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ABSTRACT: *Microbial fuel cells (MFCs) are regarded as one of the best potential natural resources to be discovered as a way towards reducing the over-dependence on fossil-fuel-based electricity generation. But, Limitations of advanced study on MFCs have slow-downed its development. Moreover, Low power generations from MFCs, expensive electrode materials, and the inability to scale up MFCs to industrially relevant capacities have made that worse. However, the Utilization of MFC in the arena of electro-chemistry and thermal science can be very promising in other aspects. In this work, we studied various materials and processes that can be applied to construct economical MFCs on small scale. Then, a Charge-Discharge cycling experiment was conducted on the Cell. During the test, Voltage generation close to Lithium-Ion Batteries (LIBs) was identified which shows MFCs can be used as batteries. Next, a single spherical particle one-dimensional (1D) physics-based thermo-electrochemical model was developed to investigate the potential overall performance of MFC as an energy storage device. Using our model in simulation, we validated the experimental results to predict the techniques required to analyze the system's optimum performance and provided recommendations on theories and parameters to include in MFC studies to achieve the best possible outcomes. The outcome of this work will provide useful information on the concept of MFC and design guidelines for various applications.*

Keywords: MFC, Economical, Thermo-electrochemical, Experiment, Simulation,

1. INTRODUCTION

The consumption of energy is increasing exponentially every year. There are two types of energy sources as Non-Renewable energy sources [1] and Renewable energy sources [2]. Fossil fuel and Nuclear Sources are known as non-renewable energy sources. But Fossil fuel has a major drawback that it is harmful for the environment as it emits air polluting gases while burnt. On the other hand, extracting energy from nuclear sources is very costly. However, miscellaneous countries around the world have made remarkable efforts to find a piece of the cogent solution for energy crisis by turning the eyes into renewable energy sources such as solar energy, the energy produced from wind and water [3, 4]. Another kind of renewable energy source is Fuel cell (FC).

Microbial Fuel Cell (MFC) is a type of FC, where microorganisms are used as catalysts. The conventional MFC design consists of two chambers, an anaerobic anodic chamber and an aerobic cathode chamber [5]. In a double chamber MFC, bacteria release electron to anode with the help of organic materials present in the anode compartment. Electrons pass through an external wire to the cathode. Usually, wastewater is put in anode compartment as there are a lot of microorganisms and clean water is kept into the cathode compartment. Thus, we get an amount of voltage and current reading. MFC has a drawback that it needs a considerable amount of mass to generate energy. With lower mass, we get lower energy. In practice, with 5 [L] of wastewater, a maximum 1.01 [V] (open circuit voltage) and constant 0.2 [mA] current was measured. So, it can be used as a battery as it generates voltage almost the same as a Li-ion battery. However, considering the lower amount of mass, MFC can be used as an energy storage device. It has been reported that when more than one individual MFC is connected in a stack or multi-electrode, the voltage and current increase, depending on the connection mode (series or parallel) [6]. The performance of the MFC can be varied by changing various factors such as temperature, the mass of wastewater, anode and cathode material, etc.

In this work, we constructed economical MFCs on small scale. Our main aim was to make an MFC setup with available materials. After fabricating the MFC setup, the Charge-Discharge cycling experiment was conducted on

the Cell. During the battery cycling test, a capacity gap is witnessed at the beginning and the endpoint of the Voltage vs. Normalized Capacity cycling loop. This capacity gap during battery cycling is reduced by correcting side-reaction on the exchange current density using the TAFEL kinetics formula. In our experiment, voltage generation close to Lithium-Ion Batteries (LIBs) was identified which shows MFCs can be used as batteries. A single spherical particle one-dimensional (1D) physics-based thermo-electrochemical model without any electrolyte was developed to investigate the potential overall performance of MFC as an energy storage device. We used mass balance equation (Fick's second law), Traditional Butler-Volmer Equation, Exchange current density theory to make a Lithium-Ion Battery like a mathematical model. Using our model in the simulation, we validated the experimental results to predict the techniques required to analyze the system's optimum performance and provided recommendations on theories and parameters to include in MFC studies to achieve the best possible outcomes. Details of our study will provide more explanation on how MFC can be treated as a portable energy storage device like Lithium-Ion Batteries.

