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A Hybrid Lithium ion Energy Storage System using Aqueous Electrolyte Solution

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Abstract: We can make much safer and cheaper Lithium-ion batteries by using aqueous electrolyte when compared to today's commercial cells which use organic electrolytes. In this work, an aqueous hybrid storage system consists of LiCoO_2 as cathode and Vulcan carbon as anode in an aqueous electrolyte solution of LiNO_3 (5 M), is studied using electrochemical experimentations. The electrochemical behavior of electrodes and cell are studied in neutral aqueous electrolytes using cyclic voltammetry (CV), galvanostatic charge-discharge. This system has shown 110 mAh/g specific capacities at a charge rate of 1C, but poor capacity is observed after 40 cycles. This low cycle life is reported as the common problem in ARLBs by many research groups. Solving the low voltage and poor cycling capacities of ARLBs will address many problems of present large scale energy systems.

Key words: ARLB, Batteries, Energy storage, Electric vehicles, and electrode materials.

I. INTRODUCTION

Energy storage devices are very essential, for the storage of energy from the large scale renewable resources and electrical vehicle applications. Lithium-ion (Li-ion) battery with organic electrolyte has been used widely in many electronic devices, as power storage devices for renewable energy and energy sources in electric vehicles in recent times. They offer high energy capacity, longer lifetime and light weight compare to other secondary batteries such as the nickel-cadmium, lead acid and nickel-metal hydride batteries. Despite the superior performance of organic Li-ion batteries, safety concerns and high fabrication cost have been a big drawback and limiting the usage of these batteries in many applications especially in electrical vehicles and large scale energy storage applications[1].

One of the major issues with organic electrolyte based Li-ion battery is safety. Flammable organic electrolyte is responsible for the high risk of safety incidents in LIBs. The thermal runaway caused by the reactivity of the electrode materials with electrolytes is major safety issue in lithium-ion batteries with organic electrolyte. The cost of organic electrolyte Lithium-ion battery is relatively high due to the requirement of a strictly dry environment conditions during assembly processes of the cell, and it is also attributed to the high cost of organic electrolytes, transition metals, and lithium salts. Furthermore, the limited ion conductivities of the organic electrolytes require

battery designs with thin electrodes for high power and energy efficiency. All of the above problems are responsible for low manufacturing of lithium-ion batteries in our country.

Most of these problems can be solved by using aqueous rechargeable Lithium batteries (ARLB) [1]. That is by using aqueous electrolyte in the place of organic electrolyte in Li-ion battery. They are alternative source of energy storage for large-scale applications, which can resolve many challenges of organic electrolyte lithium ion batteries: (i) fundamentally the safety issue of flammable organic electrolytes can be resolved, (ii) the electrolyte solvent and salts are much cheaper, and (iii) aqueous electrolyte is having higher ionic conductivity compared to organic electrolytes, resulting in high energy density and better round-trip efficiency [2,3]. In addition, they are environmental friendly as they are aqueous electrolyte.

