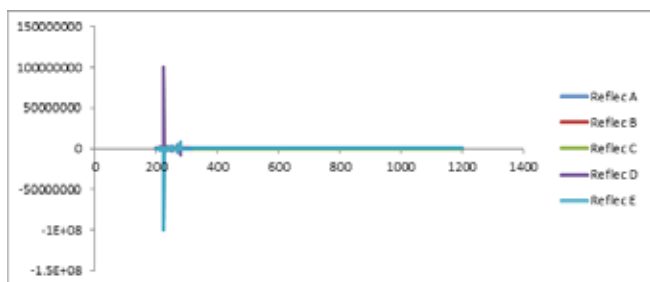


FIG. 3. Showing reflectance as a function wavelength ( $\lambda$ ) MnO thin film.

## CONCLUSION

Undoped and Iron (II) doped MnO thin films with different samples A, B, C, D, and E have been successfully synthesized by CBD technique on glass substrates. Optical analysis showed that MnO high transparency at the near infra-red (NIR) region could be possibly be used as material for poultry roofs and walls which is more advantageous than using the conventional methods of heating.

## REFERENCES

- Boden, D., Venuto, C.J., Wisler, D., and Wylie, R.B. (1967). The Alkaline Manganese Dioxide Electrode. The Discharge Process. doi: 10.1149/1.2426618 *J. Electrochem. Soc.* 1967 volume 114, issue 5, 415-417
- Burke, L.D., and Murphy, O.J. (1980). Electrochromic behaviour of electrodeposited cobalt oxide films. *J. Electroanal. Chem.*, 109, 373 (1980).
- Chang, J.K., Lee, M.T., Huang, C.H., and Tsai, W.T. (2008). Physicochemical properties and electrochemical behavior of binary manganese–cobalt oxide electrodes for supercapacitor applications, *Mater. Chem. Phys.* 108, 124-131.
- Chang, J.K., Chen, Y.L., and Tsai, W.T. (2004). Effect of heat treatment on material characteristics and pseudocapacitive properties of manganese oxide prepared by anodic deposition, *J. Power. Sources*, 135 (2004) 344-353.
- Charles, J.C., and Jun, J.X. (2003). Vanadium-doped manganese oxides as cathode materials for rechargeable lithium batteries. The Rutgers Scholar “An Electronic Bulletin of Undergraduate Research”. Vol. 5.
- Chi, H., Li, Y., Xin, Y., and Qin, H. (2014) “Boron-doped manganese dioxide for supercapacitor,” *Chemical Communications*, vol.50, pp.13349–13352.
- Cordoba de Torresi, S.I., and Gorenstein, A. (1992). The effect of manganese addition on nickel hydroxide electrodes with emphasis on its electrochromic properties *Electrochim. Acta*, 37, 2015.
- David, L., Bradford, C., Tang, X., Graham, T.C.M., Prior, K.A., and Cavenett, B.C. (2003). Growth of zinc blende MnS and MnS heterostructures by MBE using ZnS as a sulfur source. *J. Cryst. Growth* 251, 591.
- Faustini, M., Louis, B., Albouy, P.A., Kuemmel, M., and Grosso, D., (2014). Synergic combination of the sol-gel method with dip coating for plasmonic devices – NCBI – NIH. *J. Phys. chem. C* 114, 7637.
- Fan, D.B., Wang, H., and Zhang, Y.C. (2003). Preparation of crystalline MnS thin films by chemical bath deposition. *J. Cheng, B. Wang, H. Yan, Mater. Chem. Phys.* 80, 44. [https://doi.org/10.1016/S0254-0584\(02\)00518-7](https://doi.org/10.1016/S0254-0584(02)00518-7)
- Garnich, E., Yu, P.C., and Lampert, C.M. (1990). Preparation of Microcoiled Si<sub>3</sub>N<sub>4</sub> Fibers by Impurity Metal Activated Chemical Vapor Deposition and Their Mechanical Properties. *Sol. Energy Mater.*, 20, 265.
- Hanaor, D., Triani, G., and Sorrell, C.C. (2011). Morphology and photocatalytic activity of highly oriented mixed phase titanium dioxide thin films. *Surface and coatings technology* .205(12), 3658-3664. Marcel Dekker, Inc. New York, 89, ISBN: 0-8247-0851-2.
- Jahne, E., Goede, O., and Weinhold, V. (1988). *Phys. Status Solidi B* 146, K157 (1988).
- Kim, K.J., and Park, Y.R. (2004). Structural and optical investigation of manganese oxide thin films by spray pyrolysis technique. *J. Cryst. Growth* 270, 162(2004).
- Lopez de Mishima, B.A., Ohtsuka, T., and Sato, N. (1988). *ibid.*, 243, 219.
- Maruyama, T., and Arai, S. (1993). Nanostructured Nickel Oxide Films Prepared by Chemical Vapor Deposition and Their Electrochromic Properties *Sol. Energy Mater. Sol. Cells*, 30, 257.
- McBreen, J. (1975). Rapid electrochemical characterization of battery electrode materials in the solid state. *Electrochim. Acta*, 20, 221 (1975).
- Mayen-Hernandez, S.A., Sandoval, S.J., Perez, R.C., Delgado, G.T., Chao, B.S., and Sandoval, O.J. (2003). *J. Cryst. Growth* 256, 12.
- Mu, J., Gu, Z.F., Wang, L., Zhang, Z.Q., Sun, H., and Kang, S.Z. (2008). *J. Nanopartic. Res.* 10, 197.
- Nardi J.C. (1985). Characterization of the Li/MnO<sub>2</sub> Multistep Discharge. *J. Electrochem. Soc.* 132, 1787.
- Pathan, H.M., Kale, S.S., Lokhande, C.D., Han, S.H., and Joo, O.S. (2007). Synthesis and characterization of manganese sulphide thin films deposited by spray pyrolysis *Mater. Res. Bull.* 42, 1565.
- Reddy, R.N., and Reddy, R.G. (2004). Electrochemistry of Novel Electrode Materials for Energy ..., Issue 25. *J. Power Sourc.* 132, 315 (2004).