2. EXPERIMENT

2.1 Experimental Setup

The experiment was conducted in plastic containers which can contain 5 liters of water. Two identical containers were used. One as anode compartment and other as cathode compartment. Wastewater was taken in the anode compartment. Then the container was sealed so that it could be airtight. Surface water was taken in the cathode compartment. The cathode compartment was kept open so that air can pass over the water. To complete the cell 2 electrodes were dipped into the anode and cathode compartments. Copper electrodes were used for the purpose of the experiment. Then, the electrodes were connected by external wire (Figure-1). Both compartments were connected by a U-tube for ion transfer. The solution of the U-tube was made with KCL (Potassium Chloride) and Agar Agar Powder.

2.2 Measurements and Outputs

The volume of water was 4000 [ml] on both compartments. Copper electrodes were used which is of rectangular-shaped with a surface area of 141.12E-4 [m^2]. Initially, the open circuit voltage was calculated 700 [mV]. After 8 hours it was increased to 1.051 [V]. The current was 0.1846 [mA]. The external wire was made of copper and it was insulated by rubber. The U-tube was made of glass.

2.3 Working Principle

An MFC works like a galvanic cell which uses the energy that is released from spontaneous redox reaction to generate electricity. Wastewater consists of many organic compounds and microorganisms. Microorganisms i.e. Bacteria require oxygen and organic material for respiration. As the anode compartment is airtight is has lack of oxygen. So, Bacteria releases electron to the anode. The electrons flow through the circuit to the cathode. As the cathode compartment is open, it has much oxygen. The electrons are accepted by oxygen. For example, if acetate is used as an organic substance then the redox reaction would be (Rozendal et al., 2008) as shown in Equation (2.1)[1],
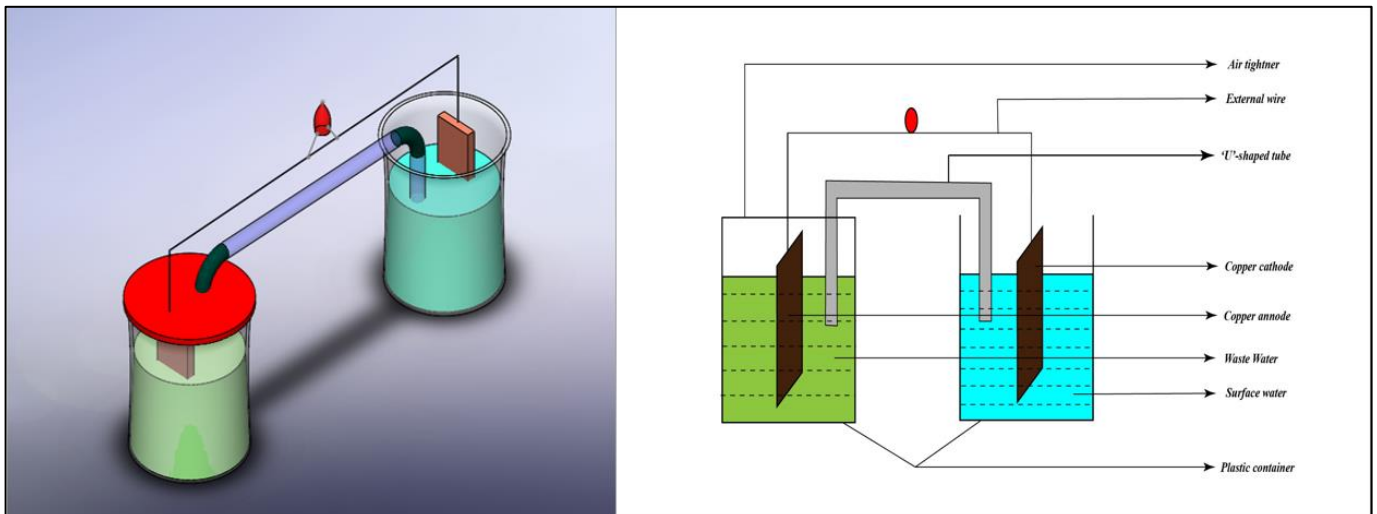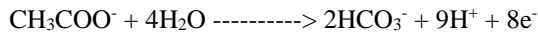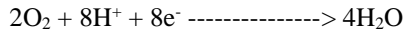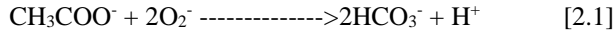
Anodic Reaction:

