

CREATING IMPROVED CATHODE MATERIALS FOR LITHIUM-ION BATTERIES\*

by

EMMA WISNIEWSKI-BARKER\*\*  
BRYN MAWR COLLEGE  
BRYN MAWR, PA  
CORRESPONDENCE: EWISNIEWSK@BRYNMAWR.EDU

CHRISTOPHER S. JOHNSON  
CHEMICAL SCIENCE AND ENGINEERING  
ARGONNE NATIONAL LABORATORY

\*Work performed at Argonne National Laboratory, a contract Laboratory of the United States Department of Energy

\*\*Participant in the Summer 2009 Student Program. This program is coordinated by the Division of Educational Programs.

## Table of Contents

Abstract.....	3
Introduction.....	4
Materials and Methods.....	5
Results.....	7
Discussion and Conclusion.....	8
Future Work.....	9
Acknowledgements.....	10
References.....	10
Figures.....	12

Creating Improved Cathode Materials for Lithium-Ion Batteries. EMMA WISNIEWSKI-BARKER (Bryn Mawr College, Bryn Mawr, PA, 19010) CHRISTOPHER S. JOHNSON (Argonne National Laboratory, Argonne, IL, 60439).

Lithium-ion (Li-ion) batteries are key to the development of Hybrid Electric Vehicles (HEVs) and Plug-in Hybrid Electric Vehicles (PHEVs). One challenge to overcome that will lead to better-working and longer-lasting batteries for more efficient hybrid vehicles is to change and refine the cathode material. The objective of the research was to create a new cathode material that could overcome the constraints associated with the traditional  $\text{LiCoO}_2$  cathode by reducing or eliminating the amount of costly cobalt and adding a combination of nickel and manganese to the transition metal layer. The compound  $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$  has previously been shown to increase the capacity and energy of the battery while still retaining the layered formation of the  $\text{LiCoO}_2$ . The precursor material, which consisted of either nickel cobalt manganese hydroxide or nickel manganese carbonate, was reacted with sodium carbonate in an oven at varying temperatures. The  $\text{Na}[\text{M}]\text{O}_2$ , with M being the combination of cobalt, nickel, and manganese, underwent an ion exchange in hexanol with an excess of lithium bromide to obtain  $\text{Li}[\text{M}]\text{O}_2$ . Initial rate tests examining the performance and life of the batteries have demonstrated that this new cathode material operates slightly better than the current baseline material and has the potential to lead to better batteries for HEVs and PHEVs. Further studies must be done to continue to maximize the performance of these materials.

## 1. INTRODUCTION

The development of lithium-ion (Li-ion) batteries is an important area of current research. One facet of this research in which there have been many interesting discoveries is the area of cathodes [1]. Previous research has shown how using the ion exchange method to create the Li-ion cathode increases the specific capacity of the battery [2, 3]. This current research investigates how to increase battery cycling life when the cathode material is  $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ , where  $x$ ,  $y$ , and  $z$  vary. Discussions on the effect of the crystal structure of the compound on the performance of the battery led the researchers to focus on maximizing the mobility of the lithium within the cathode. The easier it is for the lithium to flow in and out of the substance, the greater the power of the battery.

There are three main types of cathodes for Li-ion batteries, all discovered by and credited to Dr. John Goodenough [4]. The first type,  $\text{LiMO}_2$ , with  $M = \text{Co}$ , is currently featured in most cell phone and laptop batteries.  $\text{LiMO}_2$  cathodes have a layered structure. The structure is composed of alternating layers of transition metals and lithium. This structure allows the lithium to flow without obstructions in two dimensions. While this type of battery cathode has been very successful, there are a number of issues with it. First, because of the layered structure and site disorder of the Ni, some of the lithium cannot move about freely, because if all of it were to leave the layer, the structure would collapse. This design flaw limits the amount of lithium that can move, which ultimately reduces the power and capacity of the battery. As mentioned previously, the more lithium that can flow in and out of the cathode, the better the battery will function. Another problem with this type of cathode is that at higher temperatures, the compound loses oxygen. This poses a danger hazard when the battery is stressed or overheated [5].

The second type of cathode,  $\text{LiMPO}_4$ , has an olivine structure. The capacity of this type of cathode is similar to that of the  $\text{LiMO}_2$  type. However, it is much safer up to higher temperatures than the layered type of cathode, because the  $\text{PO}_4$  (3-) polyanion is quite stable at high-temperatures [6]. The lessened safety risks associated with this type of cathode makes it an appealing option for use in batteries.

The third type,  $\text{LiM}_2\text{O}_4$ , has a spinel structure [7]. One of the benefits of having the spinel structure is that the battery works at a higher voltage, which increases the specific energy. In addition, the spinel structure features three dimensional pathways for the migration of lithium, thereby making the spinel a high-power cathode material. However, cathodes with a spinel structure have two drawbacks. First, they have intrinsically lower capacity. Because research is continually attempting to increase the capacity and power of batteries, this is the cause of some obvious problems. Second, this spinel-structured cathode has been shown to be less safe than the olivine-structured  $\text{LiMPO}_4$  cathode, although it has been found to be more safe than the layered  $\text{LiMO}_2$  cathode.

This research focuses on the layered  $\text{LiMO}_2$  cathode. If a balance could be found to increase the freedom of the lithium without having a collapse in the layered structure, the specific capacity and power of the battery would be greatly increased.

## **2. MATERIALS AND METHODS**

In order to investigate the possibility of increasing the performance of Li-ion batteries, carbonates were used as precursor materials. Representative compounds were made by combining the carbonates, such that the product consists of an  $\text{ANi}_{0.25}\text{Mn}_{0.75}\text{O}_2$  configuration, with “A” being a new variant element. They were put on a shaker for 24 hours as a dry mix. When removed from the shaker, there remained some precursor separation. The combination was

then lightly ground to make the powder homogenous. All subsequent mixtures were simply ground together until homogenous, instead of placed on the shaker, as the shaker had been found to be largely ineffective. These mixtures were heated to 900 degrees Celsius over three hours. They were held at that temperature for 16 hours. Then the furnace was turned off and they were allowed to cool to room temperature. This heating was used to create pure-layered oxide compound.

