EFFECT OF DIFFERENT CURRENT COLLECTORS IN Mg BATTERY WITH CONVENTIONAL PEO BASED GEL POLYMER ELECTROLYTE

H.N.M. SARANGIKA.[1*], M.A.K.L. DISSANAYAKE[3,4], G.K.R. SENADEERA[2, 3], J.A.K. SAMPATH[1] AND T.T.M. PERERA[1]

[1]*Department of Physical Sciences and Technology, Sabaragamuwa University of Sri Lanka, Belihuloya, Sri Lanka.*
[2]*Department of Physics, The Open University of Sri Lanka, Nawala, Nugegoda, Sri Lanka.*
[3]*National Institute of Fundamental Studies, Kandy, Sri Lanka.*
[4]*Postgraduate Institute of Science, University of Peradeniya, Sri Lanka*

Corresponding Author, e-mail: *sarangikah@gmail.com*

ABSTRACT

The electrochemical behavior and stability of several current collectors such as Copper(Cu), Nickel(Ni), Stainless Steel(SS), Aluminum(Al), Compressed Carbon(Comp C) and Fluorine doped Tin Oxide (FTO) potentially employed in magnesium batteries have been investigated with non-aqueous gel electrolyte. Polyethylene oxide (PEO) complexed with magnesium triflate (MgTf or $Mg(CF_3SO_3)_2$), Ethylene Carbonate(EC) and Propylene Carbonate(PC) was used as Gel Polymer electrolyte(GPE). The electrochemical stability of the polymer electrolyte Vs different current collector has been examined by linear sweep voltammetry (LSV). A battery of the configuration Mg/PEO:$Mg(CF_3SO_3)_2$:EC:PC/TiO_2-C/Different current collectors was assembled and characterized using Open Circuit voltage, constant load discharging measurements and charge/discharge cycles. Preliminary studies showed that Copper, Nickel, and Aluminum, widely used in the literature as a current collector is not stable for magnesium batteries using PEO:$Mg(CF_3SO_3)_2$:EC:PC electrolyte at potential above 1.8 V. Fluorine doped Tin Oxide, Compressed Carbon and Stainless Steel were found to be electrochemically stable in this electrolyte. Among the current collectors studied, FTO exhibits excellent stability up to 3.0 V in the electrolyte and is a good candidate for current collector in Magnesium batteries.

1. INTRODUCTION

Electrical energy must be available for 24 hours a day to meet the continuous energy demand and for this, a greatly improved and reliable electrical energy storage system is required. Batteries are devices used to convert chemical energy directly to electrical energy and they are the leading energy storage technologies today that are capable of releasing a flow of charge when required. Rechargeable battery (secondary battery) technology is the most promising because the chemical reaction employed to generate electricity is reversible. Rechargeable batteries are being developed by researcher in past few decades. At present, most commercial rechargeable battery types are Li – ion and Li – Po (Lithium Polymer) batteries [1-3].

The major challenges of developing Li ion batteries are performance, safety and cost. Problems such as dendritic deposition of Lithium, growth of passive layer on Lithium surface leads to poor rechargeability of the Li anode based battery. Additionally Lithium is high reactive towards oxygen and humid, so this is also an important factor to concern. Limited availability of Li as poorly accessible forms is another challenge in the Li-ion battery system.

Magnesium is positioned next to the lithium in the periodic table and its electrochemical properties are comparable with Li. Due to its higher volumetric capacity and lower cost (3862 mAh cm^{-3} and \$270/ton respectively for Mg metal anode) compared with Li metal anode, (2062 mAh cm^{-3} and \$64800/ton respectively) Mg rechargeable batteries can be considered as one of the most promising alternative to the current battery technologies [4]. Despite these attractive attributes of Mg batteries, there are several challenges pertaining to the use of cathodes, electrolytes, anodes, and current collectors. Extensive research has focused on the development of a feasible system for rechargeable magnesium-ion batteries, including identification and development of new insertion/extraction cathode materials, new anodes and a variety of electrolytes [5-7].