Figure-1(a) Schematic diagram of the experimental Setup of Microbial Fuel Cell (MFC), Figure-1(b) 2D diagram of different components of the experimental Setup of Microbial Fuel Cell (MFC)

$CH_3COO^- + 4H_2O \text{ ----------> } 2HCO_3^- + 9H^+ + 8e^-$

Cathodic Reaction:

$2O_2 + 8H^+ + 8e^- \text{ ---------------> } 4H_2O$

Overall Reaction:

$CH_3COO^- + 2O_2^- \text{ --------------> } 2HCO_3^- + H^+$ [2.1]

After preparing the cell, the battery charging (charging-discharging) test was done. First, the cell was automatically charged from Bacterial reaction to the highest cut off 1 [V]. After gaining stability, the cell was discharged back to the minimum cut off 0.099 [V]. After the charging-discharging process, one entire cycle was completed. Then, we calculated the specific capacity for each voltage point of all the cycles for all the cells. We applied measured 0.1846 [mA] current in this experiment.
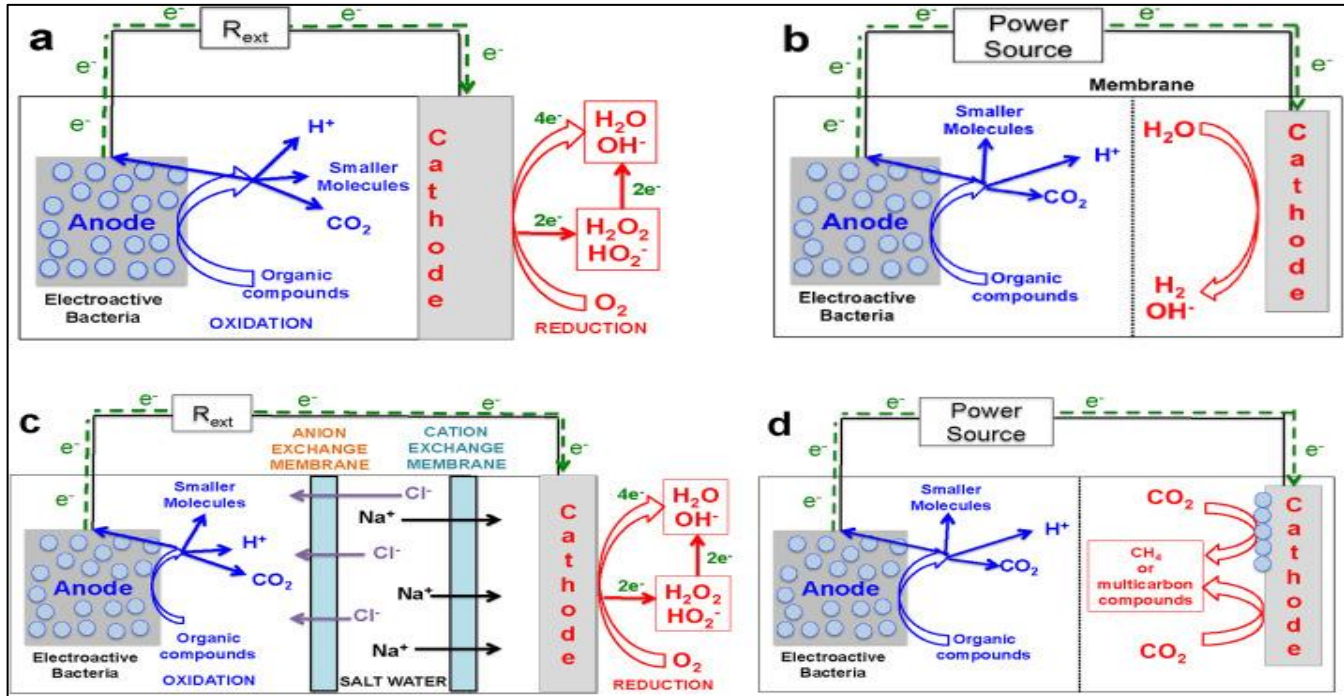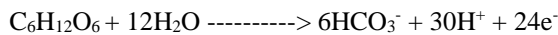

