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ORIGINAL RESEARCH

Parametric Evaluation of Li-ion Battery for Different Anode Materials

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Abstract

Activated carbons and metal organic frameworks foster the efficient use of Li-ion batteries in high-power applications. They are well-established in energy storage applications, but have not yet been incorporated into the conceptual field. This trend is expected to continue as an increasing number of researchers concentrate on energy storage concepts. The distance between theory and practice has to be narrowed, and this takes effort. Studies show that Li-ion batteries are heavily reliant on the anode materials for their capacity, rate performance, and cycle stability. Thus, improvements in anode materials are more significant than those in cathode materials when it comes to developing improved Li-ion battery. This study emphasizes on the electrochemical properties of materials derived from metal-organic frameworks (MOFs) and activated carbon, evaluating their material characteristics and notable advancements as anode materials in Li-ion battery. To better understand the design parameters of anode materials, 1D COMSOL Multiphysics modelling technique is presented and discussed along with standard literature values. Different anode materials were analyzed in terms of charge/discharge capacity, cycle life performance, surface morphology, and ac impedance value. It was found that Waste plum trunk (WPT) exhibit lower impedance under electrochemical impedance test. Also, WPT has increased current density of 0.080 mA/cm^2 more than other anode materials and provides higher mobility for Li^+ diffusion. As a whole, this study contributes to the development of simultaneous computer modelling of physical systems and electrical engineering construction in Li-ion battery with suitable anode materials for commercial and industrial application.

Key words: Parametric Evaluation, Li-ion Battery, Anode Materials, Higher mobility

1 | INTRODUCTION

In recent years, rechargeable batteries can be found in almost every household. Consumer devices such as laptops, mobile phones as well as household appliances, all make use of lithium-ion batteries, which are comprehensively utilized energy preservation arrangements at the present time. That's why they're so important to the process of digitizing our society as a whole. Constant improvements in battery technology have led to an increase in their capacity, energy, and power density. Although there is significant advancement in battery sales globally, its technology's is sometimes criticized for its lagging growth and development. Energy storage simply cannot keep up with the exponential growth of the information technology sector; according to Moore's law, memory within computers doubles every two years. The only battery technologies that stand out are those based on nickel and lithium, which have made amazing advancements in chemistry and engineering. Li-based batteries outperform several previous technologies because of their high energy density and versatility in design, which now account for 63% of the global market value for portable batteries [1]. This is the reason of being the subject of the majority of research on both the elementary and operational levels [2]. Having higher electro-positivity and being one of the thinnest and lightest metals was initially the driving force behind the use of a Li as the anode in battery technology. Also, Li battery has fewer side reactions compared to other battery systems as it intercalates or desorbs from anode or cathode materials memory effects that would eventually reduce energy density [3].

In 1970s the construction of basic Li cells, such as non-rechargeable one is the first example of employing Li metal. Their huge capacity and adjustable discharge rate made them appropriate for use in a wide variety of implanted medical devices, in addition to wristwatches, calculators, and other small electronic devices [4]. In 1972, Exxon initiated an experiment employing TiS_2 as positive electrode, lithium perchlorate in dioxolane as electrolyte, and lithium metal as the negative electrode [5][6]. At that time, TiS_2 was the most effective intercalation chemical available with its good multilayer structure. But with each consecutive discharge-recharge cycle Li metal underwent irregular (dendritic) growth in the reaction by creating a risk of explosion. In between that time Bell Labs' observation showed better capacities and voltages which led to substantial improvements in intercalation materials [7]. For the purpose to avoid the dangers associated with using Li metal, there were a number of different approaches that either adjusted the negative electrode or the electrolyte. Delays in implementing the Li-ion battery concepts are due to the scarcity of appropriate components regarding the negative electrode and the failure of electrolytes to meet the required performance parameters for a battery technology.

Compared to cathode materials, anode materials have been studied in greater depth and more options are available. The electrochemical properties of Li-ion batteries, such as their cycle charging rate, and energy density are very dependent to the anode materials used in their construction [8]. Since the introduction of carbonaceous anodes to mass production, carbon has remained the material for commercial Li-ion batteries [9]. But carbon anodes are almost at their estimated maximum power rating of 372 mAh/g after two centuries of investigation. Carbon replacements with high density of energy and improved safety are required to address the requirements for increasing energy densities, notably to meet the requirements for electric automobiles. There is another type of carbon material namely disordered carbon that also show possibility to serve as anode material. Carbons with a disordered structure have their atoms grouped in a plane hexagonal network but lack a strong long-range order. Disordered carbon typically exhibits high specific capacity but with concerns of significant, permanent capacity loss during the first cycle and capacity fading [10] [11]. There has been a lot of attention given to disordered carbon as of late, but how exactly it's high capacity can be achieved is still unanswered. Metal-organic frameworks (MOFs) are a kind of crystallographic porous materials that have received attention as a candidate of electrode for lithium-ion battery because of their enormous specific surface area, high porosity, and high lithium storage ability [12] [13]. The potential application of metal-organic framework (MOF) in electrochemical applications recently caught the attention of many scientists across the globe [14]. Their increased surface area is a key contributor to their superior electrochemical characteristics.