Compatibility between current collectors and electrolyte, particularly the stability of current collectors, is an important factor for designing a rechargeable battery with a long cycle life. Therefore, in this paper we have reported a fundamental study of electrochemical behavior of current collectors in PEO/EC/PC/MgTf electrolyte.

2. EXPERIMENTAL

The electrolyte used for the Mg battery was prepared according to the following receipt. 0.12 g of Magnesium Trifluoromethanesulfonate ($Mg(CF_3SO_3)_2$) was dispersed in 0.3 g of propylene carbonate (PC), 0.3 g of ethylene carbonate (EC) and the mixture was stirred for few minutes for complete dissolution. Then, 0.1 g of PEO was added to this solution and the mixture was heated up to 80°C under continuous stirring until a homogeneous viscous gel is formed. This viscous gel was then allowed to cool down to room temperature.

The electrochemical stability of the GPEs was investigated by linear sweep voltammetry to measure the breakdown voltage for the electrolyte so that it can withstand the operating voltage in the battery system. The measurements were carried out using Current collector/GPE/Mg cell. During LSV analyses conducted on the selected current collectors, the scan potential was controlled from open circuit potential (OCP) to 3.0 V. The three-electrode cell consisted of a working electrode (Cu, Ni, SS Al, SS, FTO and compressed carbon), a counter electrode (Mg), a reference electrode (Mg), and the PEO:$Mg(CF_3SO_3)_2$:EC:PC electrolyte.

A powder mixture (0.2 g) of 80wt% TiO_2, (0.025 g) of 10 wt% carbon powders, (0.025 g) of 10%Pvdf and few drops of acetic acid were thoroughly ground with ethanol. This mixture was used to prepare the 5 mm diameter and two tape thickness pellet on different current collectors Copper(Cu), Nickel(Ni), Stainless Steel(SS), Aluminum(Al), Compressed Carbon(Comp C) and Fluorine doped Tin Oxide (FTO) and then sintered at 450 °C for 45 minutes. The weight of the prepared TiO_2 electrode was 1 mg. The weight of the magnesium pellet used as the anode was 0.07 g.

The cells with the configuration, Mg/PEO:EC:PC: $Mg(CF_3SO_3)_2/TiO_2$-C/different current collectors were assembled and tested their open circuit voltage and discharge plot under 100 kΩ load.

3. RESULTS AND DISCUSSION

Fig.1 shows the linear sweep voltammetry for the cells containing different current collector/GPE/Mg. From the graph, it can be observed that there is a very low background current measured in a potential region between 0.5 and 3.0 V for SS, FTO and compressed carbon. The small current might be attributed to the change of the current collector surface. Cu and Al which are widely used as current collectors for Mg ion battery show significant electrochemical corrosion in the voltage range 1.80–2.40 V. At higher voltage the current began to flow and increased rapidly upon reaching the cut-off voltage indicating that the electrolyte decomposition process has taken place [8, 9]. Ni current collector shows different electrochemical behavior against the PEO based gel electrolyte.

