



The Efficiency of Titanium-Graphite Electrode Cells in the Presence of Ionic Liquids and Deep Eutectic Solvents as Electrolytes

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Abstract

Prior to the start of production, several factors must be considered, including the price, effectiveness, and environmental friendliness of batteries. Ionic liquids and deep eutectic solvents have shown significant success when employed as electrolytes with Titanium-graphite cells, especially when combined with additives that enhance their conductivity by reducing the high viscosity of these liquids. Evaluating the discharge voltage of the $AlCl_3$ -chloroacetamide IL with DCM as an additive revealed a voltage of 1.16V and an internal resistance of 11 Ohm. These electrochemical cells exhibited an intriguing response. Otherwise, when utilizing $CaCl_2 \cdot 2H_2O$: Acetamide DES with DI water as an additive, the cell voltage measured 0.97V, with an internal resistance of 23 Ohm. Moreover, these cells demonstrated thermal stability during both charging and discharging processes, which can be attributed to the concentration and quality of the ionic species. Furthermore, the surfaces of the Titanium electrodes were examined using FESEM and EDXA equipment to assess the impact of the ionic liquid and DES on these electrodes.

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1. Introduction

Climate change and air pollution are major challenges facing our energy-dependent society. To address these risks, the generation of renewable energy and the electrification of transportation are widely recognized as effective solutions. However, the success of these solutions relies heavily on efficient electrical energy storage. Rechargeable batteries offer great potential for large-scale energy storage due to their high energy density and conversion efficiency [1-4]. Rechargeable batteries, also known as secondary batteries, allow for the reversible conversion of chemical energy into electrical energy with higher efficiency compared to traditional heat engines, and without emitting harmful gases. Various commercial rechargeable battery technologies exist, with lithium-ion and graphite (LIB)

batteries currently dominating the market [5-7]. However, researchers seeking batteries that embody perfectionism in terms of performance face concerns regarding flammability and the toxicity of certain battery materials [8-10]. Consequently, extensive research is being conducted to identify the best electrodes and electrolytes that meet the desired requirements while keeping up with modern demands. As a result, aluminum-based batteries (ALBs) [11,12] with graphite electrodes [13-17] have been developed as a safer, more accessible, cost-effective, and lightweight alternative. These batteries utilize ionic liquids (IL) and deep eutectic solvents (DES) as electrolytes [18-20]. These liquids and solvents possess high ionic conductivity, thermal stability, wide electrical windows, and do not interact with the electrodes, allowing the electrodes to maintain

their shape and properties. Furthermore, ILs and DESs are cost-effective and exhibit non-toxic properties [21]. Examples of such electrolytes include calcium chloride/acetamide DES [22] and aluminum chloride anhydrous/amide IL [23, 24]. In this study, titanium electrodes were employed as anodes in electrochemical cells using ionic liquids and deep-melting solvents as electrolytes. The electrical properties of these cells were investigated, contributing to the ongoing efforts to develop advanced battery technologies.

2. Materials and Methods

Titanium foil, Dichloromethane (DCM) (Sigma Aldrich), deionized water (DI water) (HACH business), aluminum chloride (AlCl_3) (Carloerba), chloroacetamide (CA) (Sigma-Aldrich), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) (Chem-Supply), and acetamide (AC) (Fluka) were all used without any purification. Using a field emission scanning electron microscope (FESEM) (INSPECT S50), the surface morphology of specimens was examined. FESEM and the X-Flash 6110 Bruker EDX were combined to estimate the surface composition of the samples. The Etekcity Infrared Thermometer (Temp Gun) 1080, utilized to record heat temperature, and the Digital Multimeter Electric Tester, INGCO DCM200, were used to measure the impedance and record the open circuit potential, respectively. In a glove box filled with argon gas, experiments were carried out, and results were obtained at room temperature.