Figure-2: (a) Schematic of a Microbial Fuel Cell (MFC) (b) Microbial Electrolysis Cell (c) Microbial Desalination Cell (d) General Microbial Electro synthesis Cell [15]

The main organic substrate in wastewater is Glucose ($C_6H_{12}O_6$). The oxidation reduction reaction in a MFC is given below,

Oxidation Reaction (Anode):

$C_6H_{12}O_6 + 12H_2O \text{ ----------> } 6HCO_3^- + 30H^+ + 24e^-$

Reduction Reactions (Cathode):

$O_2 + 4H^+ + 4e^- \text{ ---------------> } 2H_2O$
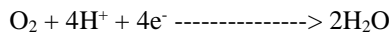
Because of these reactions at electrodes, electron is released and transferred through external circuit and electricity is produced. Figure 2 illustrates the electrochemical mechanism inside the Microbial Fuel Cell system.

Theoretically, the voltage or emf of the reaction is calculated by the equation,

$\Delta E^\circ_{cell} = \Delta E^\circ_{cathode} - \Delta E^\circ_{anode}$ [2.2]

2.4 Battery Cycling Test

2.5 Side-Reaction Correction

During battery cycling experiment, each time we noticed capacity gap between starting and ending point of the cycling loop as shown in Figure-3(a). This capacity gap was generated because of side-reaction formation by the by-product when chemical kinetics occurred at the interphase between separator and anode. It could be reduced by implementing wide side-reaction correction formula on the exchange current density [7,8]. Sethuraman et al. implemented TAFEL regime formula for SR correction in their work [7,8]. We also applied the same following formula for Side Reaction correction on the exchange current density in our experiment.

$$i_{0,SR} = i_0 * \exp\left(\frac{\alpha_{SR}F}{RT}\left(V - U_{SR}\right)\right)$$ [1]

The transfer coefficient for the side reaction, α_{SR}, was

assumed to be 0.5 [7,8]. While Tafel kinetics did not provide an explicit equilibrium potential (i_0 and U are related), we assumed a value of U_{SR}= 0.8 vs. Li/Li+ to estimate $i_{0,SR}$ [7,8]. This side-reaction current, $i_{0,SR}$ was then calculated through the cycle assuming an i_0 such that the marching was eliminated from the cycling data. The voltages we got from the experiment was applied in this study.

We demonstrated the Side-reaction correction for cycling cell in the following two figures. Figure-3(a) in the Voltage vs Normalized Capacity graph, it showed the capacity gap at the end of the cycling before the side reaction correction. Whereas figure-3(b), Voltage vs Normalized Capacity graph depicted the cycling scenario

Butler-Volmer (BV) equation to describe the electrochemical reaction at the interface. To estimate diffusion coefficients in the particle using data, Fick's law (Eq. [2]) was numerically solved in spherical coordinates.

$$\frac{\partial c_s}{\partial t} = D_s \frac{\partial^2 c_s}{\partial r^2} + 2\frac{D_s}{r}\frac{\partial c_s}{\partial r} \qquad [2]$$