Once this was created, a metal bromide was combined with the oxide compound using ion exchange method to create composition X, which takes the form of  $ABMO_2$ , with “B” being a second variant element. Previous research had shown this to be a successful method of creating the desired compound [3]. However, to continue the increase of the specific capacity of Li-ion batteries, this research aimed to not completely exchange all of the new “A” variant for “B” variant. The goal was to have a few of the “A” variant ions left in the lithium layer as pillars to hold open the space, keep the layer from collapsing, and allow for greater movement and quantity of lithium charged and discharged in the battery. The ion exchange was executed over a period of approximately seven to eight hours at 165 degrees Celsius.

Once the desired compound was created, electrodes and coin cell batteries were made from that material. The batteries were assembled in a glove box at room temperature under Helium using an electrolyte from Tomiyama. The batteries were run through a rate study to test their power and capacity. The batteries were cycled from 2 to 5 volts.

This process was repeated for combinations of the same carbonates and a different metal carbonate,  $Ni_{0.33}Co_{0.33}Mn_{0.33}CO_3$  to create composition Y. Composition Y takes the same form as composition X,  $ABMO_2$ . However, the metal component of Y differs from that of X.

It should be noted that the material that went through the ion exchange process for composition X was originally heated at 800 degrees Celsius, instead of 900 degrees Celsius like the others. However, this does not appear to have greatly influenced the results in any way.

### **3. RESULTS**

The baseline sample created from composition X, showed a very clean X-Ray Diffraction (XRD) pattern (see Figure 1). As seen in this figure, secondary phases did not appear in the XRD pattern, reinforcing that the synthesis of the compound occurred as desired. Composition X was tested on a cycler from 2 to 5 volts. Although the capacity did decrease with the increased rate, when the rate was slowed, the battery recovered almost all of its original capacity. When cycling at C/16, the capacity was 212.65 mAh/g. Even when cycling at 2C, the lowest capacity reached was 164.28 mAh/g. At the end of the rate study, the current went back to C/16, and the capacity climbed all the way back to 226.95 mAh/g, exceeding even the starting capacity (see Figure 2 for details).

A baseline was created for composition Y that also had a clean XRD pattern (see Figure 3). Once it was determined that composition Y had been created satisfactorily without evidence of secondary phases, it was tested on a cycler from 2 to 5 volts. Composition Y had a capacity of 174.21 at C/16. Composition Y reached a capacity of 150.58 at 2C, and it recovered to 165.20 when the current returned to C/16 (see Figure 4 for details).

The experimental compound created for composition X had a fairly clear XRD pattern before the ion exchange. After the ion exchange the XRD pattern was also very clear, although the peaks, excluding the first one, were broader than they were on the XRD pattern before the ion exchange (see Figures 5*a* and 5*b*). The presence of a smaller, second peak on both the pre- and post-ion exchange XRD pattern indicates that some lithium was present in the metal layer.

Although there remains some data to be collected, the capacity of this compound at the rate of C/16 was 228.04 mAh/g, which suggests that this ion exchange material will do as well as, or possibly better than, the baseline composition for this material (see Figure 6).

The experimental compound created from composition Y through ion exchange had a very clean XRD pattern, both before and after the ion exchange process (see Figures 7a and 7b). When cycling at C/16, it had a capacity of 180.81 mAh/g. When increased to 2C, the capacity dropped to 117.60 mAh/g, but then when the rate was increased to C/16 again, the capacity came back up to 154.38 mAh/g (see Figure 8 for details).

When looking at the voltage profile for the baseline and experimental compounds made from composition Y (see Figure 9a and 9b), one can see that, once normalized for weight, the drop-off in capacity for these two batteries is equal. Because of their unequal weights, the rates of the slowest cycles are different for these two compounds, with six hours for the lighter and eleven hours for the heavier. Figure 9b shows that the experimental compound, made through the ion exchange method, has higher impedance, which results in a decreasing voltage and a lower energy.

#### **4. DISCUSSION AND CONCLUSION**

In this research, both a standard baseline material and the same material made through an ion exchange were created for two different starting metal carbonates. The goal of the ion exchange method was to increase the power and capacity of the cathode by increasing the freedom of movement of the lithium. The layered structure of this type of cathode allows for two dimensional movement of the lithium. However, because the layers would collapse if all of the lithium were removed, the research aimed to keep some of the “A” variant ions in the lithium layer through the ion exchange. If not all of the lithium were removed and some “A” variant ions



remained, those “A” variant ions could act as pillars and hold open the lithium layer. This would allow more of the lithium to flow in and out of the structure, increasing the power and specific capacity of the cathode.

The XRD patterns and cycling data showed that the ion exchange method did help increase the specific capacity of the batteries. When Figure 7a is compared to Figure 7b, it becomes clear that the first peak moved significantly to the right after the ion exchange, indicating that the d-spacing has decreased. It is believed that the d-spacing decreased because many of the “A” variant ions, which are larger than lithium ions, had been exchanged for the smaller lithium ions. However, looking at Figure 7b also suggests that the ion exchange method left a few “A” variant ions in the lithium layer, which caused the primary peak to shift to the left of what was expected, as seen in the XRD pattern of the baseline material in Figure 1. This implies that the ion exchange method has created a more open layered structure with a large d-spacing, which allows more freedom of movement of the lithium.

Because the specific capacity of the experimental compounds created through ion exchange for both composition X and composition Y are higher than those of their respective baseline compounds, it is believed that this new method of creating cathode material could lead to more efficient and powerful lithium ion batteries. However, the large decrease and smaller recovery in capacity of the experimental compound from composition Y raise some questions as to how much better this material will be than the baseline one.

## **5. FUTURE WORK**

This research has investigated some promising possibilities for increasing the specific capacity and power of Li-ion battery cathodes. Further research is needed to maximize the benefits of this ion-exchange process and determine the correct ratio of “A” variant ions to

lithium ions in the lithium layer. To do so, researchers should vary the amount of time over which the ion exchange happens, as well as the temperature at which it happens.

## 6. ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy and the Division of Educational Programs' Summer 2009 Student Program at Argonne National Laboratory. I would like to thank John T. Vaughey and my mentor Christopher S. Johnson for their support and knowledge.