2.1 Preparation of titanium-graphite cells by the presence of AlCl_3 :CA IL and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$: Ac DES as electrolytes with and without additives. [25]

To demonstrate the applicability of the discussed data, titanium-graphite cells were constructed using two different electrolyte systems. In the first system, an ionic liquid (AlCl_3 :CA) with a mole ratio of 2:1 [24] was utilized without any additives. The second system involved diluting the ionic liquid with dichloromethane (DCM) organic solvent at percentages ranging from 25% to 75%, depending on the highest measured conductivity

[26]. For the second system, a $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$: Ac DES with a mole ratio of 1:7 [22] was employed as the electrolyte. Additionally, water was added before and after the DES in a ratio of 35% deionized (DI) water to 65% DES, respectively. This water addition served to enhance ion mobility by reducing the high viscosity of the DES [26]. The negative electrode was constructed using titanium, with dimensions of $1\text{cm} \times 2\text{cm}$, while the cathode consisted of a graphene electrode with a column diameter of 5 mm. To prevent potential oxidation processes or contamination of the cell with other chemical pollutants, all these components were enclosed in a sealed glass container under an inert argon gas atmosphere, as depicted in Figure 1. Note that the distance between the two electrodes is 1 cm for all electrochemical cells

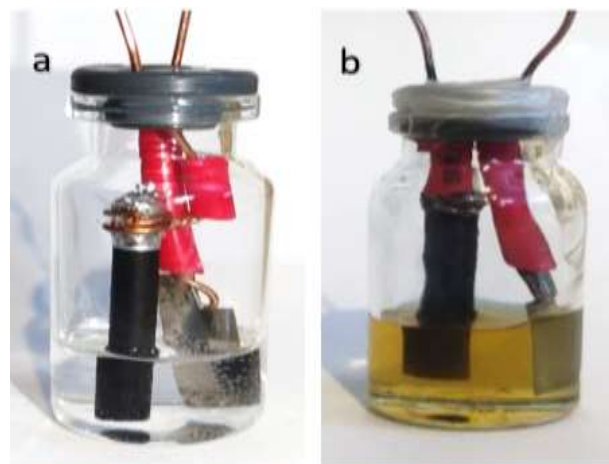


Figure 1. Illustration of a titanium-graphite electro-chemical cells (a) with DES + DI water (b) with IL + DCM

3. Results and Discussion

3.1. The self-discharge for Titanium-graphite battery cells

Following the completion of preparing four battery cells with different systems and additives, all cells underwent a charging process with a continuous voltage (DC) of 3 volts for 5 minutes. Subsequently, the cell voltages were measured using a digital multimeter over a period of 7 days, and the readings were recorded to assess the extent of energy retention within the cells. The recorded data is presented in Table 1 and Figure 2.

Table 1. The voltage measurements of all Titanium-graphite battery cells during one week.

Titanium-graphite battery cells with	Self-voltage discharge per unit time							
	First Voltage	Voltage after 1 day	Voltage after 2 day	Voltage after 3 day	Voltage after 4 day	Voltage after 5 day	Voltage after 6 day	Voltage after 7 day
IL	0.79	0.77	0.72	0.67	0.61	0.54	0.51	0.45
IL+DCM	1.16	1.11	1.08	1.03	0.98	0.94	0.92	0.86
DES	0.41	0.38	0.35	0.30	0.27	0.22	0.18	0.12
DES+ DI water	0.97	0.94	0.90	0.87	0.82	0.75	0.71	0.64

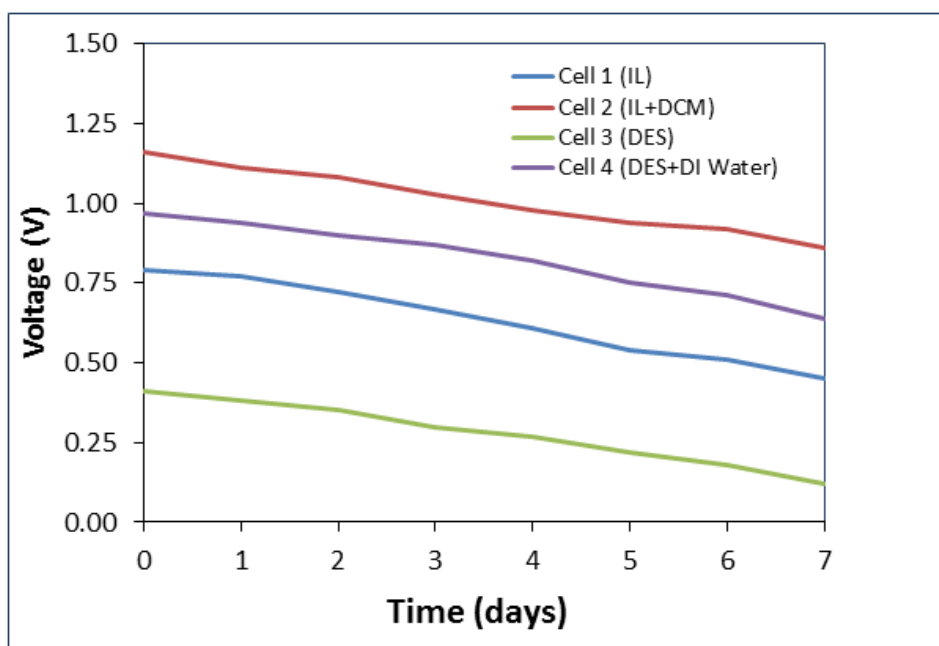


Figure 2. The voltage measurements of all Titanium-graphite battery cells during one week.