The boundary and initial conditions are,

$$D\frac{\partial c_s}{\partial r} = -\frac{i_{app}}{a_V LF} \quad \text{for} \quad r = r_0 \qquad [3]$$

$$D\frac{\partial c_s}{\partial r} = 0 \quad \text{for} \quad r = 0 \qquad [4]$$

$$c_{s,0} = c_0 \quad \text{for} \quad t = 0 \qquad [5]$$
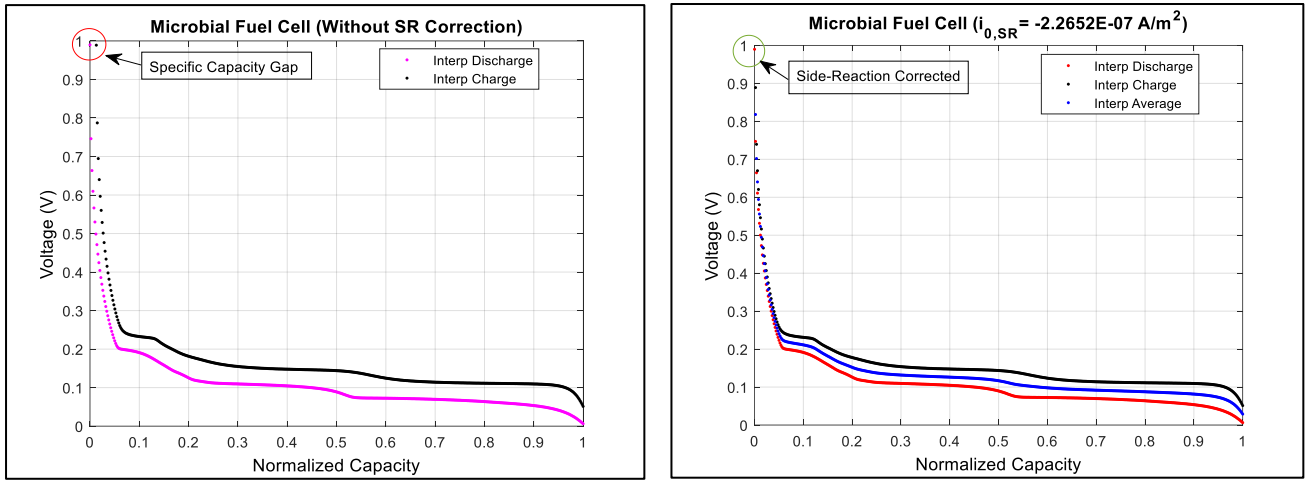

Figure-3: (a) Voltage vs Normalized before Side Reaction correction. Pink dots indicated discharging and Black dots indicates charging. Red circle denotes voltage gap, (b) Voltage vs Normalized Capacity after Side Reaction correction. Red dots indicated discharging and Black dots indicates charging. Green circle denotes voltage gap reduction after side reaction correction. Blue dots denote the average plot between discharging and charging

after side-reaction correction. For MFC, $i_{0,SR}$ value was calculated as -2.2652E-07 A/m^2. The blue dots in the figure-3(b) in the defined average of charging-discharging plots which was used in our simulation model as well.

3. MODEL DEVELOPMENT
3.1 Mass Balance Equation

Since our model is a single particle one-dimensional half-cell model without any electrolytes, the model developed in this study assumed the graphite particle to be a single phase, rather than a two-phase system [9,10,11]. A simple electrode model that reflects this schematic was developed in order to estimate the reaction distribution across the electrode. The governing equations and boundary conditions (Table I) for this model have been discussed in the literature. These equations are composed of mass balance in the solid phases and the traditional

Where r_0 is the particle radius, c_s is the lithium concentration, $c_{s,0}$ is the initial lithium concentration, D_s is the diffusion coefficient, i_{app} is the current density, a_V is the surface-to-volume ratio, L is cell thickness, F is the Faraday's constant. In estimating the diffusion coefficients, both particle volume changes and stress effects were ignored.

3.2 Butler-Volmer Equation

In this model we included traditional Butler-Volmer equation. These equations include exchange current density, i_0 (A/m^2) [10-13]. In our case, we used constant value for that. BV Equation can be expressed,

$$j_n = \frac{i_0}{F}\left\{\exp\left[\frac{F(V-U)}{2RT}\right] - \exp\left[-\frac{F(V-U)}{2RT}\right]\right\} \qquad [6]$$

Table I. Governing equations and boundary conditions for porous electrode (half-cell) model.