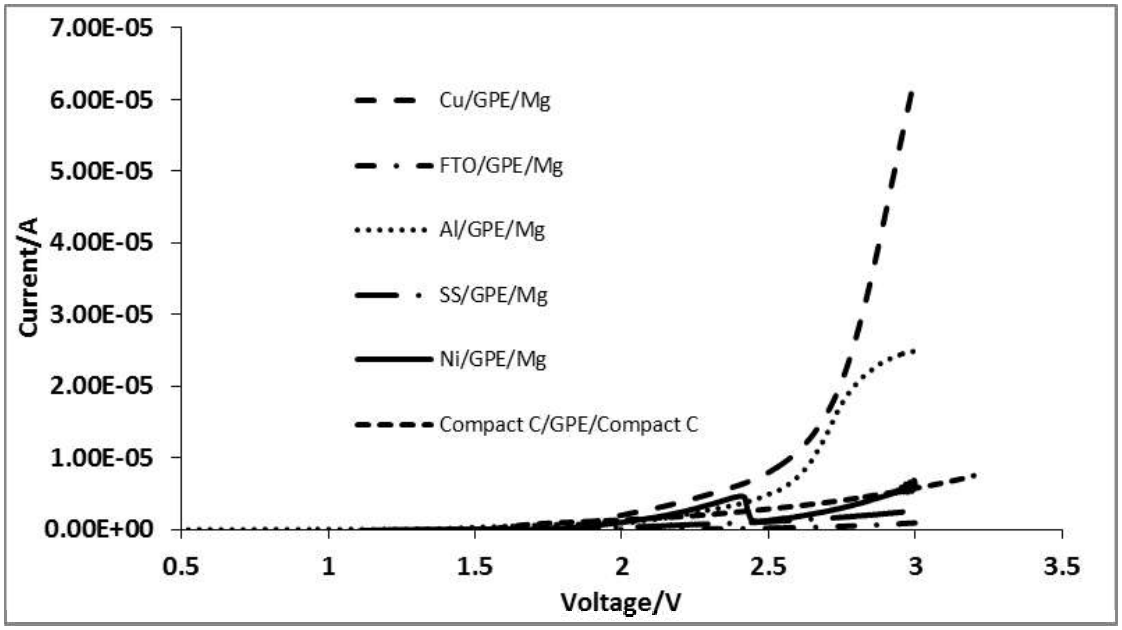

Fig.1. Linear sweep voltammograms of Copper(Cu), Nickel(Ni), Stainless Steel(SS), Aluminum(Al), Compressed Carbon(Comp C) and Fluorine doped Tin Oxide (FTO) in PEO:EC:PC: $Mg(CF_3SO_3)_2$ electrolyte within the potential range between 0.5 V and 2.4 V (vs. Mg2+/Mg) collected at a voltage scan rate at 1 mVs^{-1}.

To better understand the electrochemical behavior of Ni in the present electrolyte, CV analyses were also performed using Ni as the working electrode [10]. Fig.2 shows the first CV cycle obtained from 0.5 V to 3.0 V using a Ni working electrode and PEO:EC:PC: $Mg(CF_3SO_3)_2$ electrolyte. As shown in Fig.2, during the first positive scan, the anodic current was observed beginning from 1.8 V and there was an oxidation peak at 2.4 V, which is consistent with the LSV analysis. Beyond 2.4 V electrochemical corrosion can be clearly observed.

The decomposition voltage is higher for SS, FTO and compressed carbon electrodes compared with Al, Cu electrodes. This shows that SS, FTO and compressed carbon current collectors are more electrochemically stable as the capability of the polymer electrolyte to withstand at high voltages. As rechargeable batteries generally operate between 3.0 V and 4.5 V, it can be concluded that SS, FTO and compressed carbon are suitable to be used as current collectors in rechargeable magnesium battery [11].