The data in the table indicates that the IL and DCM system exhibited superior performance compared to the DES and other cells. This suggests that the additives employed in the IL and DCM system effectively reduced viscosity and enhanced ion mobility within the electrolyte, resulting in higher cell voltages. The collected data aims to provide an understanding of the concept of self-discharge, which refers to the gradual loss of stored energy in batteries due to various chemical reactions occurring within the cells. However, this self-discharge phenomenon can be mitigated or reduced by applying an appropriate passivating layer on the electrodes. Such a passivating layer acts as a protective barrier, minimizing undesired

chemical reactions and preserving the stored energy within the cells for a longer period.

3.2. Internal Resistant Test for Titanium-graphite battery cells

Internal resistance is a crucial parameter that provides valuable insights into the efficiency and energy generation capabilities of battery cells. It measures the resistance to current flow within the batteries. In the case of the four titanium cells, the internal resistance was measured using a digital internal resistance tester. Additionally, the amount of current flowing through each cell, without the assistance of an external load, was calculated using Ohm's law (equation 1).

$$R = \frac{V}{I} \quad \dots (1)$$

where V represents the voltage across the cell, I denotes the current flowing through the cell, and R signifies the internal resistance of the cell. By measuring the voltage and knowing the internal resistance, the current flowing through the cells can be determined using Ohm's law. This provides valuable information about the behavior and characteristics of the battery cells in terms of current flow and internal resistance. Based on the recorded data in Table 2, it can be observed that various factors, including the quality, concentration, and distance between the electrodes, among others, have an influence on the internal resistance of the battery cells. It is worth noting that as the cell efficiency increases, the internal resistance tends to decrease [27]. The internal resistance of a battery is affected by several factors. The quality of the materials used in the electrodes, electrolyte, and other components of the cell can impact the internal resistance. Higher quality materials often exhibit lower resistance to the flow of current. The concentration of the electrolyte can also play a role. Optimal concentration levels ensure better ion conductivity and reduce internal resistance. Additionally, the distance between the electrodes affects the path length for the ions to travel, and a shorter distance can result in lower resistance. Overall, the recorded data in Table (2) emphasizes the relationship between cell efficiency and internal resistance. When a cell operates with higher efficiency, it typically exhibits lower internal resistance, indicating a more favorable and efficient flow of current within the battery.

3.3. Scanning Electron Microscope (FESEM) and Energy dispersive X-ray analysis (EDXA) examination results for Titanium-graphite battery cells.

The surface of the titanium electrode was initially examined using a scanning electron microscope (FESEM) both before and after treatment with the two electrolytes (IL+DCM and DES+DI water) used in this study. The results revealed that the electrolytes had a noticeable effect on the titanium surface. When the titanium electrode was exposed to the DES+DI water electrolyte, it is likely that a very thin oxide layer (TiO_2) formed on the surface of the electrode (Fig. 3b). The presence of water in the DES+DI water composition may have contributed to the production of this oxide layer

[28]. Similarly, when using the IL+DCM electrolyte, the electrochemical reactions induced the formation of an oxide layer (Al_2O_3) in the presence of the corrosive Al_2O_7 ion, which is one of the components of the ionic liquid (Fig. 3c) [29]. The formation of this oxide layer is expected to increase with repeated charging and discharging, depending on factors such as the duration of charging/discharging cycles and the thickness of the titanium electrode. This oxide layer formation can potentially impact the efficiency of the cell. However, it is important to note that the ionic liquid may also serve as a coating material during the charging process [29]. This can provide an additional advantage by preserving the surface of the titanium electrode and extending its lifespan. Overall, the FESEM analysis revealed the influence of the electrolytes on the titanium electrode surface, with the formation of oxide layers. Managing these oxide layers and utilizing the coating properties of the ionic liquid can be advantageous in maintaining the efficiency and longevity of the titanium electrode in the electrochemical cell.