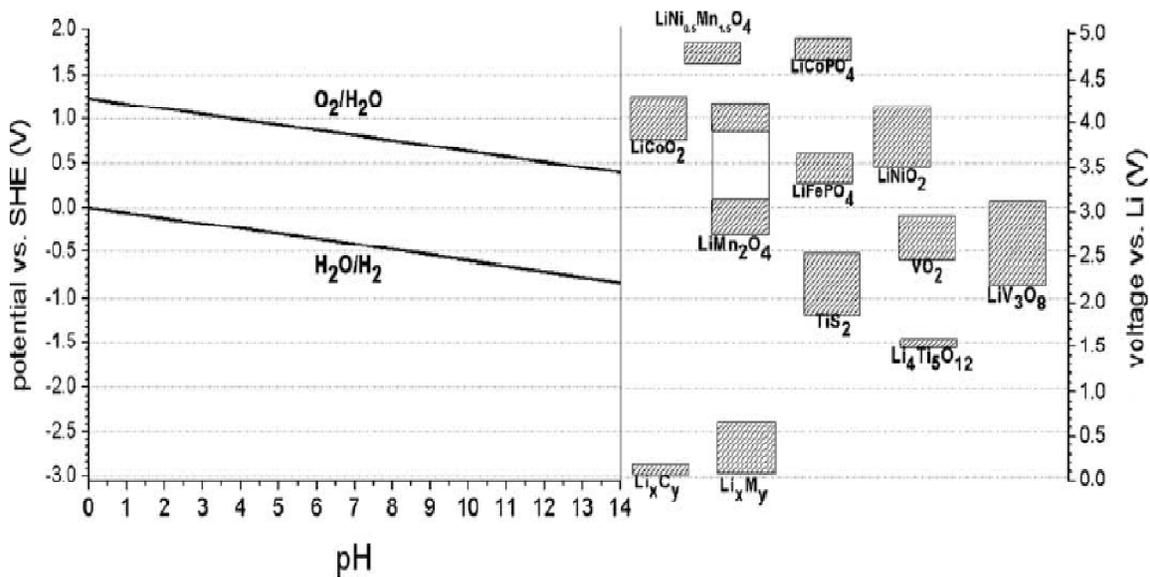


Figure 1: Water stability window and reaction potentials of lithium in LIBs

The overall electrochemistry of ARLBs is identical to that of the conventional rechargeable battery system based on organic electrolytes. However the stable voltage window is narrow for aqueous electrolytes when compared to the organic electrolytes used in the conventional LIBs. The intercalation potential range of the electrode should lie within the electrochemical stability windows of the aqueous electrolyte to allow the reversible reaction of Li ions into/from the host of electrode materials in water, [5-8]. In Fig. 1 we can see a Pourbaix diagram which shows both the theoretical water stability range, and its pH dependence. It also gives details about the operating potentials of different lithium battery electrode materials [9-15]. The electrochemical stability window of water is about 1.23 V. The structure of lithium batteries are shown in Fig. 2, which contains cathode, anode and electrolyte as main elements.

(A) Objective of the study

Many studies have reported the necessity of anode material in ARLBs to improve the performance and to reduce the cost of batteries [12-15]. Vulcan carbon which is most commonly used in fuel cells and it is one of the good materials known for its conductivity. So, we wanted to test the employability of Vulcan carbon in ARLBs as anode material. In this work, we have tested electrochemical behavior of Vulcan carbon in aqueous LiNO_3 electrolyte. LiCoO_2 , which is most commonly used as cathode material in Li-ion batteries because of availability and performance, is used as cathode material in this study. LiCoO_2 is used as cathode material in many studies [4-6].

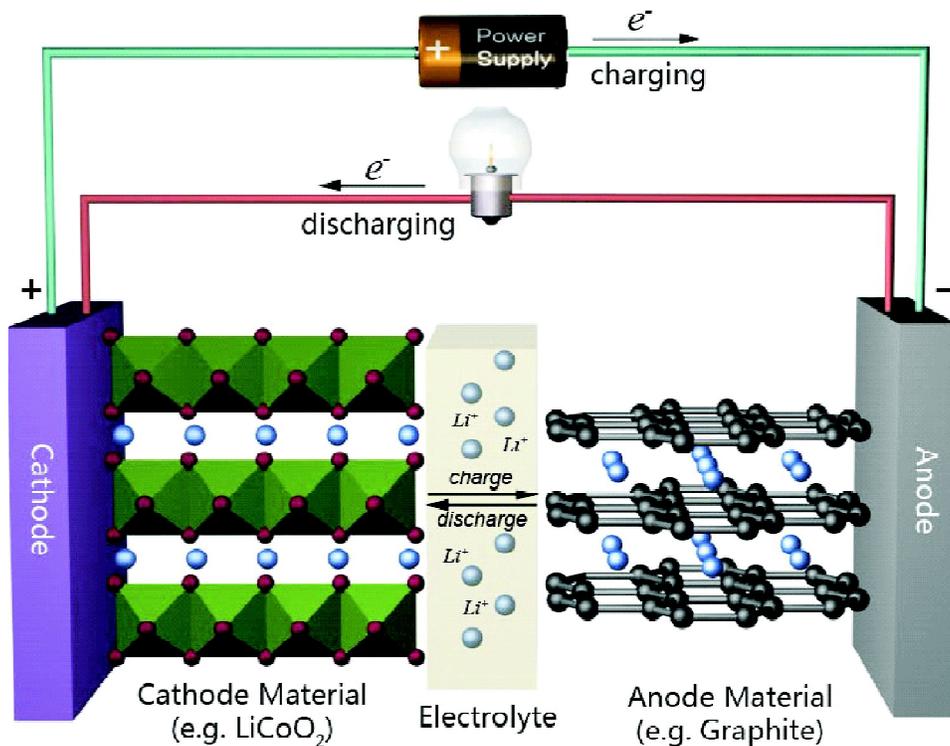


Figure 2: Structure of lithium battery with cathode and anode

I. EXPERIMENTAL SETUP

(A) Electrode preparation

Commercial LiCoO_2 powder was obtained from Aldrich and used without any further treatments. We have prepared Working electrodes by mixing LiCoO_2 powders with carbon black and an organic binder –PVDF (poly vinyl di-fluoride), in a weight ratio of 80:10:10 in NMP (n-methyl pyrrolidone), also from Aldrich. After stirring, the mixture was deposited on stainless steel mesh by coating as shown in the Fig. 3, and then dried at