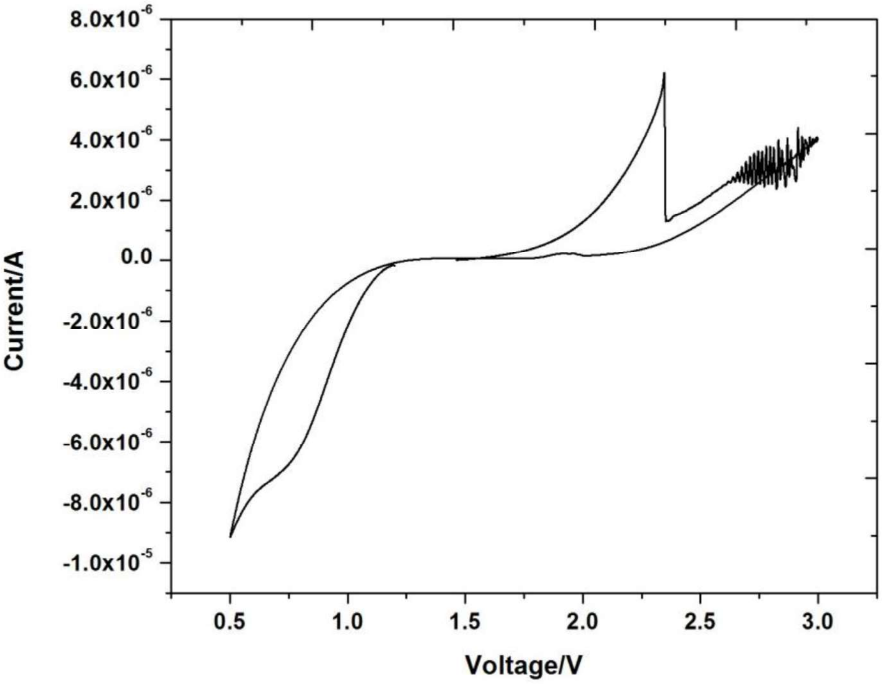

Fig.2. Cyclic voltammograms of a Ni electrode in PEO:EC:PC: $Mg(CF_3SO_3)_2$ electrolyte within the potential range of 0.5–3.0 V (vs. Mg^{2+}/Mg) collected at a voltage scan rate of 1 mVs^{-1}.

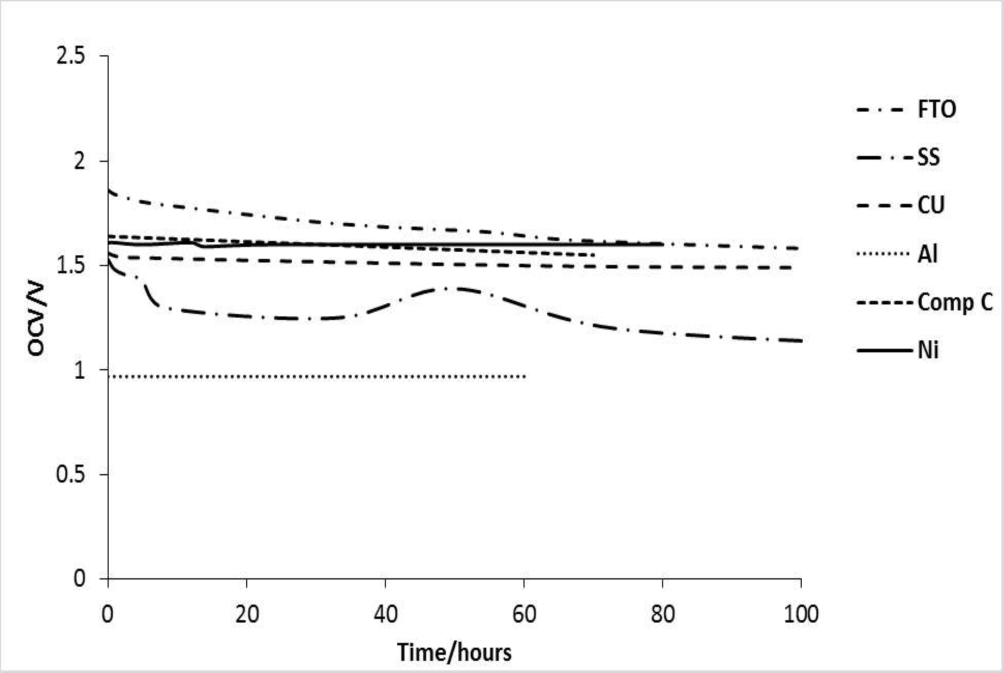

Fig.3. Open circuit voltage of Mg/Electrolyte/TiO_2-C cell during 80 hours of storage.

The applicability of the current collector to rechargeable magnesium battery system has been examined by fabricating a prototype cell. For the cathode material of the cell, TiO_2 based mixture was coated on different current collectors. Prepared cathodes were used to assemble a battery with the configuration Mg/PEO:EC:PC: $Mg(CF_3SO_3)_2/TiO_2$-C/different current collectors and open circuit voltage (OCV) was observed (Fig.3). The highest OCV was observed for the FTO while Al which is widely used as a current collector in Mg battery reported the lowest OCV. Due to the cell formation reaction at the electrodes the initial drop in the voltage of the cell after fabrication has been observed for FTO. However, the OCV was stabilized at 1.5 V after 60 hours. Ni and compressed carbon showed stabilized OCV throughout the 120 h duration.