Table 2. Voltage, Internal Resistance and Current measurements for Titanium-Graphite cells with different electrolytes.

Titanium-Graphite cells with:	Voltage (V)	Internal Resistance (Ohm)	Current (A)
IL	0.79	19	0.042
IL+DCM	1.16	11	0.105
DES	0.41	45	0.009
DES+ DI water	0.97	23	0.042

To provide evidence of the presence of metal oxides on the titanium electrode, an Energy Dispersive X-ray Analysis (EDXA) test was conducted. This test helps determine the elemental composition of the titanium electrode's surface after exposure to the two electrolytes. Figure (4a) represents the titanium electrode prior to immersion in the electrolyte, showing only the presence of the titanium element. However, Figures (4b) and (4c) display the titanium electrode after immersion in the electrolyte (DES+DI water and IL+DCM respectively), revealing the presence of additional elements such as nitrogen, oxygen, aluminum (Al), calcium (Ca), carbon, and chlorine. These elements are components present in the used electrolytes. The EDXA analysis confirms the formation of metal oxides on the titanium electrode's surface after exposure to the electrolytes. The presence of

these additional elements, such as oxygen and aluminum, indicates the formation of titanium oxide (TiO₂) and aluminum oxide (Al₂O₃) layers, respectively, as discussed earlier. This analysis provides further evidence of the chemical changes occurring on the titanium electrode's surface due to its interaction with the electrolytes.

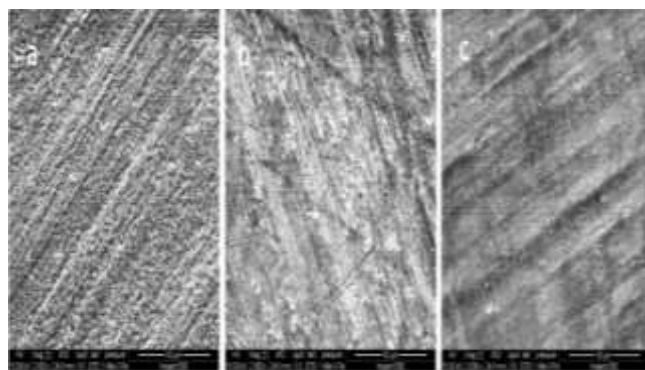


Figure 3. FESEM images of Titanium electrode at 50 μm (a) without any action, (b) after immersion in DES+ DI water and (c) IL+DCM.

3.4. Thermal charge-discharge test for Titanium-graphite battery cells

To assess the charging and discharging behavior of each cell, the temperatures of all four titanium-graphite battery cells (IL, IL+DCM, DES, and DES+DI Water) were measured both inside the cell and in the external ambient environment. The results of these temperature measurements are depicted in Figures (5) and (6). Where figure (5) represents the temperature measurements recorded inside the battery cells during the charging processes, while charged for a duration of 5 minutes at a voltage of 3 volts (DC). The data provides insights into the temperature changes occurring within the cells throughout these operations. Figure (6) displays the temperature measurements taken the discharging of the battery cells, while applying a resistance with a current of 0.5 A for 5 minutes. These measurements help assess the impact of the cell's operation on the surrounding temperature conditions. By analyzing the temperature profiles depicted in these figures, it is possible to gain a better understanding of the thermal behavior and performance of the titanium-graphite battery cells under different electrolyte compositions. These temperature measurements provide valuable

information regarding the heat dissipation, thermal stability, and overall efficiency of the cells during the charging and discharging processes (equation 2).