## 7. REFERENCES

- [1] Whittingham, M. S. (2004). Lithium batteries and cathode materials. *Chemical Reviews*, *104*(10), 4271-4301. Retrieved July 23, 2009.
- [2] Armstrong, A. R., & Bruce, P. G. (1996). Synthesis of layered LiMnO<sub>2</sub> as an electrode for rechargeable lithium batteries. *Nature*, *381*(6582), 499-500. Retrieved July 23, 2009.
- [3] Kang, K., Meng, Y. S., Breger, J., Grey, C. P., & Ceder, G. (2006). Electrodes with High Power and High Capacity for Rechargeable Lithium Batteries. *Science*, *311*, 977-980. Retrieved May 27, 2009.
- [4] Goodenough, J. B. (2008). *Witness to Grace*. Frederick, MD: Publishamerica.
- [5] Wang, Y. D., Jiang, J. W., & Dahn, J. R. (2007). The reactivity of delithiated Li(Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>)O<sub>2</sub>, Li(Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>)O<sub>2</sub> or LiCoO<sub>2</sub> with non-aqueous electrolyte. *Electrochemistry Communications*, *9*, 2534-2540. Retrieved July 20, 2009.
- [6] Padhi, A. K., Nanjundaswamy, K. S., & Goodenough, J. B. (1997). Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *Journal of The Electrochemical Society*, *144*(4), 1188-1194. Retrieved July 20, 2009.

- [7] Thackeray, M. M., Dekock, A., Rossouw, M. H., Liles, D., Bittihn, R., & Hoge, D. (1992). Spinel Electrodes from the Li-Mn-O System for Rechargeable Lithium Battery Applications. *Journal of The Electrochemical Society*, 139(2), 363-366. Retrieved July 23, 2009.

## FIGURES

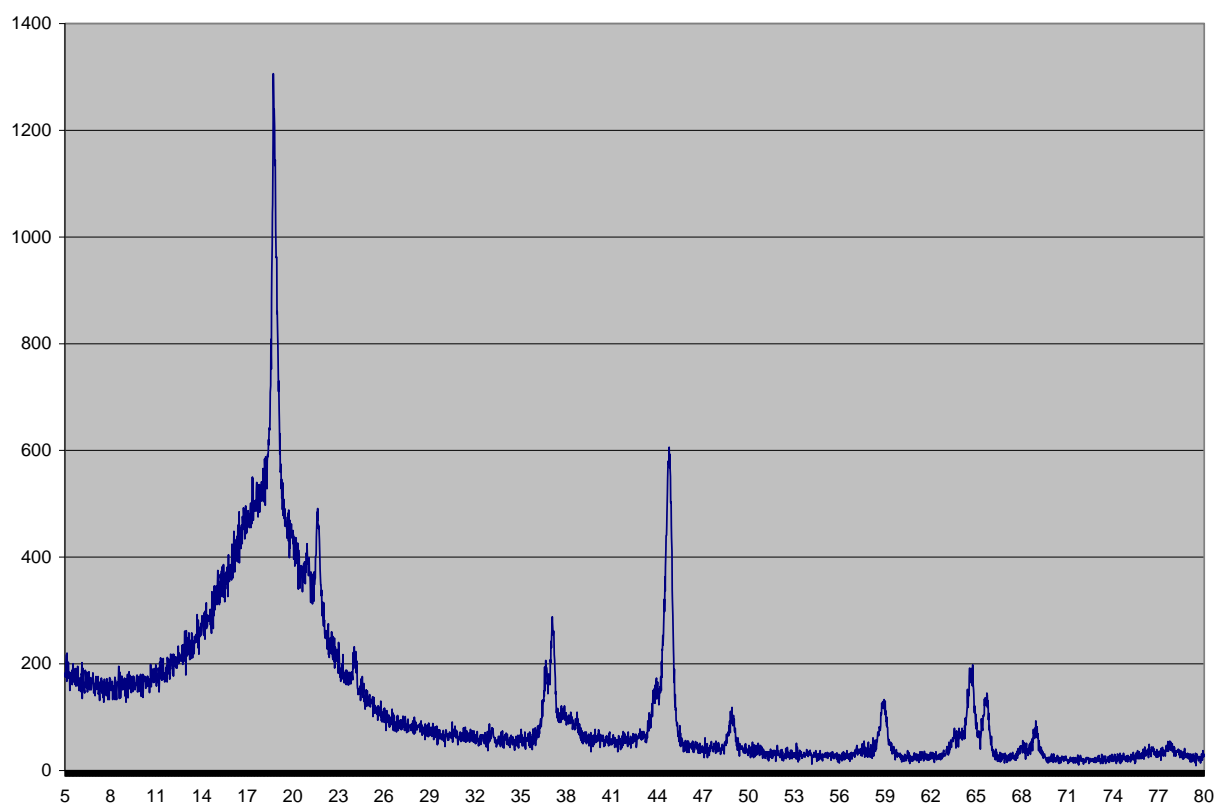


Figure 1: XRD pattern of baseline material for composition X.