Governing Equations	**Boundary Conditions**

Mass balance in solid phase (spherical coordinate) (c_s: lithium concentration),

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial r^2} + 2 \frac{D}{r} \frac{\partial c}{\partial r}$$

$$D \frac{\partial c}{\partial r}\big|_{r=R} = -\frac{i_{app}}{a_V LF}; \qquad D \frac{\partial c}{\partial r}\big|_{r=0} = 0$$

Modified Butler-Volmer Voltage Equation,

$$V = U + \frac{2RT}{F} \sinh^{-1}\left(\frac{i_{app}}{2i_0 a_V LF}\right)$$

Table II. List of model parameters used in this study

Parameters	**Values**	**Description**	**Remarks**
r_0	500 X 10^{-9}	Initial Particle Radius [m]	Reference [10]
D_S	2 X 10^{-15}	Initial Solid Diffusivity [m^2/s]	"
Capa	Calculated from experiment	Columbic Capacity [mAh/g]	"
i_0	0.0037	Exchange Current Density-1 [A/m^2]	Measured
c_{max}	ρ X $\dfrac{Capa}{F}$	Maximum Concentration [mol/m^3]	"
C-rate	Calculated from experiment	C-Rate [1/h]	"
c_{01}	x_0 X c_{max}	Initial Concentration [mol/m^3]	Reference [13],[14]
aV	3.91 X 10^6	Surface to Volume Ratio [1/m]	"
L	116 X 10^{-6}	Thickness of Electrode [m]	"
F	96487	Faraday Constant [C/mol]	"
R	8.314	Universal Gas Constant [J/mol/K]	"
T	298	Temperature [K]	Reference [16]
ρ	2000	Density of Graphite [kg/m^3]	"
x_0	0.0001	Initial SOC of graphite	"

j_n is net flux, mol/m^2/s. It defines as,

$$j_n = \frac{i_{app}}{a_V LF} \qquad [7]$$

Therefore, equation [7] can be expressed as follows,

$$\frac{i_{app}}{a_V LF} = \frac{i_0}{F}\left\{\exp\left[(1-\alpha)\frac{F(V-U)}{RT}\right] - \exp\left[-\alpha\frac{F(V-U)}{RT}\right]\right\} \qquad [8]$$

Where, α is the symmetric coefficient, i_0 is the exchange current density, R is the universal gas constant, T is the temperature. If we use α= 0.5, equation [6] can be written as,

$$V = U + \frac{2RT}{F} \sinh^{-1}\left(\frac{i_{app}}{2i_0 a_V LF}\right) \qquad [9]$$

Initial voltage, U (V) is derived in equation [10] and U_0 value is the experimental Open circuit voltage values.

$$U = U_0\left(\frac{c_s}{c_{max}}\right) \qquad [10]$$

In our physics based mathematical model, we identified key parameters which were essential for our experimental validation. We used constant values for the parameters to make our model as simple as possible. We implemented these values in our model and checked with experimental results.

3.3 Solution Procedure

The mathematical model equations were solved using a finite-element package COMSOL Multiphysics 5.5. Model parameters such as electrode design, thermodynamics, transport, kinetic, and mechanical properties are listed in Table-I. In our experiment, we completed the battery cycling test in Standard Condition such as 25℃ (room temperature). The validity of the parameter choice is checked by comparing the physics model to experiments, as shown in Table-II described above. The mesh for the setup was selected as extremely fine coarse. The computation was performed on Intel core i7 CPU using 5 cores.

4. RESULTS AND DISCUSSION

In testing electrodes at high C-rates, comparatively thin-layer electrodes are considered to be an ideal design because the transport limitations in the electrolyte phase are neglected. It is confirmed in our ideal electrode using the porous electrode model. At first, we generated a Voltage vs. Normalized Capacity graph from our experimental data. Then, we corrected side-reaction generated from chemical kinetics using the TAFEL regime. Using all the equations we developed in our mathematical model, we tried to validate our experimental result.