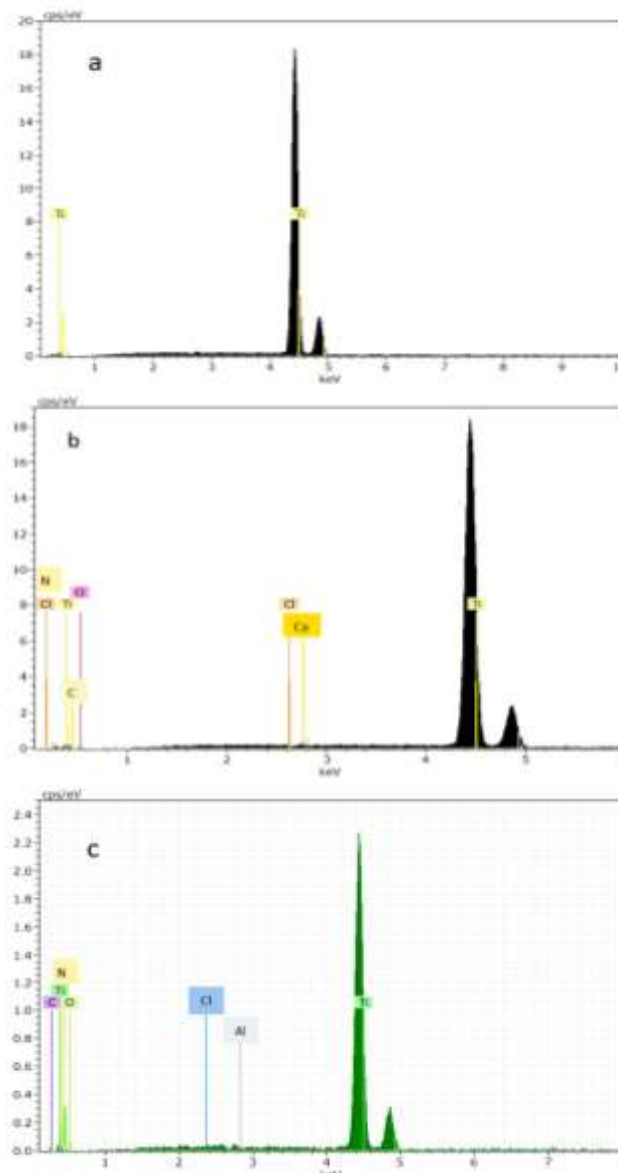
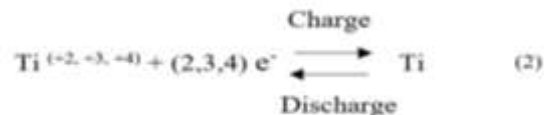


Figure 4. EDXA images of Titanium electrode (a) without any action, (b) after immersion in DES+ DI water and (c) IL+DCM.

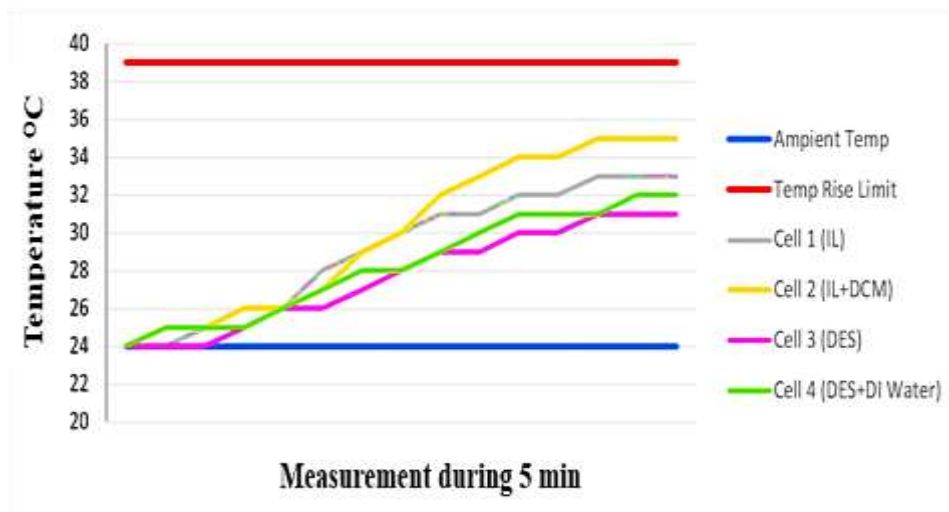


Figure 5. Thermal charge test for Titanium-Graphite cells with different electrolytes.

