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Fabrication of Magnesium ion Rechargeable Battery Using Dolomite as the Cathode Material

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ABSTRACT

Nowadays, Magnesium ion batteries have become a popular subject in the field of rechargeable cells. Due to the exhaustion of Lithium resources and vast availability of Magnesium deposits compared with Lithium resources, Magnesium is currently emerging as a substituent. One of the natural resources enriched with Magnesium is dolomite which is an abundant mineral in Sri Lanka bearing Calcium and Magnesium carbonates. But it is mostly utilized in construction industry at present.

In this study, a rechargeable battery constructed using dolomite as the cathode, Magnesium metal as the anode with $MgCl_2$ based electrolyte is presented. The procedure of cell fabrication, preparation of electrolyte and characterization of dolomite based rechargeable battery have been investigated. The functionality is based on the interchange of Mg^{2+} ions during charging and discharging process where open circuit voltage and short circuit current recorded for this dolomite cell were 0.89 V and 0.13 mA respectively. In addition, the charging current was 0.5 mA and discharging current was maintained at 0.1 mA. The total discharge capacity of the dolomite cell was found to be about 1.492 mA h g^{-1}.

1. INTRODUCTION

Rechargeable batteries have shown greater potential in the evolution of technology with energy storage for a wide range of applications from small to large scale [1]. Yet, there is a need for economical, faster charging, ecologically favourable battery with high capacity as there are concerning issues such as safety, efficiency and cost in widely used Lithium-ion batteries (LIB) as well [2].

Hence, the development of new battery systems has become an unavoidable research challenge with multi-valent ion batteries as there is limited and uneven distribution of Lithium resources in the earth's crust (0.002%). Among the candidates, Magnesium seems to be a favourable substitute as it has a similar ionic radius compared to Lithium (Li =0.76 Å, Mg = 0.72 Å) with 1.35% abundance in the earth's crust. Even its oxidative stability is higher than Lithium [3].

Magnesium (Mg) is mostly originating in huge deposits of magnesite ($MgCO_3$), dolomite ($MgCO_3 \cdot CaCO_3$), brucite ($Mg(OH)_2$) [4]. Among them, dolomite has been identified as the most common Mg rich mineral which is readily available in Sri Lanka. It can be used as a potential electrode material constituent for Mg rechargeable batteries.

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A specific rechargeable battery cell was fabricated using dolomite cathode and Mg metal anode in this study. It was a research attempt which was aimed to produce a Mg ion rechargeable battery with low cost, safe and ecologically friendly characteristics.

3. METHODOLOGY

3.1. Instruments and Equipment

Following are the instruments that were used for this study: electronic balance, hot plate, Potentistat/Galvanostat, Autolab FRA 32, ultrasonic cleaner, digital multimeter and necessary glassware.

3.2. Preparation of Electrolyte

In this study, Magnesium Chloride ($MgCl_2$) and Ethylene Carbonate (>99% purity) were used to prepare the electrolyte solution. $MgCl_2$ was dissolved in Ethylene Carbonate to prepare 1 M solution of $MgCl_2$ as the electrolyte solution.

3.3. Fabrication Process of Electrodes and Cells

Cathode was composed with dolomite as the active material. Activated carbon and polyvinylidene fluoride (PVDF) were added ~10% and ~15% correspondingly by weight of the active material. PVDF was indicated as binder and it was dissolved in 1- methyl-2-pyrrolidinone. The solution was heated at 50˚C on a hot plate until the solvent was completely liquified. Slurry was made by ball milling dolomite powder and activated carbon added into the above solution.

Then the slurry was coated on Aluminium foil paper and the doctor blade method was used for coating process as a thin film. The coated foil paper was dried out on a hot plate at 120˚C up to a point where the solvent totally vaporized. In this study, metallic Magnesium acted as the anode and thin film coated Aluminium foil paper was used as the cathode. A paper tissue was dipped in electrolyte and sandwiched in between anode and cathode as the electrolyte media.