MOF structures have a greater surface area than many traditional porous materials that are appropriate for electrochemical applications, with values ranging from 1000 to 10,000 m^2g^{-1} [15]. The size of the pores is also crucial. The typical pore size is 9.8 nm but it is very adjustable since the length of the organic ligand surrounding the metallic core determines the pore size[16]. Some names of MOF electrode materials are Fe-MIL-88B, Fe-MIL-100, CAU-10H, Co-BDC, Co-MOF etc. Researchers have synthesised MOFs using several synthesis techniques selected from a broad range of active metals and novel organic linkers, contributing to their flexibility in electrochemical applications[17][18]. With the introduction of MOF materials, Li-ion battery electrode chemistry research was given a fresh start. Following this trend, in this work we have chosen alternative anode materials such as MOF and biomass derived activated carbon in Li-ion battery to evaluate its electrochemical performance.

2 | DEVICE STRUCTURE AND SIMULATION

For modelling and simulating physics-based problems, COMSOL Multiphysics is a framework for doing the analysis of finite elements. It is based on the latest mathematical approaches. Coupled or multi physics phenomena in various fields can be resolved using COMSOL Multiphysics. In this work, COMSOL simulation tool has been chosen for modelling Li-ion battery due to its efficient speed and reliability which is proven by the previous researchers [19]. By providing an intuitive and comprehensive interface, the battery model can be constructed with less effort and in less time than would be required in traditional numerical synthesis and solving software. In this work, we have used one dimensional interface for modelling Li-ion battery. The interface is divided into three parts as shown in Figure 1

Figure 1: Domain region of the battery model

Here domain 1 is negative electrode, domain 2 is electrolyte and domain 3 is positive electrode. Both electrodes are porous type and follow porous electrode theory. Though electrolyte is applied only in domain 2, it is associated with both positive and negative electrodes. For positive electrode material we have used LMn_2O_4 and for negative electrode we have used waste palm trunk (WPT), Mangrove Activated Carbon, MIL-100(Fe), CAU-10H and Aluminum Fumarate. All the parameter values of the materials are declared in the global parameter section of Comsol Multiphysics interface. As the battery model cross section is one dimensional the edge effect of thickness and height of the element are neglected. Length of the domain is mentioned in Table 1

Table 1 Dimension of the model

Description	Lengths (um)
Negative Electrode	100
Electrolyte	52
Positive Electrode	174

The model established for this study is a full cell battery consisting of $LiMnO_4$ as a positive electrode with a polymer electrolyte of LiPF6 in 1:2 Ethylene carbonate (EC): Dimethyl carbonate (DMC) ratio and negative electrode. One of the advantages of using Comsol is that different types of materials can be added from its built-in node or manually material parameter can be added as input. For our study we have manually added negative electrode waste palm trunk (WPT), Mangrove activated carbon, MIL-100(FE), CAU-10H and Aluminum Fumarate and their material properties are inserted from different literature [20]-[23]. For the basic model we have used some parameters presented by the 1D isothermal model. Different types of parameters used to make this model are listed below in the Table 2

Table 2 Input parameter for anode materials

Material Name	Specific surface area(m^2/g)	Pore width (nm)
Waste palm trunk (WPT)	2927	1.68
Mangrove-AC	2924	1.42
MIL-100(Fe)	1634	11
CAU-10H	477	6
Aluminum Fumarate	847	7

3 | RESULTS AND DISCUSSION

Due to its complexity, the COMSOL implementation was checked against previously available model data before being used. The charging and discharging states of the cell have been studied to verify the accuracy of the model's assumptions. The transition between these states is controlled by the cell voltage crossing certain thresholds as shown in Figure 2

