

## Environmentally friendly aluminum-graphite battery cells based on ionic liquids and deep Eutectic solvents as electrolytes with some additives

**Bassam Baqer Hasan, Taghried Ali Salman**

Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-Iraq.

E-mail: bassam78bh@gmail.com.

### Abstract

When starting to create batteries, the cost, efficiency and safety (Environmentally friendly) of these batteries must be taken into consideration. Much has been achieved by using ionic liquids and deep eutectic solvents, when used as electrolytes with aluminum-graphite cells and in the presence of additives that improve their conductivity by reducing the high viscosity of these liquids. Where these electrochemical cells showed an interesting response by measuring the discharge voltage of the  $\text{AlCl}_3$ -chloroacetamide ionic liquid with Dichloromethane as additive which amounted to (1.73 v), in contrast, the cell voltage in the presence of the  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ : Acetamide DES with DI water as additive was (1.27 v) and the internal resistance (9.0 ohm), (22.0 ohm) respectively, which is due to the concentration and quality of the ionic species, and the cells showed thermal stability when charging and discharging. In addition, the surfaces of the aluminum electrodes and the effect of the ionic liquid & DES on those electrodes were studied via SEM, EDXA devices. Note that such battery cells can be used in the field of renewable energy, because they can be charged and discharged continuously and for a long period, as well as its high capabilities to withstand the surrounding environmental conditions.

**Keywords:** Ionic liquids, deep eutectic solvents, Aluminum chloride, urea, Aluminum batteries, renewable energy, Environmentally friendly.

### Introduction

It has been proven practically that the energy density that is extracted from lead-acid batteries (the batteries used in cars) and from nickel-cadmium batteries is low and does not fully meet the needs of the various electronic equipment that are spreading today [1-3]. It was also noted that these batteries do not work with the same efficiency and capacity at low temperatures or at relatively high temperatures [4]. Thus, the need arose for batteries that meet the needs of the modern market, which can equip modern machines, equipment and devices with a higher energy density. For the purpose of obtaining such batteries, efforts have focused on manufacturing new batteries whose negative electrodes (anodes) have higher potential compared to the potential of lead electrodes or nickel-cadmium electrodes. Where the markets are invaded at the present time by those batteries that are based on lithium and graphite (LIBs) [5-7], but despite their good specifications in terms of their long life, high energy, and rechargeability, the issue of flammability and the toxic nature [8-10] of some of the materials involved in the manufacture of these batteries remains the main concern of researchers to find batteries that improve Perfectionism with all its properties and qualities. Therefore, it was achieved to manufacture aluminum-based batteries (ALBs) [11-12] with graphite electrode [13-17] as a safer, more abundant, cheaper and lighter alternative. Besides that, Ionic liquids (IL) and deep eutectic solvents (DESs) were used as electrolytes inside these batteries [18-21], as these liquids and solvents have high ionic conductivity and thermal stability, with a wide electrical window, as well as non-interaction with the electrodes that used with them, as the surfaces of those electrodes retain their shape and properties without being affected by contact with these liquids, and also safe, non-toxic and inexpensive [22,23]. Examples of this type of electrolyte are the aluminum chloride anhydrous/urea IL [24] and the calcium chloride/acetamide DES [22]. Where it is possible to prepare these liquids and deal with them easily without additional complications, and it is also possible to add some elements

and salts that increase the efficiency of these liquids when manufacturing different types of batteries[25].

### Materials and Methods

All of the chemicals were used without any purification, Dichloromethane (DCM) (Sigma Aldrich), Deionized Water (DI water) (HACH company),  $\text{AlCl}_3$  (from Carloerba), chloroacetamide (CA) (from Sigma-Aldrich), Calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) (Chem-Supply) and Acetamide (AC) (Fluka). The surface morphology of specimens was investigated by using a high-resolution field emission scanning electron microscopy (SEM) (INSPECT S50). The (X Flash 6110) Bruker EDX was used in conjunction with SEM to determine the composition of samples surface. The Instrument for Cyclic voltammogram (CV) was recorded by using a three-electrode system Digi-lvy-Dy2300 Bipotentiostat comprising platinum plate as working electrode (WE), a platinum disc of 2 mm diameter as a counter electrode (CE), and wire of silver as a reference electrode (RE). The Open circuit potential (OCP) was recorded by Digital Multimeter Electric Tester, INGCO DCM200 and the impedance measurement was done by Digital internal resistant tester, Vapce YR1030. Etekcity Infrared Thermometer (Temp Gun) 1080, used to record Heat Temperature. Experiments were performed and results were obtained at room temperature in an Argon gas-filled glove box.

### Preparation of Aluminum-graphene cells by the presence of $\text{AlCl}_3$ :CA IL and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ :Ac DES as electrolytes with and without additives.

To demonstrate the applicability of the data that will be mentioned later, Aluminum – graphene cells were prepared from two systems of electrolytes, the first by using ionic liquid ( $\text{AlCl}_3$ :CA) (2:1 mole ratio)[26] without any additives, then with DCM delusion organic solvent that added to the IL by percentage 25% to 75%, respectively, depending on the highest value of measured conductivity[27]. The second system electrolyte is by using  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ : Ac DES (1:7 mole ratio)[22] also before and after adding water (35% DI water to 65% DES, respectively) as an assistant to increase the ion's freedom movement by reducing the high viscosity of the DES [27].

On the other hand, the graphene electrode was used as a cathode with a column of 5mm in diameter while the negative electrode was made of aluminum with dimensions of  $1 \times 10 \times 50$ mm.

In the end, all these components were placed in a sealed glass container under an inert atmosphere of argon gas, to prevent any possible oxidation process or contamination of the cell with other chemical impurities, Fig (1).