Figure 3: Stainless steel mesh coated with LiCoO_2

100 °C for 1 h. The area of electrode was about 1.0 cm², and the active material's weight was typically in the range 10–15 mg for each sample.

Vulcan carbon Xc72 is used as a negative electrode. It is also prepared by similar process but electrode area is 2.0 cm² and dried at lower temperature (80 °C).

(B) Electrochemical measurements

We have used Biologic VMP3B-20 instrument as shown in the Fig. 4, to conduct Electrochemical characterizations like Cyclic voltammetry (CV) and galvanostatic cycling with potential limitation (GCPL). All the measurements in LiNO₃ (5 M) aqueous electrolytes were made in a beaker cell using a double junction Ag/AgCl (3 M KCl), a reference electrode. For convenience, all potentials will be reported vs. the standard hydrogen electrode (SHE). Platinum electrode is used as the counter electrode (CE) in the same electrolyte compartment. The CV was conducted at 0.1mV/s scan rate. The pH value of aqueous electrolyte is 7.



Figure 4: Electrochemical workstation connected to cell

II. RESULTS AND DISCUSSION

To study the electrochemical behavior of LiCoO₂ in the lithium nitrate aqueous solutions, we first conducted cyclic voltammetry experiments from 0.4 to 1.11 V vs. the SHE using LiNO₃ (aqueous electrolyte) of 5.0 molar concentrations and platinum is used as a counter electrode.

The intercalation and de-intercalation current peaks are observed at 0.9 V as shown in the Fig. 5. These values are taken from the research paper published by R. Ruffo et al. In this paper they have studied the LiCoO₂ behavior with platinum in the presence of aqueous electrolyte. The potential window is considered based on the stability window from the Fig. 1. explained by many researchers [6-10].