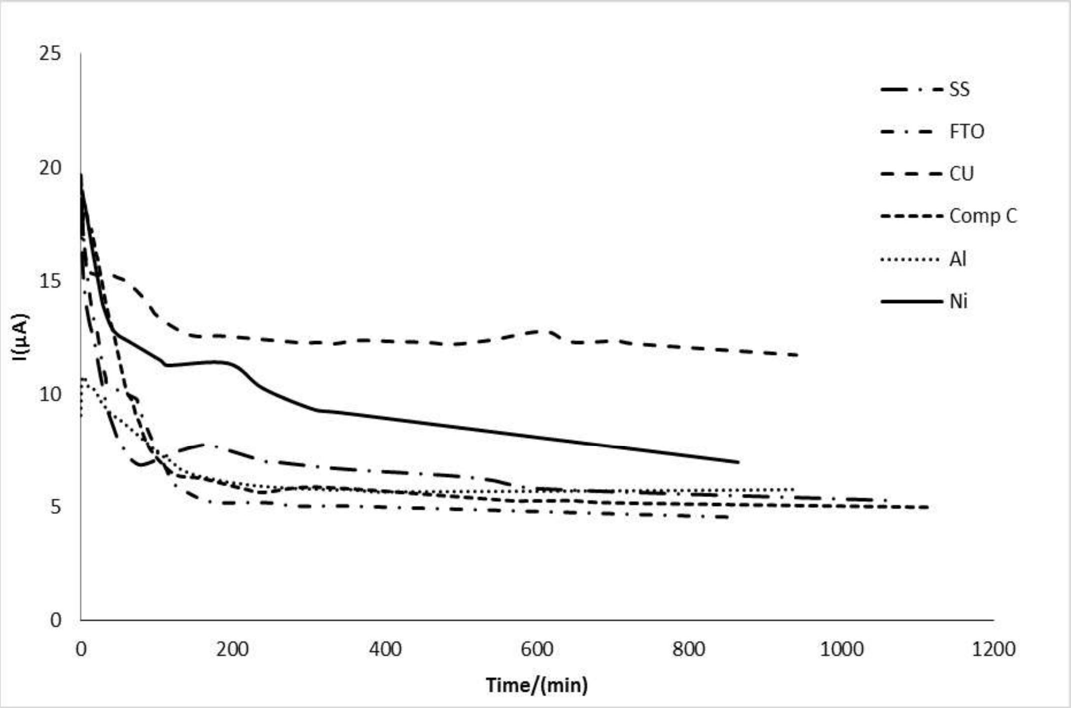

Fig.4. Discharge characteristics for Mg/PEO:EC:PC: $Mg(CF_3SO_3)_2/TiO_2$-C cell under 100 kΩ load.

Fig.3. shows the discharge characteristics of the cell Mg/PEO:EC:PC: $Mg(CF_3SO_3)_2/TiO_2$-C/different current collectors with constant load. It shows that the discharge was sustained for nearly 15 hours for 100 kΩ . Since Cu, Ni, Al, and SS are not stable in the electrolyte, these current collectors undergo oxidation and corrosion while discharging.

4. CONCLUSION

Electrochemical corrosion of Cu, Al and Ni occur in the potential range of 1.80–2.50 V (vs. Mg2+/Mg) and SS, FTO and compressed carbon exhibit electrochemical stability up to 3.0 V in the electrolyte. Open circuit voltage measurement and discharge plot further confirm this corrosion and reactions of the current collector with electrolyte. Among the current collectors studied, FTO and compressed carbon exhibit excellent stability up to 3.0 V in the electrolyte and are good candidate for current collector in Magnesium batteries.

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