3.4. Characterization of Cells

Open circuit voltage (V_{oc}) and short circuit current (I_{sc}) of the cells were measured using a digital multimeter. Charging and discharging of the cells were observed by Potentiostat/Galvanostat HA-151A and ScienceWorkshop®750 interface with a charging current of 0.5 mA and discharging current of 0.1 mA. Impedance spectroscopy (IS) was examined by using Autolab FRA 32 in the frequency range 0.1 Hz to 1 MHz and charge transfer characteristics of the cell was identified by plotting Nyquist plot.

4. RESULTS AND DISCUSSION

Figure 1 shows the charge and discharge curve of the fabricated cell with respect to 0.5 mA charging current and 0.1 mA discharging current.

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After fully charging the dolomite cell for 1 hour with 0.5 mA, the circuit voltage raised to 1.99V and the voltage of the cell dropped down to actual cell voltage of 0.8 V when it was disconnected from charging circuit. The cell was discharged with 0.1 mA at a lower C rate to achieve a higher discharge capacity. During the discharge, the cell voltage dropped gradually with time. Total specific discharge capacity of the cell was found to be 1.492 mA h g^{-1} under above conditions.

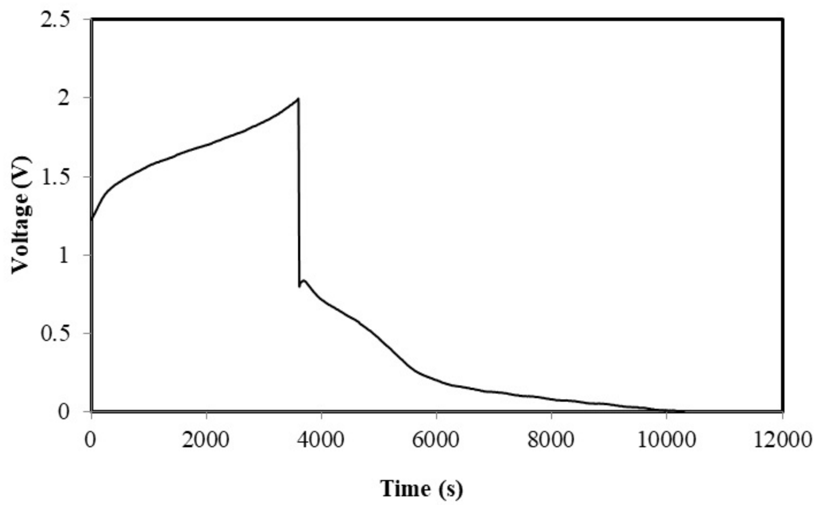

Figure 1. Charge and discharge curve of dolomite cell

Electrochemical impedance of the cell that was used to examine the movement of Magnesium ions is depicted in Figure 2. Figure 2 shows the Nyquist plot of the cell where real impedance (Z') is plotted against imaginary impedance (-Z'').