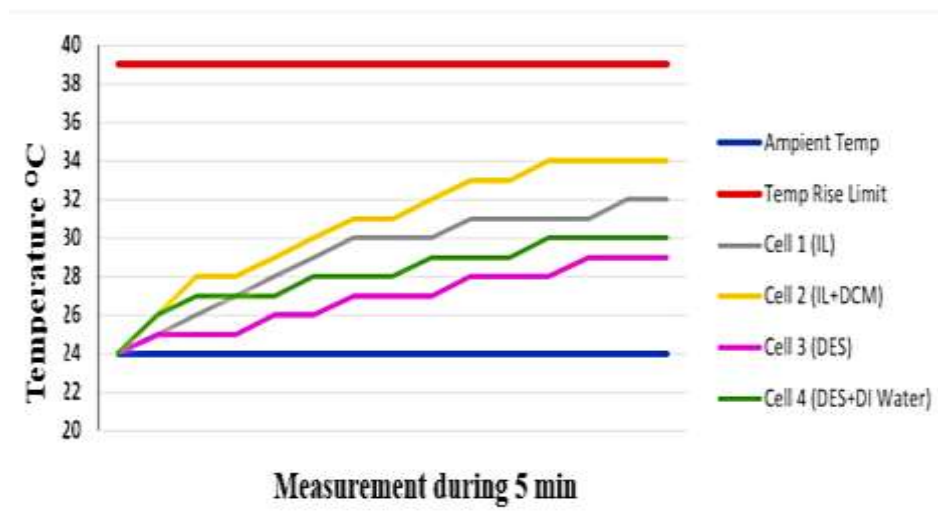


Figure 6. Thermal discharge test for Titanium-Graphite cells with different electrolytes.

The observations indicate that when the cells were fully charged for 5 minutes at 3 volts (DC) and the temperature was recorded, it did not exceed the permitted threshold of 15 degrees Celsius, which is within the approved range for charging and discharging batteries [30]. This suggests that the charging process did not lead to excessive temperature rise and the cells remained within the safe operating temperature limits. After the batteries were discharged for 5 minutes at 0.5 amperes, the temperature was measured once again. These subsequent temperature

measurements would provide insights into the temperature changes that occur during the discharging process and help assess the thermal behavior of the batteries under this specific discharge condition. By monitoring and analyzing the temperature variations during both charging and discharging, it becomes possible to evaluate the thermal performance and safety of the battery cells. Adhering to the approved temperature limits ensures the protection and longevity of the batteries, mitigating any potential risks associated with excessive heat generation during operation.

3.5. Advantages and Disadvantages of Titanium-graphite batteries.

The titanium graphene cells demonstrated an advantage over the aluminum electrode in terms of retaining their shape without corrosion or high oxidation. This indicates that the titanium electrode, when paired with electrolytes containing ionic liquid or DES, exhibited good stability and conductive efficiency even after a period of 6 months since the initial charging and discharging of the electrochemical cells. The measurements obtained during this timeframe were like those recorded at the beginning of manufacturing the cells. Increasing the charging voltage has the potential to enhance the capacity of the titanium electrode. This is because raising the oxidative number of titanium from +2 to +4 can lead to an increase in the electrical capacity of the cells that incorporate titanium electrodes. It is important to note that all the completed cells serve as experimental prototypes to showcase the viability of ionic liquids and DESs as electrolytes and titanium as electrodes. This is significant because these materials have the potential to be utilized in industrial settings for the development of batteries with high energy and storage capacities, which can be applied at various levels. Moreover, their environmentally friendly nature adds to their appeal as sustainable energy storage solutions.

4. Conclusions

The electrochemical performance of Titanium-graphite cells using two different electrolytes, an ionic liquid-based electrolyte ($\text{AlCl}_3\text{:CA}$) and a deep eutectic solvent ($\text{CaCl}_2\cdot 2\text{H}_2\text{O}\text{:Ac DES}$), was reported for the first time. The cells utilizing the ionic liquid electrolyte exhibited an open circuit potential (OCP) of 1.16 volt, an internal resistance of 11.0 ohm, and a current of 0.105 ampere without the need for an external resistance. On the other hand, the cell based on the deep eutectic solvent showed an OCP of 0.97 volt, an internal resistance of 23.0 ohm, and a current of 0.042 ampere. Thermal stability was observed in all the cells during the charge and discharge processes, indicating their ability to maintain stable performance under different operating conditions. The electrochemical cells displayed consistent behavior across all measurements, including surface oxidation, participation of ionic species, and their concentration in the electrolytes, as confirmed by the EDXA and FESEM measurements. These findings highlight the potential of both the ionic liquid-based electrolyte and deep eutectic solvent-based electrolyte for use

in Titanium-graphite cells. The ionic liquid cells exhibited higher OCP and lower internal resistance, indicating their superior performance compared to the cells based on the deep eutectic solvent. These results provide valuable insights into the electrochemical behavior and stability of Titanium-graphite cells when utilizing different electrolyte compositions.

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