We implemented all our mathematical equations (From eqn. [2] to eqn. [10] and parameters in table-2 in COMSOL Multi-physics 5.5. We ran simulation and observed following results.
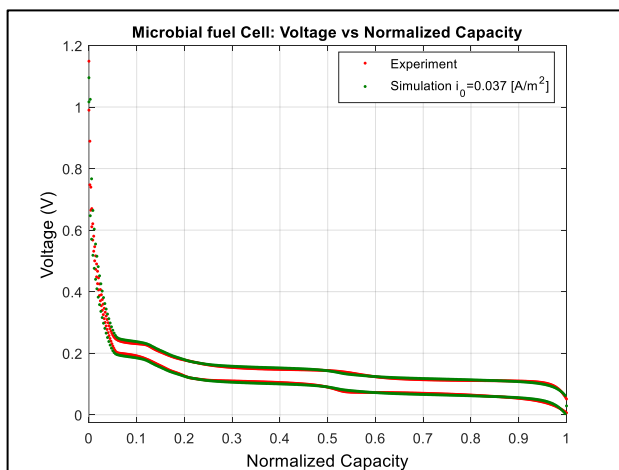

Figure-4: Experimental Validation of Voltage vs. Normalized Capacity graph for Microbial Fuel Cell (MFC)

Here, In the Figure-4, red dot denotes the experimental

result of Voltage [V] vs Normalized Capacity graph of Microbial Fuel Cell (MFC). Green dot indicates Voltage [V] vs Normalized Capacity graph generated using our model in the simulation. Voltage limit was well maintained between minimum 0.099 [V] and maximum 1.051 [V]. Applied current was also constant as 0.1896 [mA]. It can be noticed that the graph generated with constant exchange current density matched the best with the experimental result. Even though, during experiment, side-reaction exchange current density was calculated as $i_{0,SR}$ = -2.2652E-07 [A/m^2] whereas in simulation we didn't have to use $i_{0,SR}$. In case of simulation, exchange current density, i_0 = 0.0037 [A/m^2] value was implemented in Butler-Volmer (BV) Equation. These are exchange current densities were totally different. Moreover, the applied current during simulation i_{app} was same as experimental applied current. Therefore, from our observation, it can be stated that an electrochemical model developed here matched best with experimental data. Results clearly indicate that small scale MFC has the potential to be used as an energy storage device.

5. CONCLUSION

In this work, we thoroughly investigated the potentiality of Microbial Fuel Cell (MFC) as a next-generation energy storage device. The small scale MFC setup with readily available material around us was prepared and charging-discharging cycling was conducted. Then, we got rid of the by-products by correcting side-reaction correction. Next, we calculated specific capacity and measured voltage. Our voltage range was very similar to Lithium-Ion Batteries (LIBs). Voltage [V] vs Normalized Capacity curve was generated next. Then, we developed a physics-based electro-thermal model to validate our experimental results. We used the traditional Mass-diffusion equation and traditional Butler-Volmer (BV) in our model similar to the LIB model. Using our model in the simulation, our results were validated. From our observation, it can be stated that Microbial Fuel Cell (MFC) has the potential to be next-generation portable energy storage device. Further research on MFCs can improve its quality and eliminate its disadvantages.

6. REFERENCES

[1] V. Gude, Microbial fuel cells for wastewater treatment and energy generation, Microbial Electrochemical and Fuel Cells. (2016) 247-285. doi:10.1016/b978-1-78242-375-1.00008-3.

[2] V. Gude, Wastewater treatment in microbial fuel cells – an overview, Journal Of Cleaner Production. 122 (2016) 287-307. doi:10.1016/j.jclepro.2016.02.022.

[3] B. Logan, B. Hamelers, R. Rozendal, U. Schröder, J. Keller, S. Freguia et al., Microbial Fuel Cells: Methodology and Technology†, Environmental Science & Technology. 40 (2006) 5181-5192. doi:10.1021/es0605016.

[4] M. Rahimnejad, A. Adhami, S. Darvari, A. Zirepour, S. Oh, Microbial fuel cell as new technology for bioelectricity generation: A review, Alexandria Engineering Journal. 54 (2015) 745-756. doi:10.1016/j.aej.2015.03.031.

[5] N. Nik Azmi, N. Ghazali, A. Fikri, M. Ali, Studies on Power Generation and Wastewater Treatment Using Modified Single Chamber Microbial Fuel Cell, Advanced Materials Research. 1113 (2015) 823-827. doi:10.4028/www.scientific.net/amr.1113.823.

