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Exploring the Potential of Lithium-Carbon Dioxide Cells: Assembly, Performance, and Challenges in Pursuit of High-Energy-Density Rechargeable Batteries

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I. Abstract

This independent study investigates the assembly and performance of lithium-carbon dioxide ($Li - CO_2$) cells with a focus on their potential as high-energy-density rechargeable batteries. Despite presenting challenges, these cells offer innovative possibilities by utilizing carbon dioxide as a sustainable and abundant cathode material. While preliminary tests reveal degradation of the cells over time, the cells demonstrate significant benefits due to their high theoretical density. Factors such as cathode material (carbon cloth versus magnesium oxide), electrolyte selection, and assembly techniques profoundly influence the cell's behavior and overall performance.

II. Introduction

In recent years, lithium-ion batteries have become popular sources of renewable energy due to their high energy density, rechargeable properties, long life cycles, and versatility. As such, due to these properties, lithium-ion batteries can be found anywhere from consumer electronics such as smartphones or tablets to aircraft. At a foundational level, lithium-ion battery cells have minimal components.

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A lithium-ion cell is comprised of two electrodes, an anode, a cathode, current collectors, and a separator. The electrodes serve as the positively and negatively charged ends of the cell and are attached to the current collectors. The anode of the cell serves as the negative electrode and the cathode in contrast serves as the positive electrode. Within the cell, the electrolyte catalyzes the reaction by conducting electricity, and the separator acts as a porous film between the electrodes while exchanging lithium ions between the sides of the electrode [1]. The current collectors serve as conductive foils at each electrode connected to the terminals of the cell. The diagram of the cell can be shown in fig. 1 below.

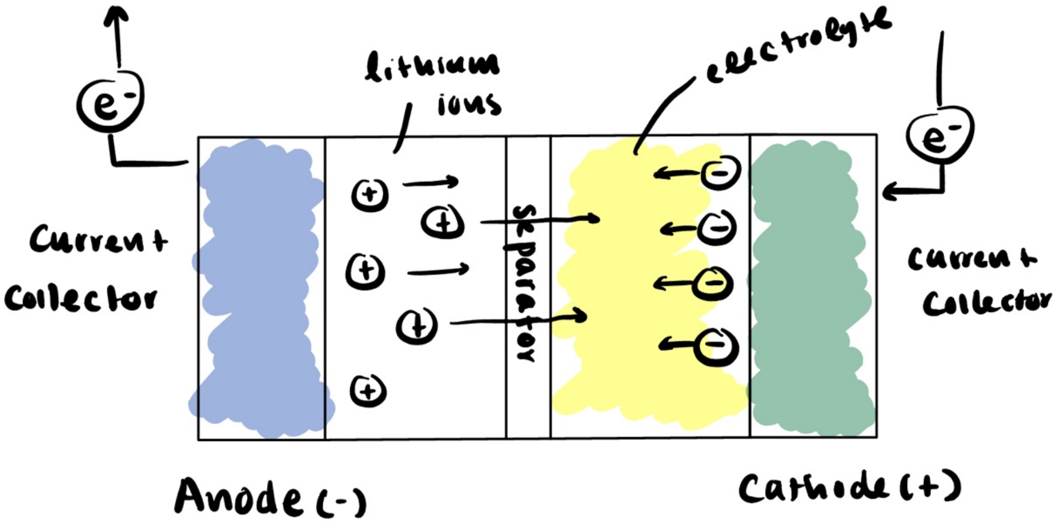

Figure 1: Diagram of Lithium-ion Cell

Within the cell of a rechargeable lithium-ion battery movement of lithium ions between the positive and negative electrodes generates electricity. The positive side of the cell or the cathode typically consists of a lithium metal oxide such as lithium manganese oxide ($LiMn_2O_4$) or lithium iron phosphate ($LiCoO_2$). During discharge, the positive lithium ions move towards the negative electrode from the positive electrode. The electrolyte within the cell serves as the conductive solution that allows the ions to move between the two electrodes, and the separator, a permeable, porous material serves as a physical separator between the two electrodes to prevent short-circuiting.