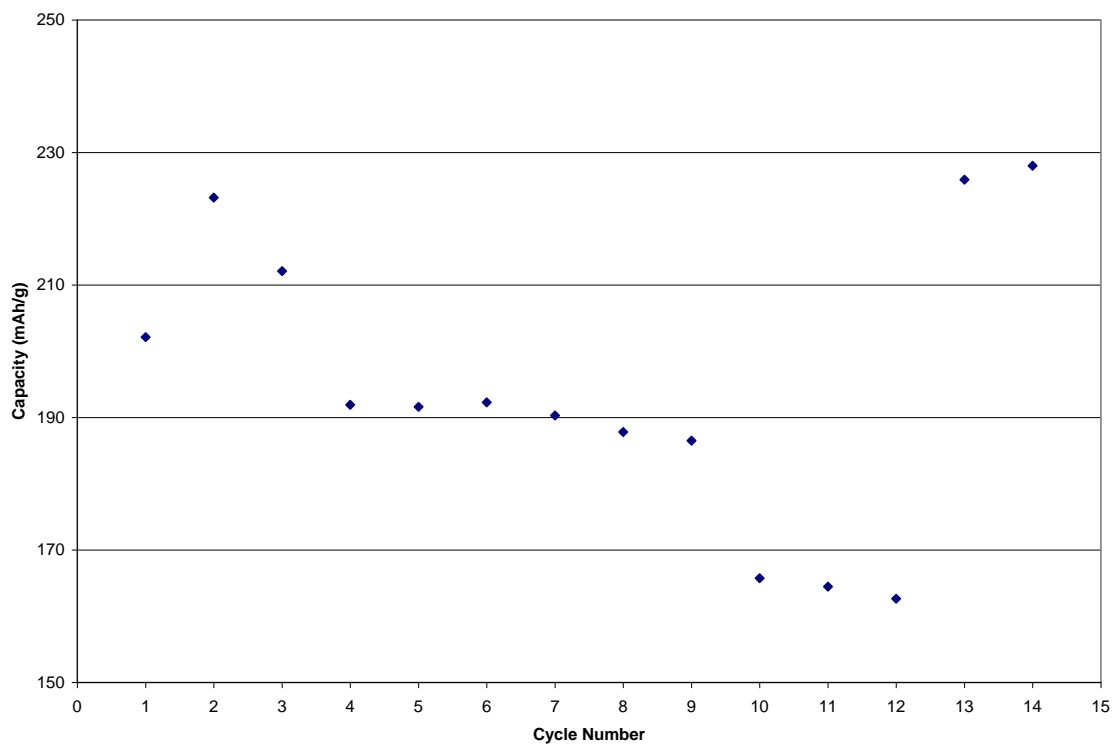


Figure 2: Cycling data from battery made of baseline material for composition X; cycled from 2-5 volts at rates ranging from C/16 to 2C.

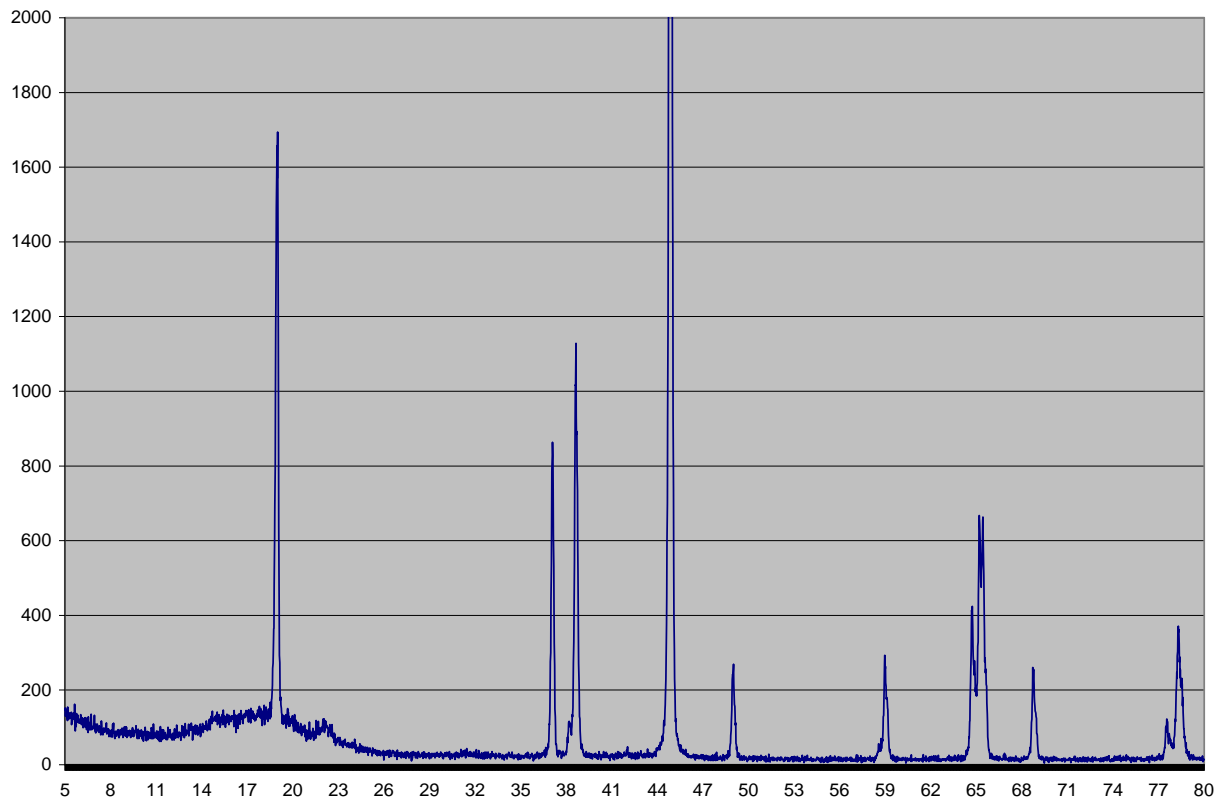


Figure 3: XRD pattern of baseline material for composition Y.