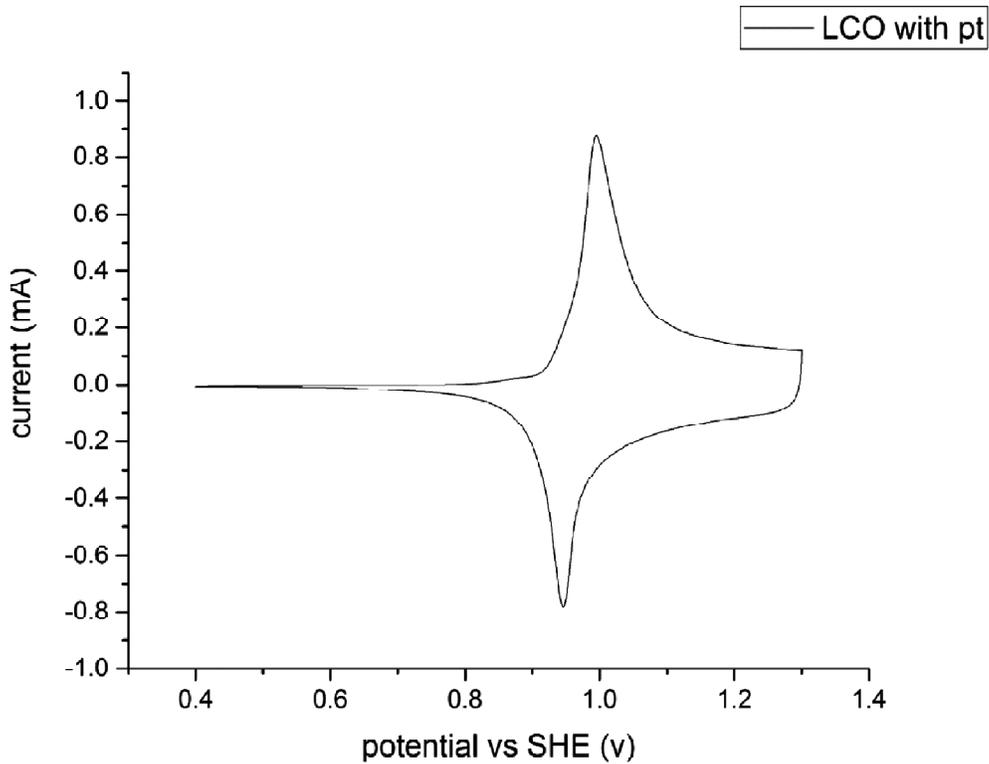


Figure 5: Cyclic voltammetry of LiCoO₂ electrode at 0.1mV/s in 5M LiNO₃ solution

The Cyclic voltammetry (CV) of Vulcan carbon is measured between -0.25 to .60 V vs. SHE to study the electrochemical behavior. This study is required to understand the behavior of Vulcan carbon at a particular potential window and also to prove the material is electrochemically active and it can be employed as an anode

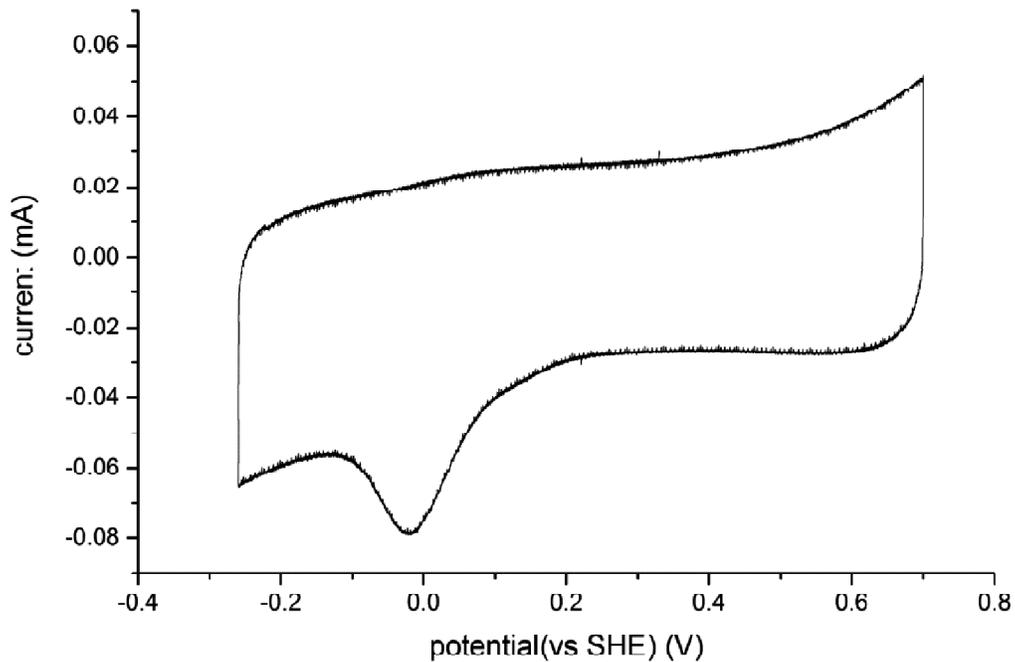


Figure 6: Cyclic voltammetry of Vulcan carbon Xc72 electrode at 0.1mV/s in 5M LiNO₃ solution

material in ARLBs. From this study, we understand that the Vulcan carbon is exhibiting electrochemical double layer capacitance behavior in aqueous LiNO_3 as shown in the Fig. 6. This CV shows no oxidation or reduction under this potential window. Hence, it can be used as an material.

To study the behavior of LiCoO_2 in aqueous LiNO_3 in presence of Vulcan carbon as negative electrode, Cyclic Voltammetry is conducted at 0.1 mV/s between 0.65 to 1.15 V vs, SHE. Maximum and minimum Current peaks are observed at 0.93 V and 1.0 V as shown in the Fig. 7. This shows the electrochemical activity of the cell between the taken potential window without any oxidation and reduction. The intercalation and deintercalation can be observed with current peaks on the both sides.