During the charging process, a voltage is applied across the cell. This applied voltage causes the lithium ions to move from the positive electrode to the negative electrode. During discharge, when the cell is providing power, the lithium ions move from the negative electrode to the positive electrode, releasing energy in the process.

Within the realm of lithium-ion batteries exist many types of cells such as lithium-oxygen batteries. In the case of the independent study, the examination was undergone with lithium-carbon dioxide cells. Lithium-carbon dioxide batteries involve a different chemical reaction compared to traditional lithium-ion cells. The chemical reaction during discharge or power delivery can be shown below in eq. 1:

$$2Li^{+} + CO_2 + 2e^{-} \rightarrow \; Li_2CO_3 \tag{1}$$

Lithium ions (Li^{+}) and electrons (e^{-}) react with carbon dioxide gas to form lithium carbonate, releasing energy as a result. During the charging process, the opposite chemical reaction occurs as the lithium carbonate decomposes back into lithium ions and electrons:

$$Li_2CO_3 \rightarrow 2Li^{+} + CO_2 + 2e^{-} \tag{2}$$

Despite this idealized reaction, there are challenges with lithium-carbon dioxide cells regarding the stability of the cell. Carbon dioxide as a cathode causes the formation of solid carbon within the cell. This formation of solid carbon can degrade the performance of the cell over time leading to reduced efficiency and capacity of the cell [2].

Though many challenges are presented with lithium-carbon dioxide cells, these cells offer many benefits due to their high theoretical density and their potential to reduce environmental impacts. Carbon dioxide is abundant in the atmosphere, making it a potentially sustainable and widely available resource for cathode material. This contrasts with other materials within the realm of lithium-ion batteries that are limited in availability.

III. Methods

Throughout the independent study, the assembly of the lithium-ion cells remained similar for the cells. The cells were constructed within a glovebox – an oxygen-free environment to ensure the lithium chips would not react to the air. After being purged of any contaminants such as liquid from the sanitation process, the cathodes and anodes were inserted into the glovebox as shown in fig. 2.

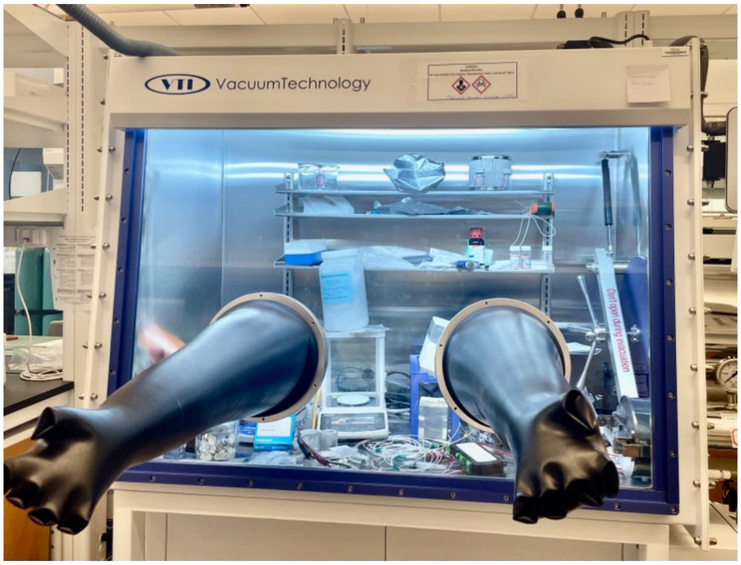

Figure 2: Glovebox

Once in the glovebox, the cells were assembled. Two types of cathodes were used, a carbon cloth MPL microporous layer and a magnesium oxide (MnO_2) cathode. The cathodes were cut to either 5/8” and ½” diameters and placed with their coated sides facing away from the current collector. The electrolyte was applied to the coated side of the cathode. Different amounts of electrolyte were applied to the different cathodes during the different trials of the experiment. The full cell assembly can be shown below in fig. 3:

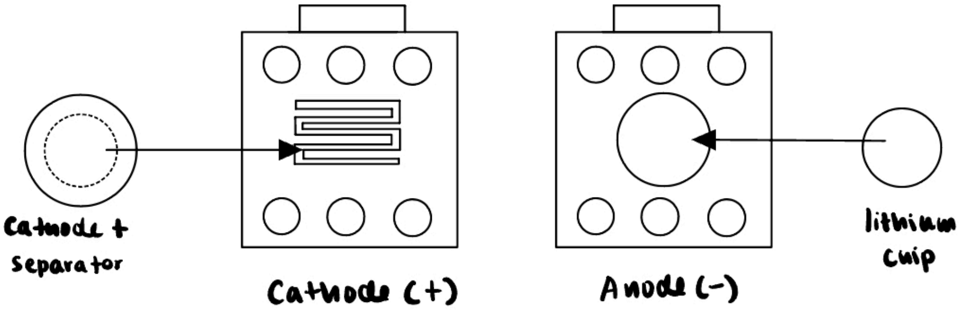

Figure 3: Full Cell Assembly

Several types of electrolytes were used throughout the experiments. These electrolytes serve as a soluble solution in which electrons can travel between the electrodes. In the case of the lithium-ion cell, the electrolyte helped release lithium ions from the lithium chip and allowed these ions to travel between the electrodes, releasing charge via electrons during such a process. The electrolytes used in the assembly included DMSO (dimethyl sulfoxide), TEGDME (tetra ethylene glycol dimethyl ether), and EMIM TSFI. In several trials, a 1:4 molar ratio of EMIM DMSO was used as an electrolyte for the cell as well. The electrolyte was applied to the cathode, ensuring the liquid was saturated into the cathode as well as the separator to ensure the reaction was catalyzed.

Once the cells were constructed within the cell, and sealed with a gasket and nuts and bolts, the batteries were removed from the glovebox and immediately connected to a flowmeter supplying carbon dioxide. The flowmeter was purged before the connection to the cells, ensuring no leftover air or oxygen within the tubes of the flowmeter. The flowmeter shown below in fig. 4 provided a consistent flow of CO_2 through the flow channel of the cell.

Figure 4: Flowmeter Supplying CO_2

Once the cells were connected to the flowmeter supplying carbon dioxide, the cells were connected at both electrodes to a Squidstat Potentiostat. After being connected to the software instrument, the cells underwent a cycle of open circuit to charge and discharge until the cells reached their capacity.

IV. Results

To observe the capacity of the assembled cells, the voltage and cumulative charge of the cells were measured over several hours. Via programming on the Squidstat apparatus, the cells underwent a cycle of open circuit, charge, and discharge with a current and voltage applied across the cells. As such, the cumulative charge was measured across the cells. With this data, the specific area capacity of the cells was calculated in eq. 3 below:

$$Q_{specific} = |Q_C \div A| - |Q_O \div A| \tag{3}$$

In eq. 3, Q_C (mAh) is the current cumulative charge value, Q_O (mAh) is the original cumulative charge at the start of discharge or charge, and the specific working area is denoted by A (cm^2). $Q_{specific}$ $(\frac{mAh}{cm^2})$ or the specific charge capacity was representative of the amount of charge that could be released from the battery relative to the cathode's area. A higher specific charge or discharge capacity denotes a higher performance of the cell.

The preliminary tests conducted were with carbon cloth MPL, comparing the specific capacity of the cells with different electrolytes to catalyze the reaction within the cells. As such, to ensure the validity of these results, the cells were assembled several times. Cells with carbon cloth as the MPL yielded discharge capacity, but low charge capacity. Figure 5 below shows the experimental results from the lithium-carbon dioxide with 120 μL of the electrolyte applied to MPL and separator.