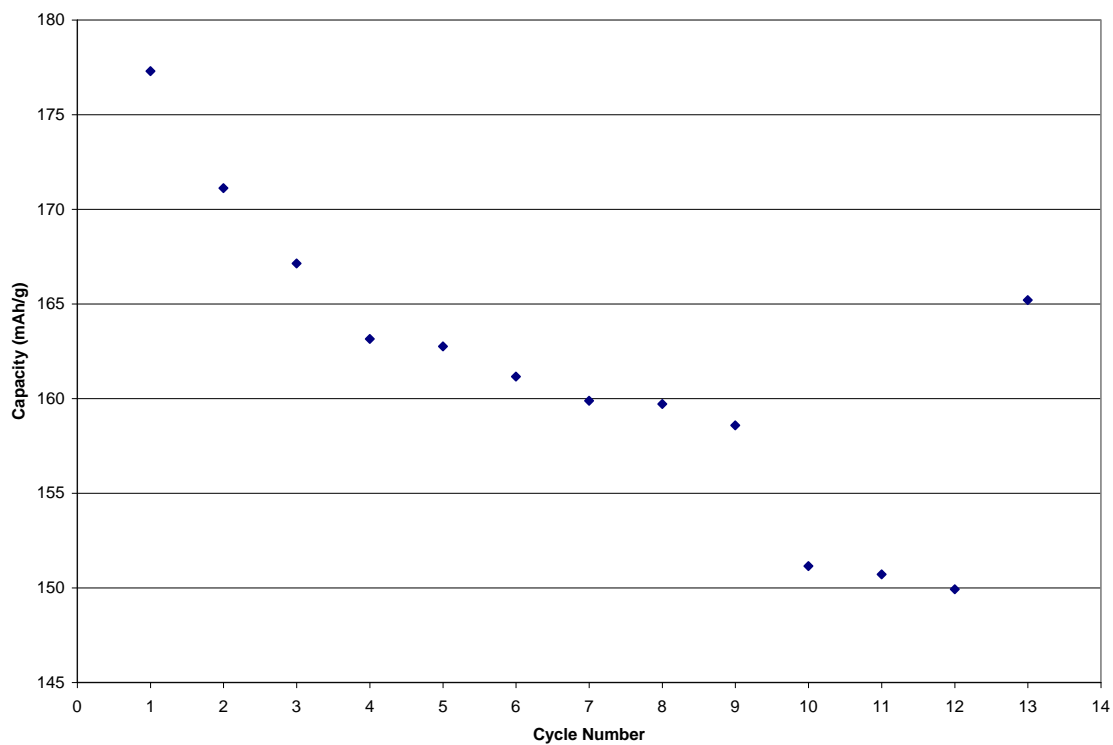


Figure 4: Cycling data from battery made of baseline material for composition Y; cycled from 2-5 volts at rates ranging from C/16 to 2C.

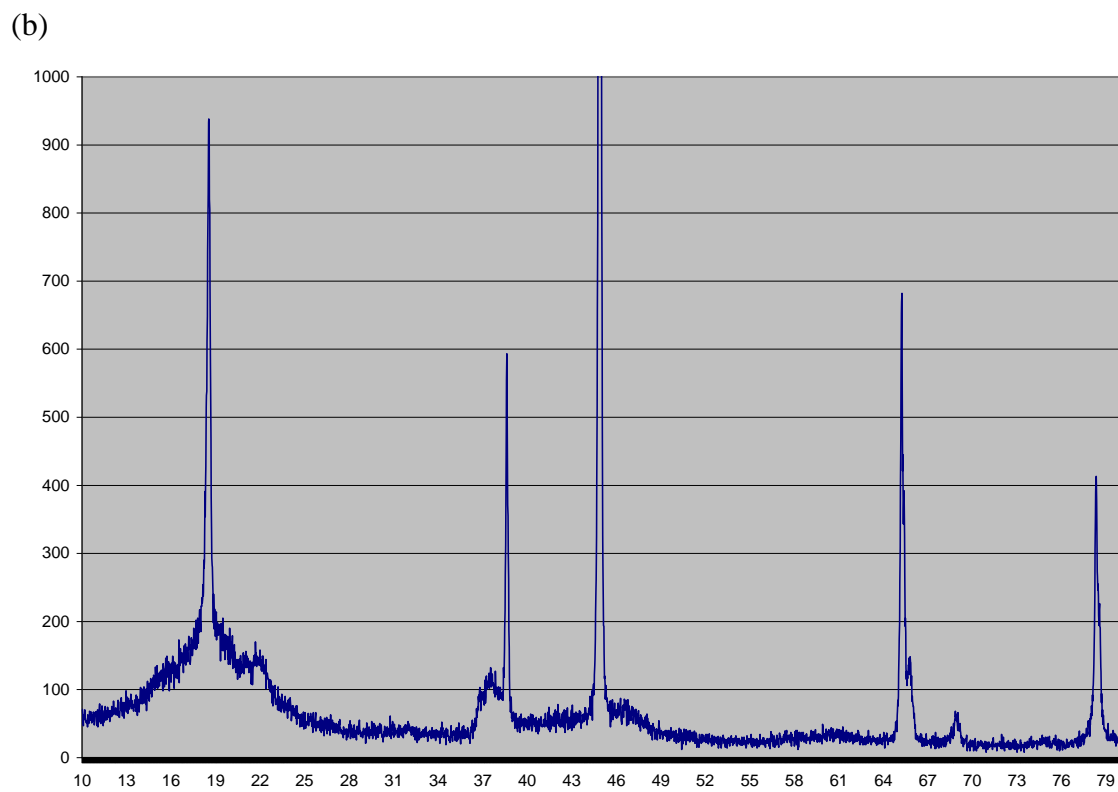
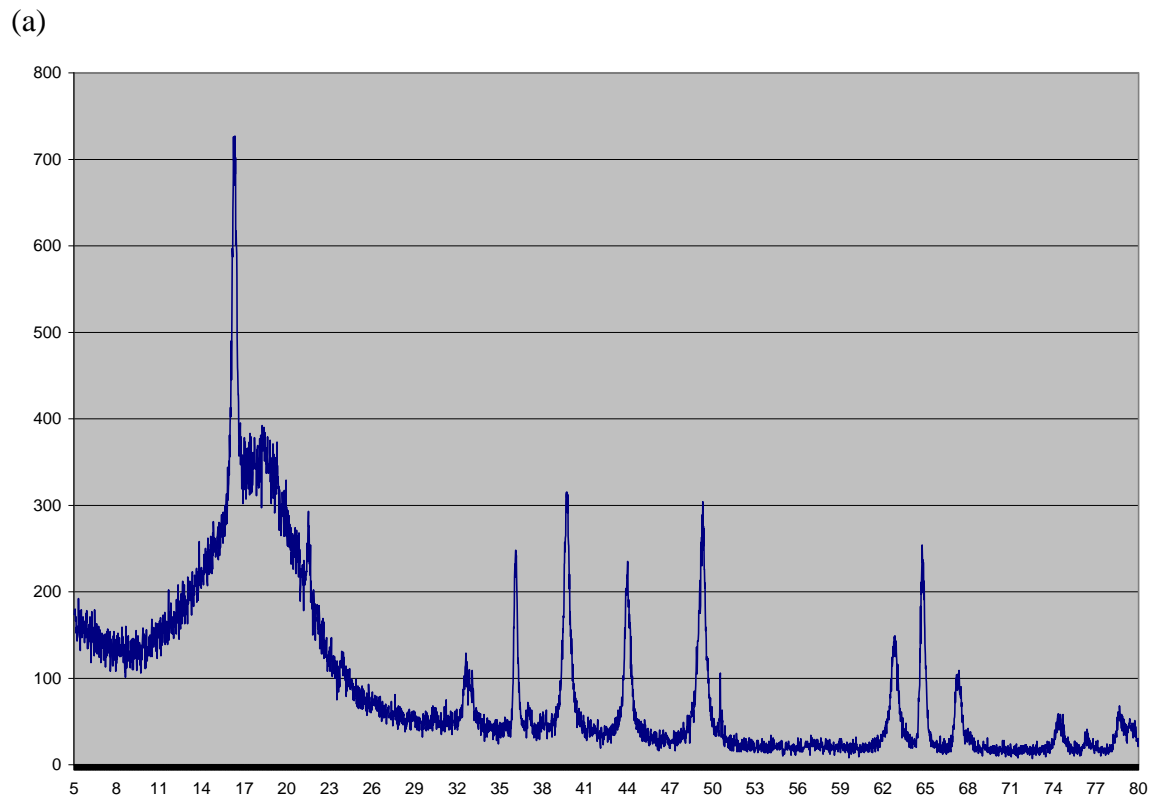