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- Reddy, R.N., and Reddy, R.G. (2006). Porous Structured Vanadium Oxide Electrode Material for Electrochemical Capacitors *J. Power Sourc.* 156, 700. doi:10.1016/j.jpowsour.2005.05.071
- Sanchez, L., Faray, J., Pereira-Ramos, J.P., Hernan, L., Morales, J., and Tirado, L. (1996). Studies on Structural, Optical and Electrical Properties of Spray Deposited Manganese Oxide (MnO<sub>2</sub>) Thin Films. *J. Mater. Chem.* 6, 37.
- Sur, S., Öztürk, Z., Öztas, M., Bedir, M., and YÖzdemir, Y. (2011). Studies on structural and electrical properties of MnO films prepared by the spray pyrolysis method. *Phys. Scr.* 84, 015701.
- Seike, T., and Nagai, J. (1991). Electrochromic Properties of Manganese Oxide Thin Films Prepared by Chemical Vapor Deposition. *J. Electrochem. Soc.*, Vol. 142, No. 9, The Electrochemical Society, Inc. *ibid.*, 22, 107.
- Sharma, R.P., Patil, S.V., Bhavsar, S.V., Patil, A.R., and Dori, L. (1999). Composition effect on optical characteristic of solution grown CdI-xMnxSe thin films. *Indian journal of pure and applied physics*, (37), 876-88.
- Toshiro, M., and Yoshinori, O. (1995). Electrochromic properties of manganese oxide thin films prepared by chemical vapour deposition (CVD). *J. Electrochem. Soc.*, Vol. 142, No. 9, September 1995 9 The Electrochemical Society, Inc.
- Thackeray, M.M. (2001). Electrochemical Technologies for Energy Storage and Conversion. *J. of Power Sources*, 97-98, 7.
- Xu, C.N., Miyazaki, K., and Watanabe, T. (1998). Humidity sensors using manganese oxides Sensors and Actuators B 46, 87.
- Venkat, S., and Weidner, J.W. (2002). Capacitance studies of cobalt oxide films formed via electrochemical precipitation, *J. Power Sources*, 108,15-20.
- Yu, G.O., Graboy, I.E., Amelichev, V.A., Bosak, A.A, Kaul, A.R, Giittler, B., Sretchnikov, V.L., and Zandbergen, H.W.(2002). Structural, Optical Investigation of Manganese Oxide Thin Films by Spray Pyrolysis Technique *Solid State Comm.* 124, 15.
- Yoshino, T., Baba, N., and S. Watanabe, (1989). *Hyomen Gigyutu*, 40, 840 (1989).
- Zhang, F., Zgala, K., and Whittingham, M.S. (2000). Vanadium-doped manganese oxides as cathode materials for rechargeable lithium batteries. *Electrochem Comm.*, 2, 445.