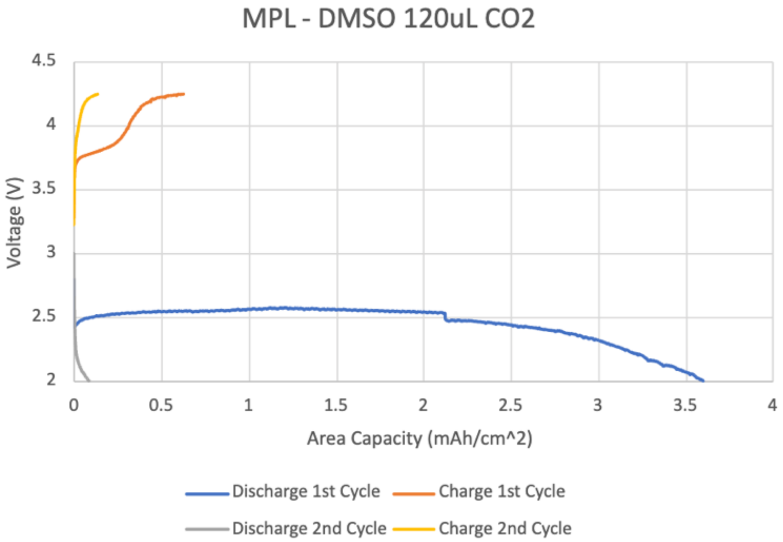

Figure 5: Graph showing the relationship between voltage (V) and specific discharge capacity $\left(\frac{mAh}{cm^2}\right)$ for 120 μL DMSO for CO_2 for two charge and discharge cycles with carbon cloth MPL

As shown in fig. 5, the discharge capacity for the first cycle of the cell was quite long, however, as indicated by the specific charge capacity, the cell's life cycle was quite short. As such, a second test was run to determine the validity of the first test as shown in fig. 6 below:

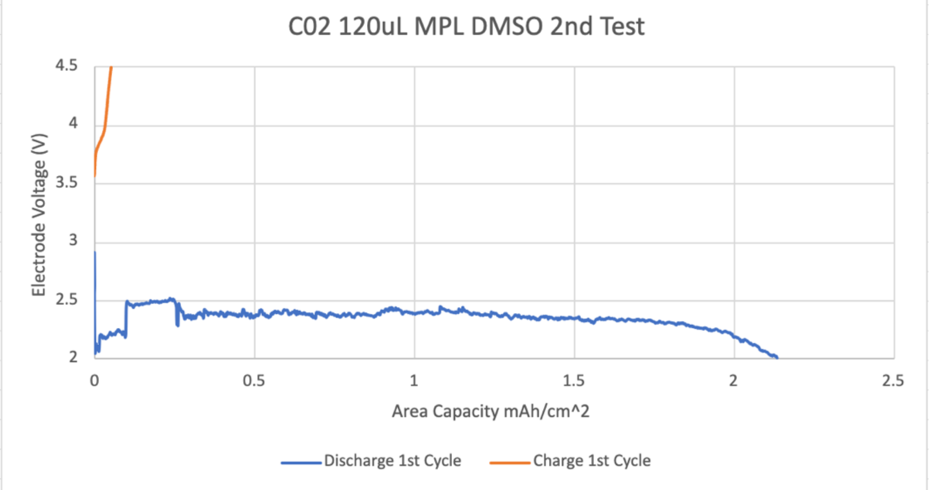

Figure 6: Graph showing the relationship between voltage (V) and specific discharge capacity $\left(\frac{mAh}{cm^2}\right)$ for 120 μL DMSO for one charge and discharge cycles with carbon cloth MPL (2nd Test)

With this second source of data from the lithium-carbon dioxide cell, a similar discharge capacity trend can be observed, though unstable. Additionally, the second test yielded only one cycle, meaning the cell failure was achieved much sooner. The instability of the discharge capacity could have been due to the assembly of the cell – either the components were too tight or too loose. In comparison, an experiment was run with the same assembly, but with a magnesium oxide (MnO_2) cathode. Due to the lack of absorbency properties for this cathode, only 60 μL was applied to the magnesium oxide cathode. The discharge capacity of the cell can be observed below in fig. 7:

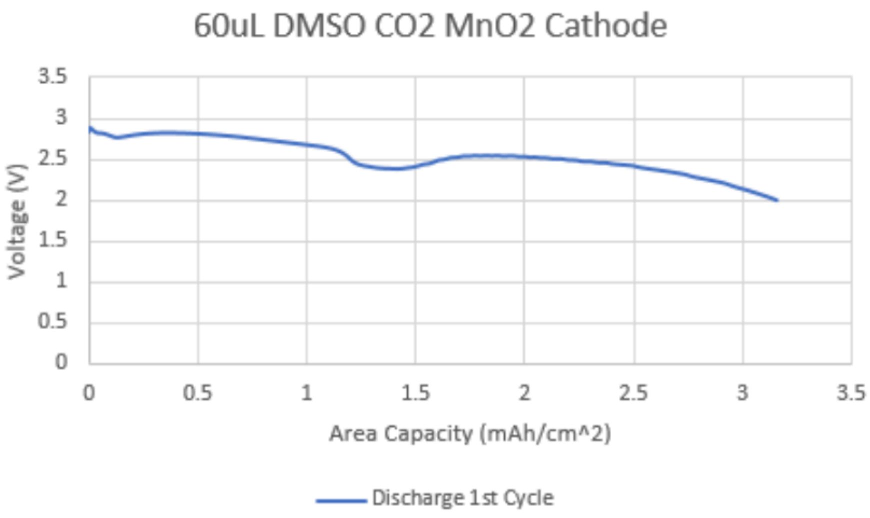

Figure 7: Graph showing the relationship between voltage (V) and specific discharge capacity $\left(\frac{mAh}{cm^2}\right)$ for 60 μL DMSO for CO_2 for one discharge cycle with magnesium oxide (MnO_2) cathode

As shown in fig. 7, while showing a stable discharge capacity, the magnesium oxide cathode did not yield any charging for the cell. However, despite the lack of charging, the magnesium oxide had a significant area capacity above 3 $\left(\frac{mAh}{cm^2}\right)$, similar to the maximum discharge capacity in fig. 5. A such, despite the uncertain results between the cathode material, the dimethyl sulfoxide (DMSO) provided the facilitation of lithium ions between the anode and cathode of the cells, as indicated by the charge and discharge capacities [3]. Similarly, a test was run with pure Ethyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide (EMIM-TSFI) as the electrolyte within the cell. The assembly of the cell remained the same with a 0.5" carbon cloth MPL. The experimental results are shown below in fig. 8:

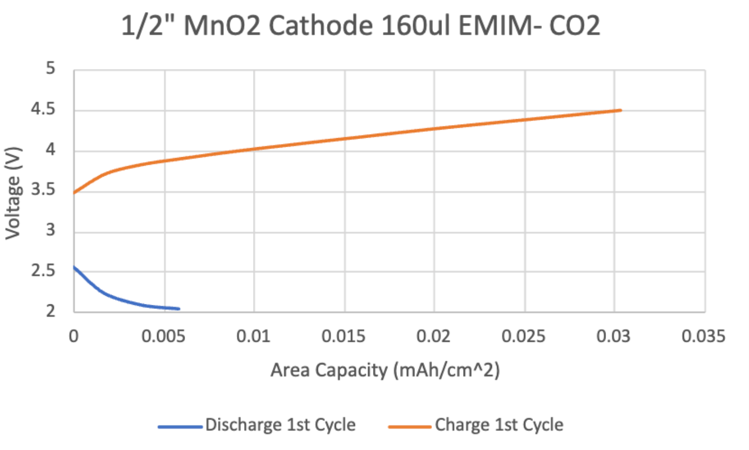

Figure 8: Graph showing the relationship between voltage (V) and specific discharge capacity $\left(\frac{mAh}{cm^2}\right)$ for 160 μL EMIM-TSFI for one charge and discharge cycles with carbon cloth MPL cathode

While the experiment yielded a charge and discharge capacity, as indicated in fig. 8, the area capacity was quite small with a maximum value of slightly greater than 0.03 $\left(\frac{mAh}{cm^2}\right)$. Due to this low charge capacity, no further tests were conducted with this electrolyte, and instead, a solution of EMIM and DMSO was created to observe the behavior of the cells under a mixture of these electrolytes.