Figure 5: (a). XRD pattern for material of composition X before ion exchange. (b). XRD pattern for material of composition X after ion exchange.



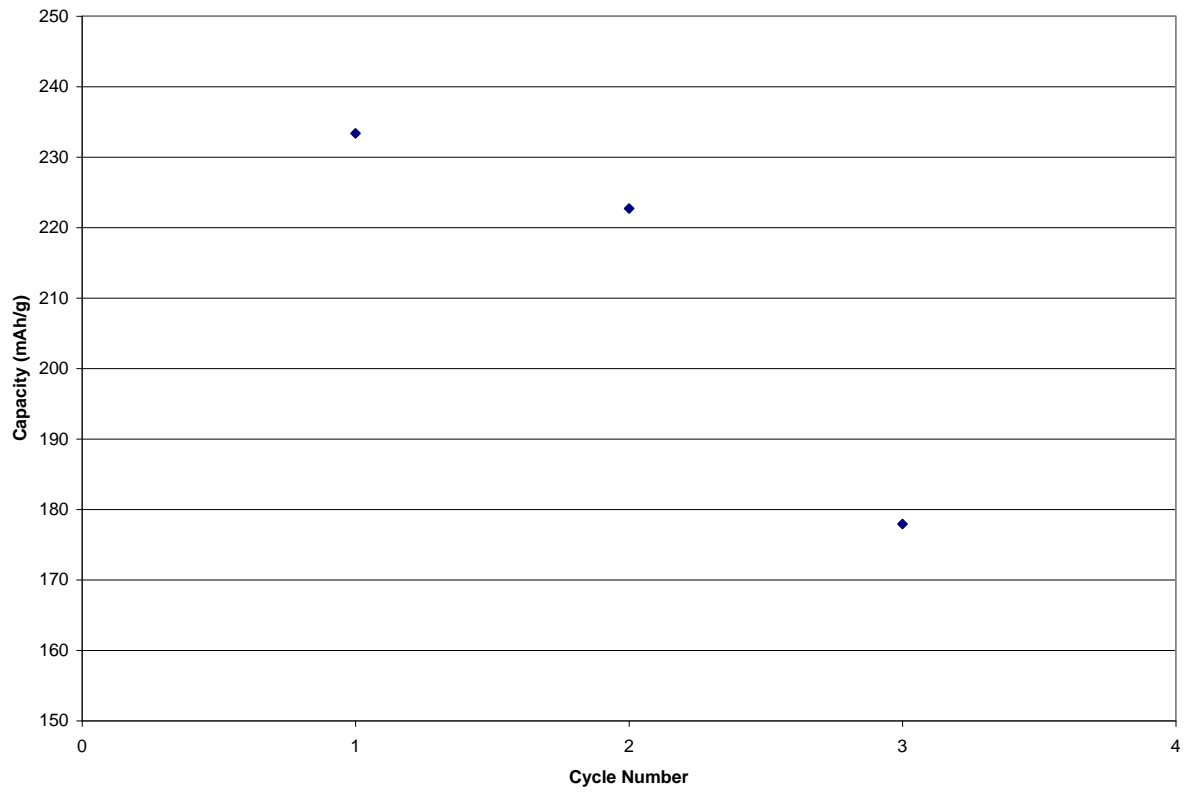
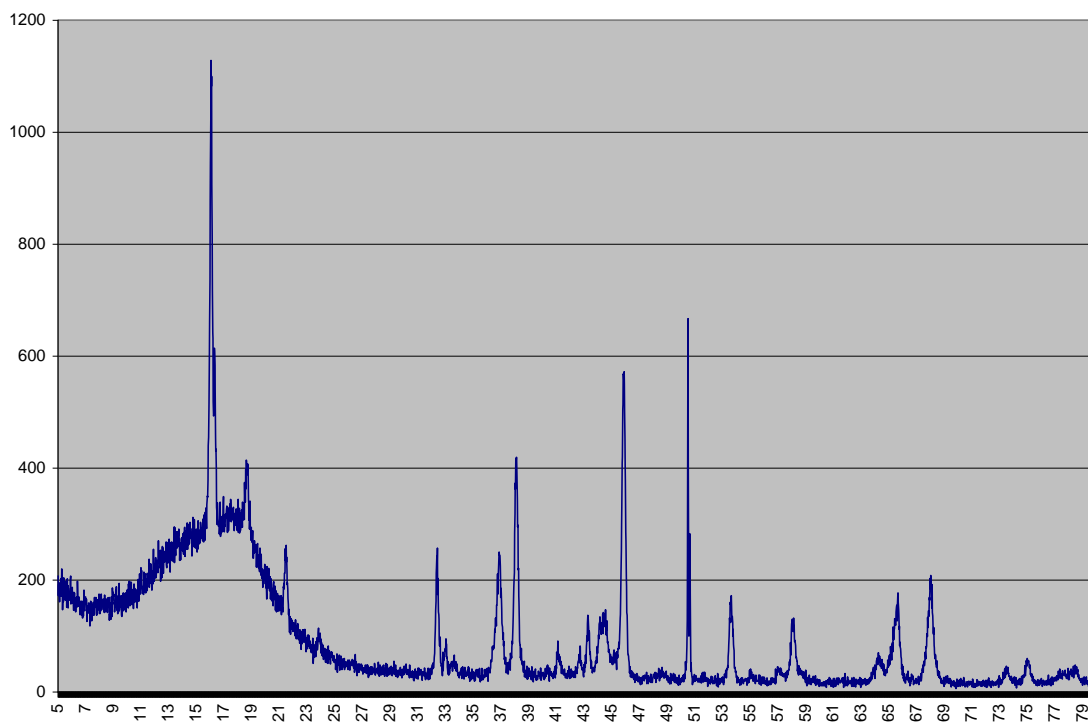