To study the charge-discharge capabilities, GCPL is performed between 0.3 to 0.93 V vs. SHE. at 1C rate, as shown in the Fig. 8. Initial charge capacity is observed to be 110 to 100 mAh/g . To test the capacity with respective number of cycles, charge-discharge is conducted for 100 cycles. Initial performance of the cell is really impressive but gradual drop in capacity is observed as shown in the Fig. 9. Many research groups have reported the poor cycle life performance of the aqueous rechargeable batteries. This is attributed to the electrochemical instability of the aqueous electrolyte and decomposition of active material in aqueous electrolyte. During the intercalation and deintercalation li-ions moves from cathode to anode through electrolyte, some of the li-ions are lost during this process because of chemical reaction between aqueous electrolyte and li-ions. This may be the one of the reason for the very poor cycling performance of the cell.

II. CONCLUSION

Insertion and extraction of lithium can readily occur in LiCoO_2 (positive electrode) in LiNO_3 (aqueous electrolyte)aqueous solutions using a three-electrode cell with a Vulcan carbon negative electrode. At salt concentrations of 5 M the kinetics are very fast, and the initial capacity is good when compared to organic electrolyte lithium batteries. But its poor cycling performance is observed, reasons for this may be decrease in

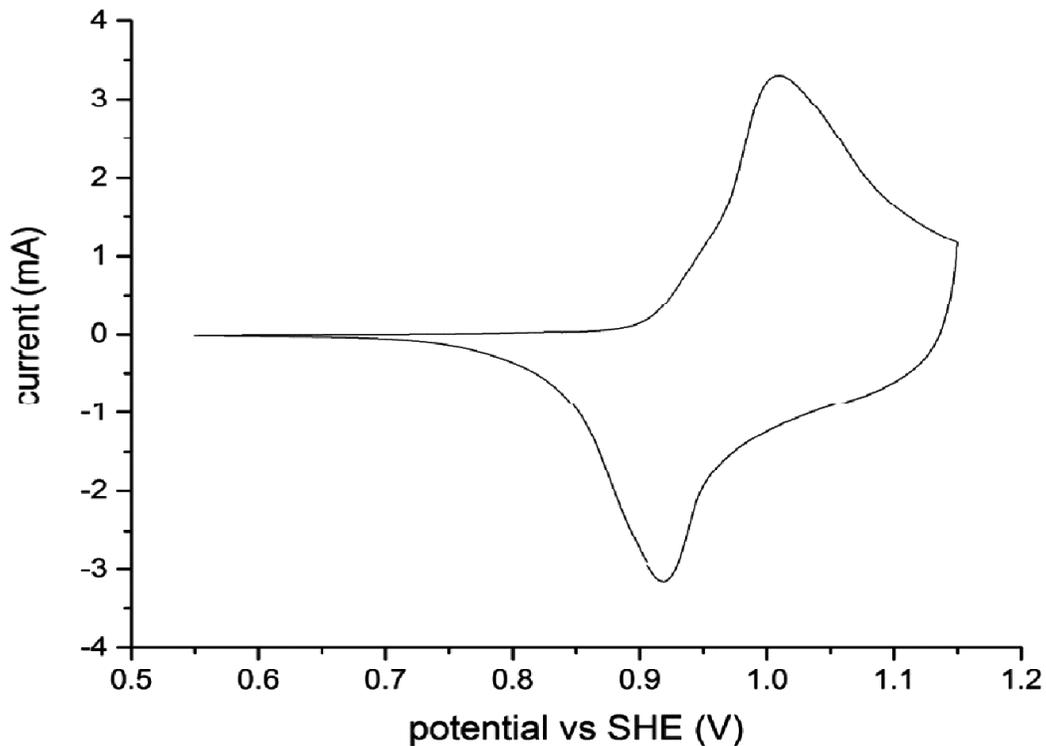


Figure 7: Cyclic voltammetry of LiCoO_2 electrode at 0.1mV/s in presence of Vulcan carbon as negative electrode