To observe the behavior of the cells under different electrolytes, a mixture of Ethyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide (EMIM-TSFI) and the DMSO was created of a 1:4 molar mass ratio. This solution was used as the electrolyte to catalyze the reaction in the cells. The results for the EMIM-DMSO 1:4 molar ratio cells can be observed in fig. 9 below. This test was conducted with the carbon cloth MPL.

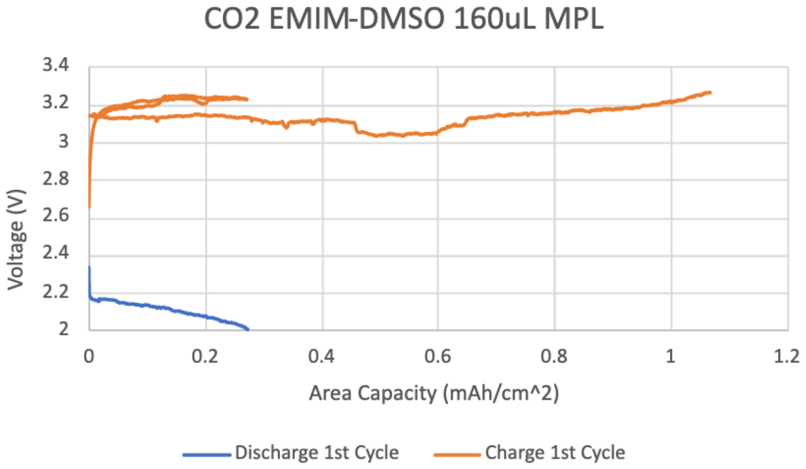

Figure 9: Graph showing the relationship between voltage (V) and specific discharge capacity $\left(\frac{mAh}{cm^2}\right)$ for 160 μL EMIM-DMSO for one charge and discharge cycles with carbon cloth MPL cathode

As shown in fig. 9, the results of this test yielded unorthodox behavior for the charge capacity of the cell. The instability of the capacity of the charge cycle could have been due to the assembly of the cell or inconsistencies of the flowmeter providing carbon dioxide to the cell. Despite the instability, the charge of the cell was far greater than the discharge capacity, indicating an imbalance in the cell's performance during the charge and discharging processes. A second test was conducted to further observe the behavior of this cell:

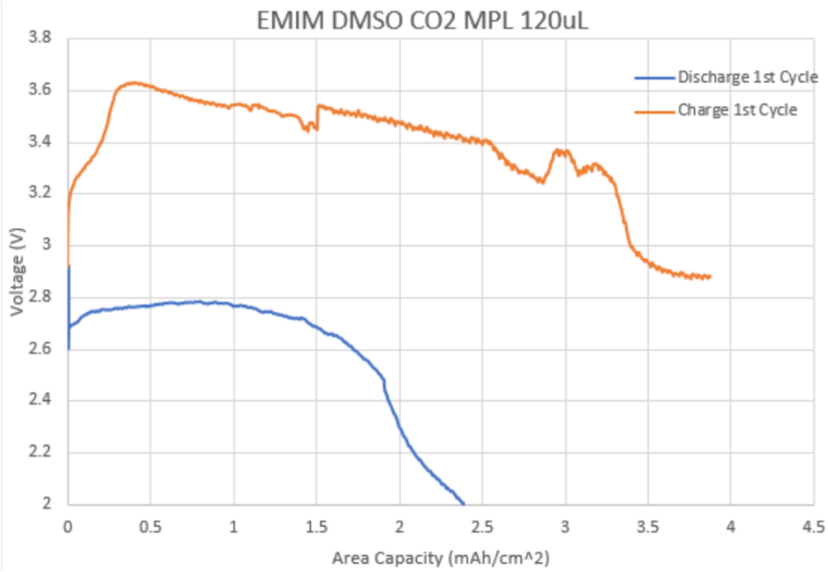

Figure 10: Graph showing the relationship between voltage (V) and specific discharge capacity $\left(\frac{mAh}{cm^2}\right)$ for 160 μL EMIM-DMSO for one charge and discharge cycles with carbon cloth MPL cathode (2nd test)