Figure 6: Cycling data from battery made of ion exchange material for composition X; cycled from 2-5 volts at rates ranging from C/16 to 2C.

Fi

(a)



(b)

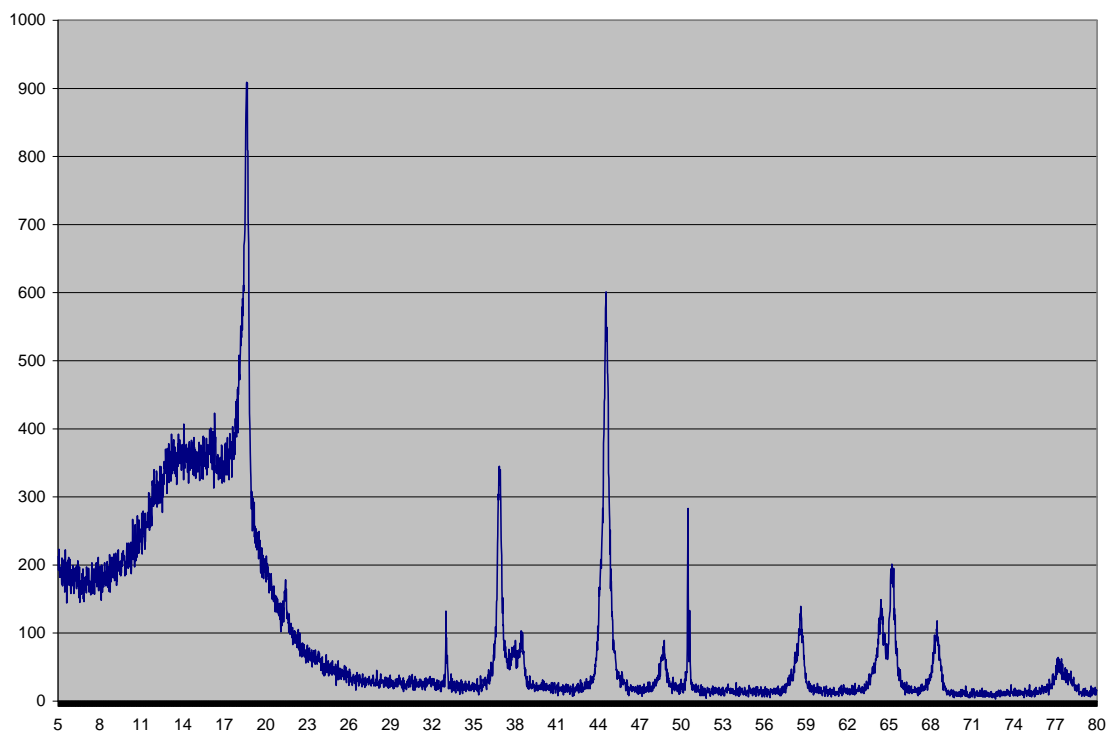


Figure 7: (a). XRD pattern for material of composition Y before ion exchange. (b). XRD pattern for material of composition Y after ion exchange.