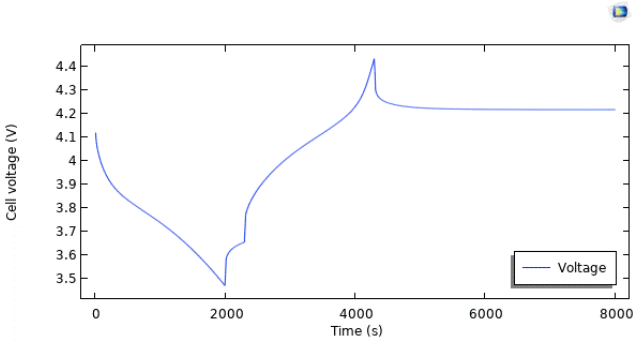

Figure 2: Charging, discharging state of Li-ion battery

This cycle is applied for discharge state lasting 2000 seconds, followed by an open circuit lasting 300 seconds, and finally a charge state lasting 2000 seconds. There was a spike in voltage at the outset of the discharge process, followed by a gradual decline due to ohmic losses. However, after the process is completed, the voltage immediately increases again. The voltage then rises steadily throughout the charging phase, reaching a maximum during the open circuit phase.

Assuming diffusion is the transport mechanism for Li-ions in the electrolyte phase in the electrolyte, a linear concentration gradient should be produced. Depending on the local over potential, Li-ions intercalate and diffuse between the two electrodes on the electrolyte potential φ_l as well as the solid matrix potential φ_s. Initially electrolyte concentration was constant presented by the flat line. As soon as the cell begins to discharge, electrolyte concentrations on the anode side begin to decrease, and this trend is also observed on the cathode side, shown in Figure 3. This is because the cell experiences significant concentration polarization due to the low effective diffusion coefficient in the electrolyte, which in turn leads to variations in ionic conductivity and concentration overpotential.

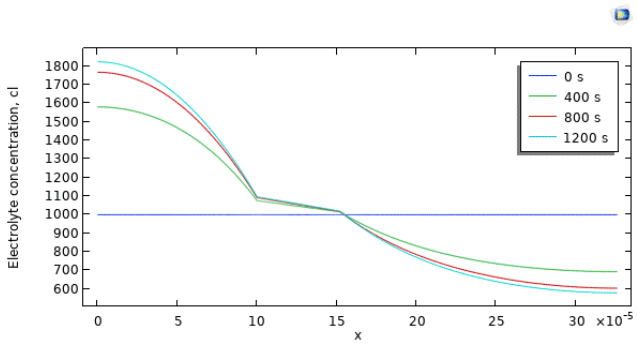

Figure 3: Electrolyte concentration of Li-ion in discharge state

EIS is a dynamic analytic tool to understand the power delivery capability of electrochemical cell and it is used to calculate the exchange current density of anode materials. Generally, AC voltage is applied to the electrochemical cell and EIS can quantify the cell resistance, charge transfer reaction, interface layer, and diffusion process of a cell only by a single experiment. The frequency range of EIS analysis in this work is 100 kHz to 10 mHz and the applied AC voltage is 10 mV for all the electrode materials. The EIS measurements profile from Comsol Multiphysics for different anode materials is shown in Figure 4

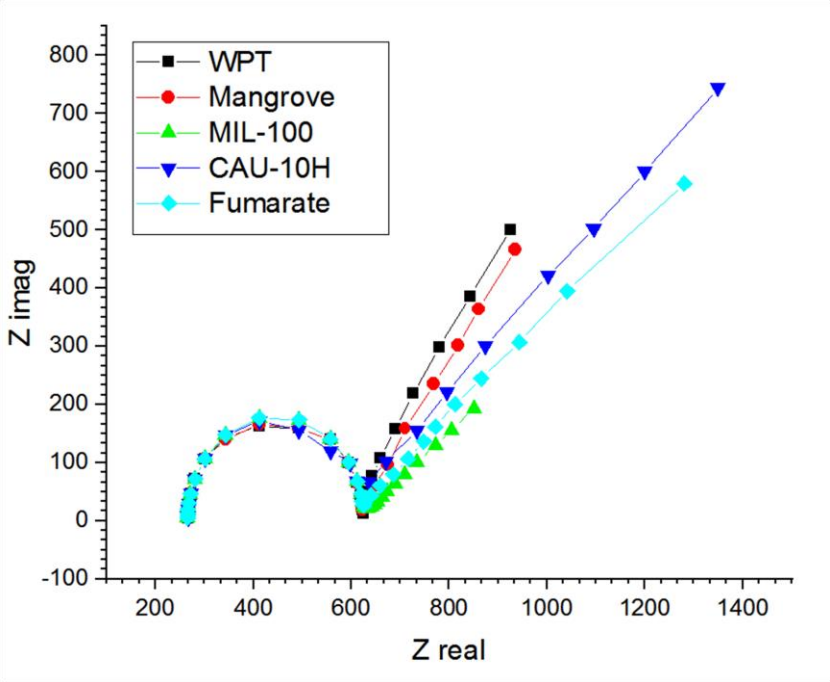

Figure 4: Electrochemical Impedance Spectroscopy (EIS) measurement for Waste palm trunk (WPT), Mangrove-AC, MIL-100 (Fe), CAU-10H, Aluminum Fumarate