As indicated in fig. 10, the behavior of the cell via discharge and charge was once again unstable. This can be observed by the turbulent line graph. These observations indicate the EMIM-DMSO electrolyte promotes an inconsistent reaction in which area capacity varies greatly during charge and discharge capacity. Regardless of these inconsistencies, the maximum area capacity of this cell was almost 4 $\left(\frac{mAh}{cm^2}\right)$, indicating this electrolyte could facilitate high-energy-density cells. As such, to examine a behavior change, the cells were assembled with the magnesium oxide cathode with the same EMIM-DMSO electrolyte, and the charge capacity was observed.

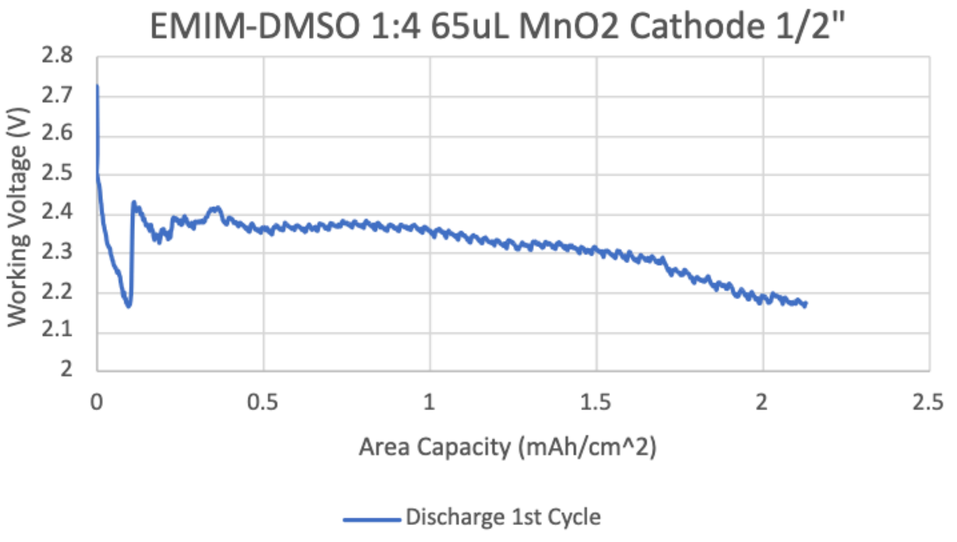

Figure 10: Graph showing the relationship between voltage (V) and specific discharge capacity $\left(\frac{mAh}{cm^2}\right)$ for 65 μL EMIM-DMSO for one discharge cycle with magnesium oxide (MnO_2) cathode

Figure 10 above shows the cell observing a single discharge cycle. Though this discharge capacity was above 2 $\left(\frac{mAh}{cm^2}\right)$, no charging of the cell occurred, and thus, the cell had a low cycle life. A second test was conducted to further understand the behavior of the cell:

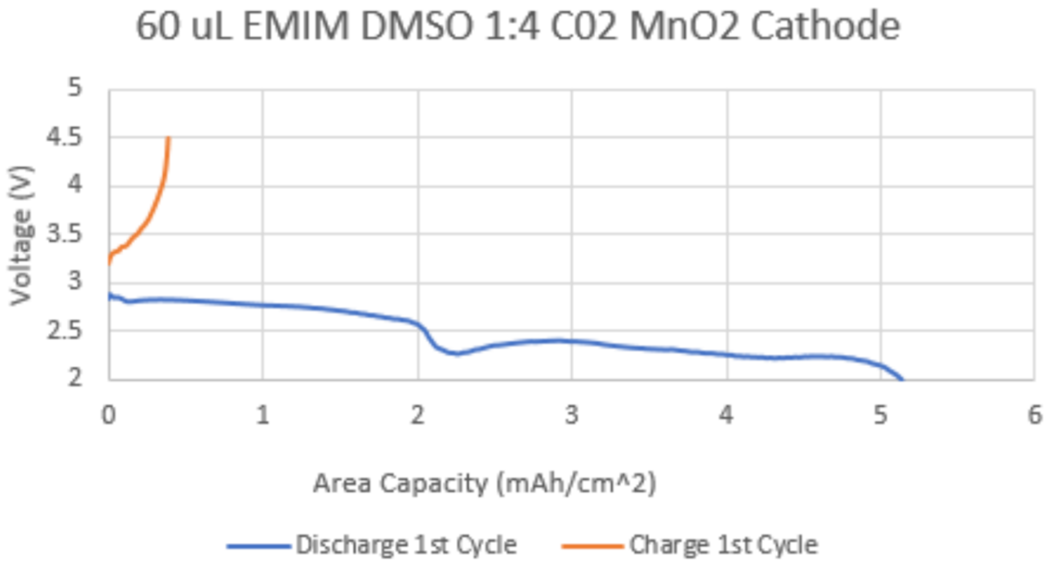

Figure 11: Graph showing the relationship between voltage (V) and specific discharge capacity $\left(\frac{mAh}{cm^2}\right)$ for 65 μL EMIM-DMSO for one discharge cycle with magnesium oxide (MnO_2) cathode (2nd test)

Figure 11 indicates a large discharge capacity of this cell, though a small charge capacity. The discharge capacity of the cell was greater than 5 $\left(\frac{mAh}{cm^2}\right)$, indicating a high energy density for this cell.

Many sources of error could have affected the low life cycles of the cells. For one, the magnesium oxide cathode was used as an alternative to the carbon cloth MPL due to internal reactions within the cells. Electrochemical reactions within lithium-carbon dioxide cells can be complex and lead to oxidation during charging. Additionally, the formation of lithium-carbonate on the cathode surface can lead to passivation layers, hindering the movement of lithium ions and electrons between the anode and cathode of the cell [4]. The cathode material could have also experienced instability during cycling, leading to structural changes, loss of conductivity or other issues negatively impacting charge capacity. Lastly, inconsistencies with the flowmeter during several trials could have impacted the supply of carbon dioxide to the cell, impacting the reaction within the cell.

V. Conclusions and Future Work

This independent study examined the assembly and performance of lithium-carbon dioxide $(Li - CO_2)$ cells exploring their potential as high-energy-density rechargeable batteries. The $Li - CO_2$ cells investigated in this study represent an innovative approach of leveraging carbon dioxide as a sustainable and abundant cathode material.

The preliminary tests revealed several challenges associated with $Li - CO_2$ cells, most notably the degradation of performance over time. Despite these challenges, $Li - CO_2$ cells demonstrated potential benefits due to their high theoretical density and the abundance of carbon dioxide as a cathode material. The choice of cathode material, such as carbon cloth MPL versus magnesium oxide (MnO_2), and the type of electrolyte impacted the cell's behavior and overall performance.

Most notably, the use of DMSO as an electrolyte proved to facilitate the movement of lithium ions between the anode and the cathode of the cells, contributing to the charge and discharge capacities. However, the cells exhibited unstable behavior at times indicating challenges in assembly, electrode materials, or the supply of carbon dioxide during the experiments.

This research underscores the complexity and intricacies associated with $Li - CO_2$ cells, and for this reason, there is still so much research that can be done on these cells. As such, further optimization and understanding of the underlying mechanisms of these cells are crucial to address challenges related to cathode stability, electrolyte selection, and overall cell design. Further work in this area should be focused on refining the cell components and assembly techniques to enhance the cycle life and overall performance of the cells. In doing so, this can contribute to the development of sustainable and efficient energy storage solutions.

VI. References

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