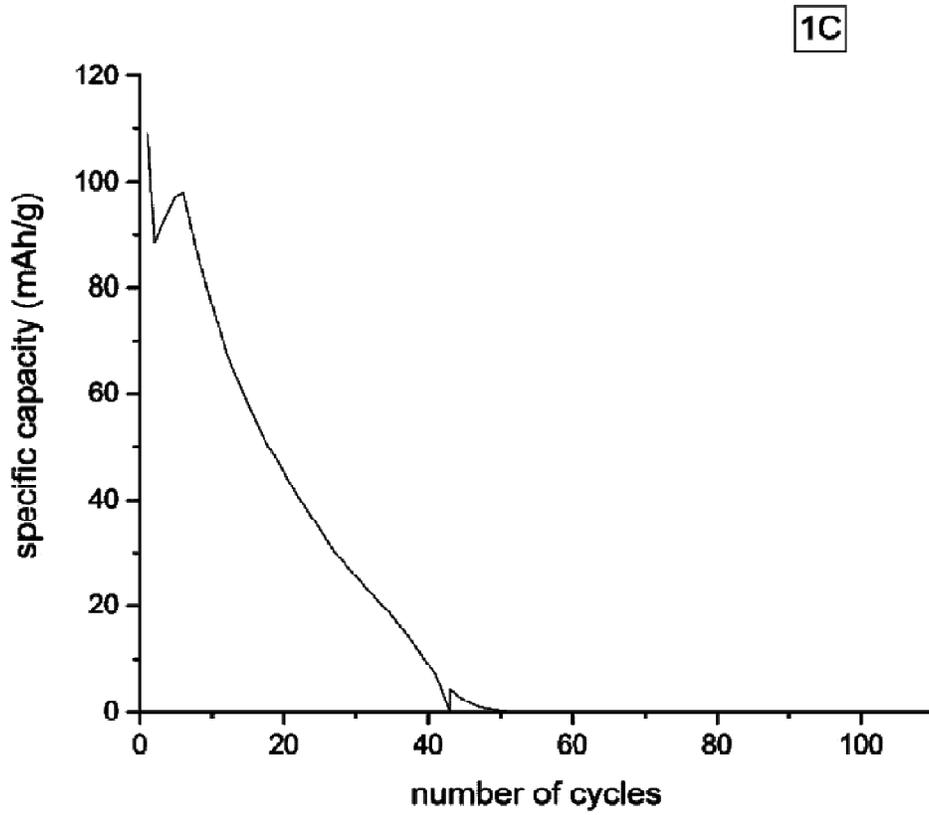


Figure 8: Charge-discharge curve for first cycle at 1 C rate

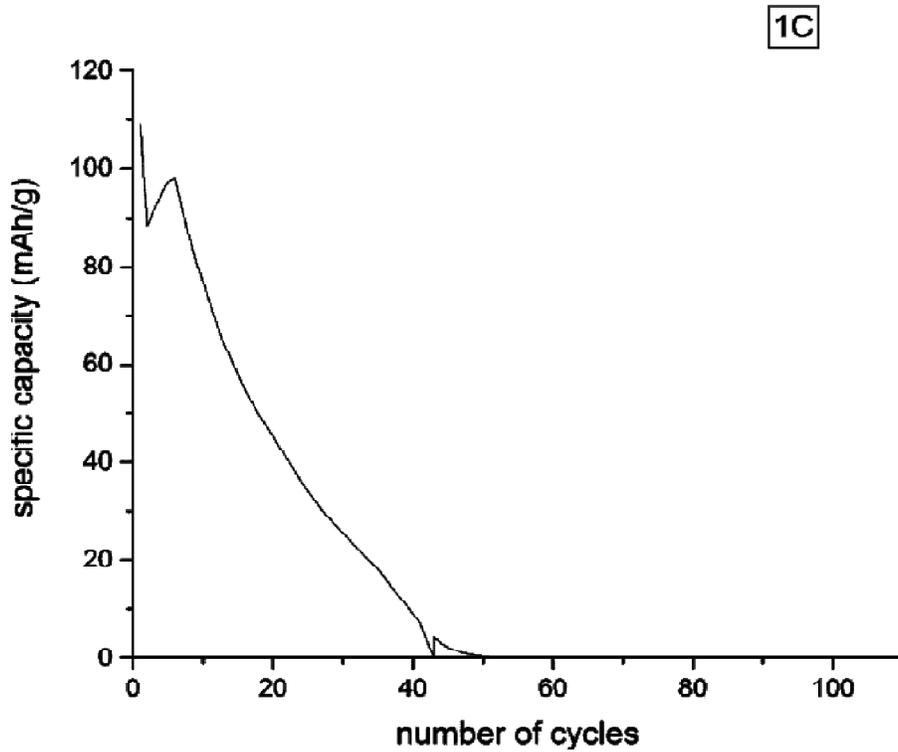


Figure 9: Capacity trend vs. number of cycles at 1C rate

lithium concentration, reaction of lithium with electrolyte. Further more research should be carried out to make aqueous rechargeable lithium batteries more efficient. This study shows the electrochemical behavior of the Vulcan carbon and its possible usage of Vulcan carbon as an anode in ARLBs.

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