Here the electrochemical impedance spectra of the cells exhibit a high frequency intercept for the electrolyte resistance R_e on the real axis Z real. The semicircle in this range characterizes the charge transfer kinetics at the interfaces and a straight line in the low frequency zone shows Warburg diffusion. The Warburg diffusion, which occurs when lithium ions diffuse into the electrode material's bulk is responsible for the straight line's low-frequency area. Actually, the Warburg diffusion indicate the migration of lithium ions into the electrode material and its value play significant role to find diffusion coefficient of Li ions. Observing the values for the various anode materials the solution resistance R_s is approximately equal for all electrodes indicating similar electrolyte and electrical resistance of about 664 Ω. This implies that all electrodes have exactly the same solution resistance. After completing the EIS measurement, EIS Spectrum Analyzer software is used to develop a circuit model for the electrode materials of a Li-ion battery. Then this model is fitted to original EIS profile for different anode materials. The obtained results from the fitting curve are not truly aligned with the actual EIS measurement profile as some parameters are assumed. However, we can say that the model is fitted with error less than 10%. The parameter values of different anode materials from the equivalent circuit model of the fitting curve are shown in Table 3

Table 3 Circuit element values of different anode materials

Circuit Element	WPT	Mangrove	MIL-100(Fe)	CAU-10H	Aluminum-Fumarate
R_s (Ω)	264.89	264.88	264.9	264.83	264.99
$CPE_{Electrode}$	3.2498E-06	3.3139E-06	3.4187E-06	3.2514E-06	3.3007E-06
R_{ct} (Ω)	321.37	326.42	358.24	325.39	343.41
Warburg impedance	108.81	102.36	50.114	184.38	125.53

Observing the values for the various anode materials the solution resistance Rs is approximately equal for all electrodes indicating similar electrolyte and electrical resistance of about 264 Ω. This implies that all electrodes have exactly the same solution resistance. However, the movement of free Li ions throughout the cell is what causes the Warburg impedance. An essential component of a battery cell's conductivity related with diffusion coefficient can be determined by knowing the value of the Warburg impedance. Another significant element influencing the electrochemical performance of the anode materials is exchange current density. Increased electrochemical activity can be inferred from a higher exchange current density. The circuit element values in Table 3 can be used to calculate the exchange current density. The value of diffusion coefficient and exchange current density for different anode materials is shown in Table 4.

Table 4 Obtained parameter values

Anode materials	Diffusion coefficient(cm2/s)	Exchange current density(mA/cm2)
WPT	1.33E-12	.080
Mangrove	1.5E-12	.078
MIL-100(Fe)	6.26E-12	.0717
CAU-10H	4.63E-13	.077
Aluminum Fumarate	9.97E-13	.075

It should be mentioned that samples with better electronic conductivity showed increased exchange current density. Due to the poor electronic conductivity of activated carbon anodes, charge transfer occurring at the electrode-electrolyte interfaces is thought to occur at a rate-determining step in these anodes. As a result, materials with greater electronic conductivity will enhance charge-transfer. From the obtained diffusion coefficient and exchange current density it can be realized that waste palm trunk (WPT) provides higher mobility for Li^+ diffusion than the other materials. That indicates strong charge transfer reaction in this cell. Thereby, WPT has the potential to replace carbon-based anode materials while enhancing Li-ion battery specific capacity. One of the most important factors in creating a highly conductive path for Li-ion diffusion is high specific surface area.

4 | CONCLUTION

In this research, to investigate the design parameters of the Li-ion battery, a one-dimensional electrochemical model was created for a variety of anode materials. The results of COMSOL Multiphysics simulation using different types of activated carbon and metal organic framework (MOF) based anode materials was presented here. According to the results of this research, electrochemical performance was improved by using a MOF since it provides greater surface area and porosity. As electronically conductive electrodes exhibited low charge-transfer resistance and, hence, high exchange current density. Results from this research confirmed that exchange current density was promoted for activated carbon like WPT as anode material in Li-ion battery. Thus, the model used in this research has the potential to be used to identify the best material for the anode in a Li-ion battery. Further it could be stated that local precursor-based material like WPT, Mangrove has adequate potentiality to contribute in energy storage device like Li-ion battery in the near future.

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Declaration of Interests

We, the authors of this research manuscript, declare that we have no financial interest. We have provided written comment to publish the paper in this journal.

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