[6] E. Estrada-Arriaga, J. Hernández-Romano, L. García-Sánchez, R. Guillén Garcés, E. Bahena-Bahena, O. Guadarrama-Pérez et al., Domestic wastewater treatment and power generation in continuous flow air-cathode stacked microbial fuel cell: Effect of series and parallel configuration, Journal of Environmental Management. 214 (2018) 232-241. doi:10.1016/j.jenvman.2018.03.007.

[7] V. Sethuraman, V. Srinivasan, J. Newman, Analysis of Electrochemical Lithiation and Delithiation Kinetics in Silicon, Journal Of The Electrochemical Society. 160 (2012) A394-A403. doi:10.1149/2.008303jes.

[8] A. Hossain, Y. Cha, M. Song, S. Kim, Side Reaction Correction and Non-linear Exchange Current Density for Mathematical Modeling of Silicon Anode Based Lithium-Ion Batteries, (2020). doi:10.13140/RG.2.2.36674.40646.

[9] X. Zhang, W. Shyy, A. Marie Sastry, Numerical Simulation of Intercalation-Induced Stress in Li-Ion Battery Electrode Particles, Journal of The Electrochemical Society. 154 (2007) A910. doi:10.1149/1.2759840.

[10] C. Jin, H. Li, Y. Song, B. Lu, A. Soh, J. Zhang, On stress-induced voltage hysteresis in lithium ion batteries: Impacts of surface effects and interparticle compression, Science China Technological Sciences. 62 (2019) 1357-1364. doi:10.1007/s11431-018-9491-6.

[11] H. Sitinamaluwa, J. Nerkar, M. Wang, S. Zhang, C. Yan, Deformation and failure mechanisms of electrochemically lithiated silicon thin films, RSC Advances. 7 (2017) 13487-13497. doi:10.1039/c7ra01399j.

[12] S. Pal, S. Damle, P. Kumta, S. Maiti, Modeling of lithium segregation induced delamination of a-Si thin film anode in Li-ion batteries, Computational Materials Science. 79 (2013) 877-887. doi:10.1016/j.commatsci.2013.06.051.

[13] Y. Cheng, M. Verbrugge, The influence of surface mechanics on diffusion induced stresses within spherical nanoparticles, Journal Of Applied Physics. 104 (2008) 083521. doi:10.1063/1.3000442.

[14] V. Sethuraman, V. Srinivasan, A. Bower, P. Guduru, In Situ Measurements of Stress-Potential Coupling in Lithiated Silicon, Journal Of The Electrochemical Society. 157 (2010) A1253. doi:10.1149/1.3489378.

[15] C. Santoro, C. Arbizzani, B. Erable, I. Ieropoulos, Microbial fuel cells: From fundamentals to applications. A review, Journal Of Power Sources. 356 (2017) 225-244. doi:10.1016/j.jpowsour.2017.03.109.

[16] J. Christensen, J. Newman, A Mathematical Model of Stress Generation and Fracture in Lithium Manganese Oxide, Journal Of The Electrochemical Society. 153 (2006) A1019. doi:10.1149/1.2185287.

[17] B. Logan, K. Rabaey, Conversion of Wastes into Bioelectricity and Chemicals by Using Microbial Electrochemical Technologies, Science. 337 (2012) 686-690. doi:10.1126/science.1217412.

[18] B. Logan, Exoelectrogenic bacteria that power microbial fuel cells, Nature Reviews Microbiology. 7 (2009) 375-381. doi:10.1038/nrmicro2113.

[19] B. Logan, D. Call, S. Cheng, H. Hamelers, T. Sleutels, A. Jeremiasse et al., Microbial Electrolysis Cells for High Yield Hydrogen Gas Production from Organic Matter, Environmental Science & Technology. 42 (2008) 8630-8640. doi:10.1021/es801553z.

[20] Y. Ahn, B. Logan, Saline catholytes as alternatives to phosphate buffers in microbial fuel cells, Bioresource Technology. 132 (2013) 436-439. doi:10.1016/j.biortech.2013.01.113.