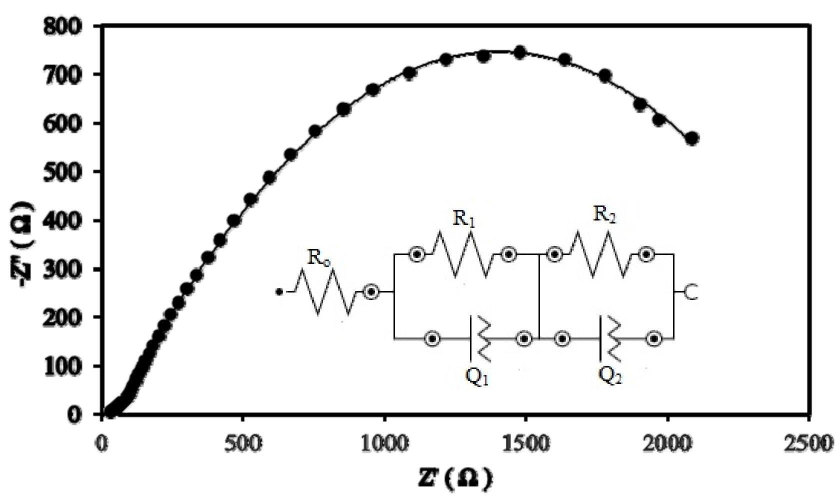

Figure 2. Nyquist plot of the dolomite cell and insert is equivalent circuit

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This impedance spectrum comprises of two uncompleted semicircles in the frequency region of 0.1 Hz to 1 MHz, which fits with the inserted equivalent circuit in Figure 2. In the circuit R_0 (23.4 Ω) value was indicated as the resistance of the electrolyte. R_1 is the charge transfer resistance against the process of electrons transfer from dolomite electrode to electrolyte and the value of R_1 was 2.58 KΩ. Q_1 is the constant phase element (CPE) which was 57.7 µMho s^N (N=0.656). In the equivalent circuit diagram, it has another part and it has acted as a secondary double layer circuit with R_2 and Q_2 values attached to the primary circuit. R_2 (96.0 Ω) has a small value compared to R_1 and Q_2 was higher (308 µMho s^N (N=0.343)) than to Q_1 due to the introduction of paper tissue which was dipped with $MgCl_2$. It supports the interchange of ions transport of both anode and cathode. According to Q values ($Q_1 < Q_2$), it shows that primary circuit has the highest impedance compared with secondary circuit part. This occurrence of the secondary circuit can be due to further electrochemical reactions occurring in between both electrodes where primary circuit is dominant with the magnitude of the values of resistance and CPE.

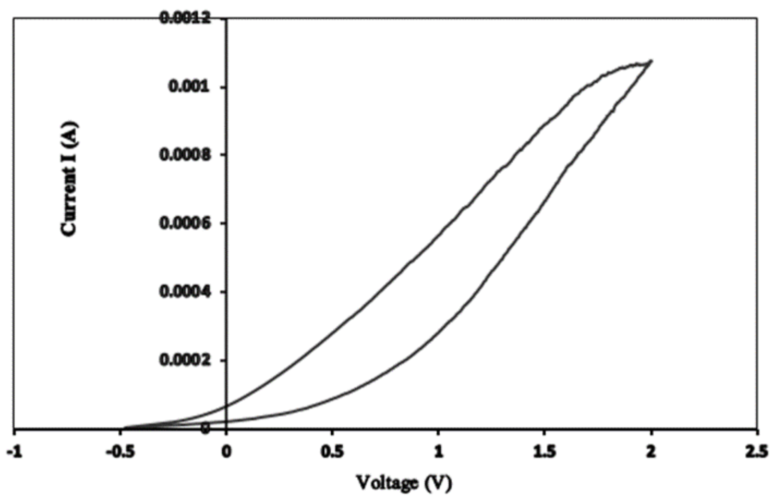

Figure 3. Cyclic Voltammetry curve obtained for the dolomite cell

Considering the cyclic voltammetry, the oxidation and reduction peaks were not clearly visible in the dolomite cell that was measured at different potential windows. Among the different cyclic voltammograms that measured at different ranges, the highest area was obtained for the -0.5 to 2.0 V range. It is possible to assume that redox reactions do not present in the device and intercalation and de-intercalation of Mg ions result the charging and discharging of the cell. This may have caused the lower capacity in the battery. Specific capacitance (C_s) of the cell was calculated using the following equation [5] using the cyclic voltammetry curve in Figure 3.

$$C_s = \frac{\int i dV}{Sm} \qquad \text{..... (1)}$$

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$\int IdV$ is the area under the cyclic voltammogram, S is the scan rate of the process and m is the mass of the anode. From the calculation it was obtained that C_s was 0.31 Asg^{-1} for a scan rate of 0.01 Vs^{-1}.

5. CONCLUSION

In this study, an investigation of Mg rechargeable battery by natural minerals was done by using dolomite as the cathode material of a rechargeable battery in the initial level. The functionality is based on the interchange of Mg^{2+} ions during charging and discharging process which was supported by the equivalent circuits drawn from the Nyquist plots. Discharging curve had 1.492 mA h g^{-1} specific discharge capacity. Specific capacitance, C_s was obtained as 0.31 Asg^{-1}. Further investigations are needed to be carried out by changing the electrolyte as the chemical reactions occurring related to functionality of this specific battery are dependent on the ion transport of Mg^{2+} ions.

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