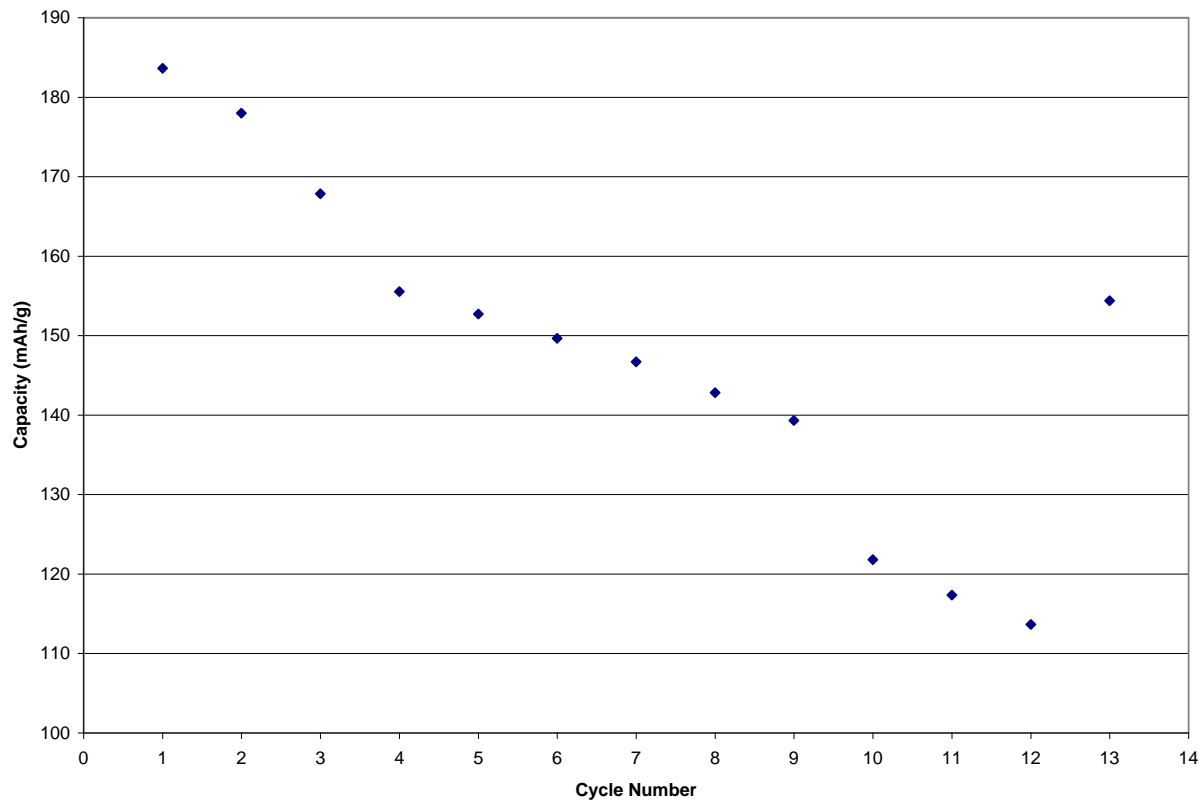
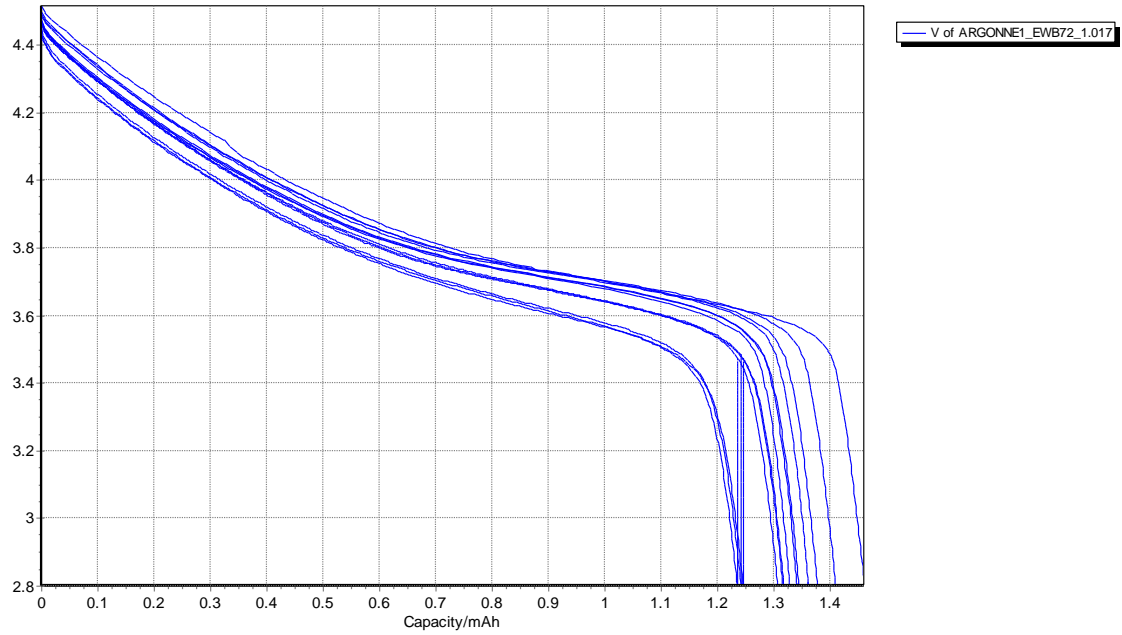


Figure 8: Cycling data from battery made of ion exchange material for composition Y; cycled from 2-5 volts at rates ranging from C/16 to 2C.

(a)



(b)

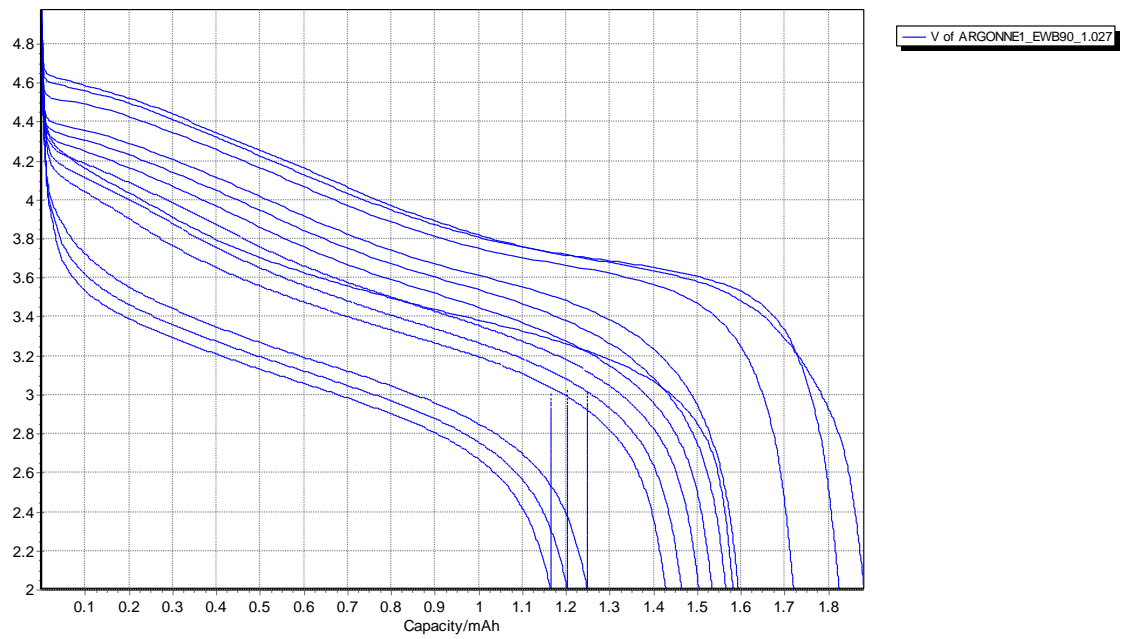


Figure 9: (a) Voltage profile for baseline material made from composition Y (slowest rate =  $C/6$ ; fastest rate =  $C$ ). (b) Voltage profile for ion exchange material made from composition Y (slowest rate =  $C/11$ ; fastest rate =  $C$ ).