Figure (1) Illustration of an aluminum-graphite electrochemical cell

**Results and Discussion**

**1. the self-discharge**

After completing the process of preparing the battery cells with various systems and additives, all cells were charged with a continuous voltage (DC) of 3 volts for 5 minutes, then the voltages of the cells were tested using a Digital Multimeter for a period of 7 days and the readings were recorded to find out the extent to which the cells concerned retain energy inside them, as shown in Table (1).

**Table (1): The voltage measurements of all cells' battery during one week.**

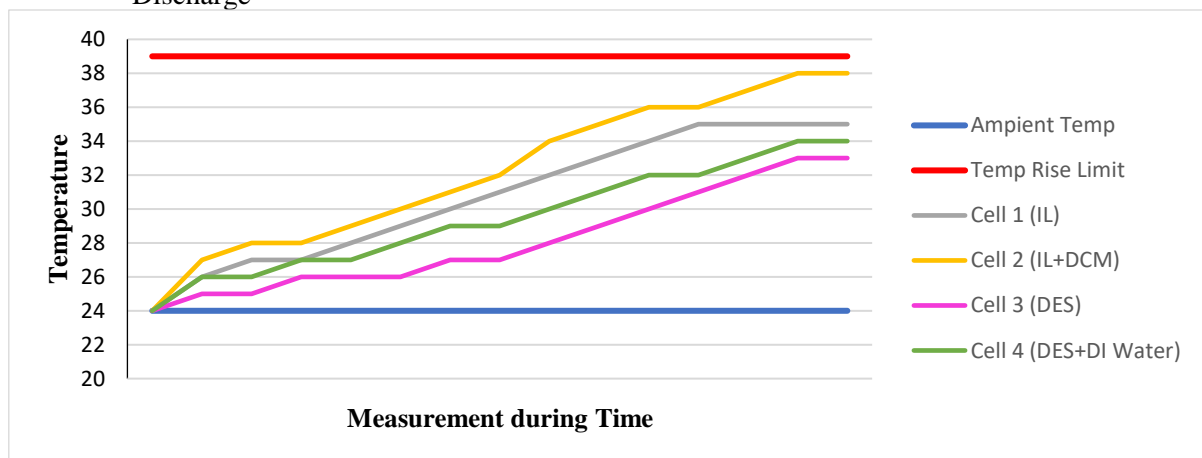
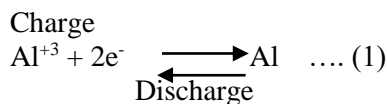
Aluminum-Graphite cells with	Self-voltage discharge per unit time							
	First Voltage	Voltage after 1 day	Voltage after 2 day	Voltage after 3 day	Voltage after 4 day	Voltage after 5 day	Voltage after 6 day	Voltage after 7 day
<b>IL</b>	1.21	1.18	1.15	1.10	1.12	1.08	1.05	1.02
<b>IL+DCM</b>	1.73	1.69	1.62	1.54	1.49	1.46	1.39	1.36
<b>DES</b>	0.64	0.60	0.57	0.53	0.51	0.49	0.44	0.39
<b>DES+ DI water</b>	1.27	1.22	1.16	1.08	0.99	0.95	0.92	0.87

Where was noted from the table values, the best results were for the IL + DCM compared with the DES or other cells. The table also shows the role of the additives in increasing the cells' voltage by reducing the viscosity and increasing the movement of ions within the electrolytes.

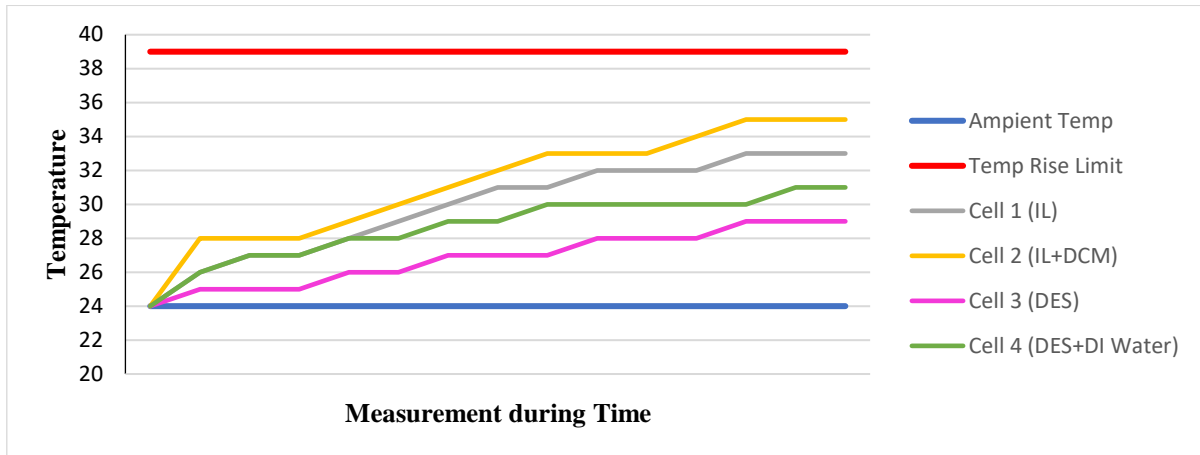
The results that have been recorded are to give an idea of the self-discharge term that occurs to the batteries as a result of some chemical reactions inside the cells, which can be avoided or reduced by using a suitable passivating layer on the electrodes.

**2. Thermal charge-discharge test**

By using an electronic thermometer, the temperature of all four Aluminum-Graphite cells (IL, IL+DCM, DES and DES+DI Water) were measured from inside the cell and the external ambient temperature to measure the charging and discharging of each cell (equation 1) the results appeared as shown in the following figures



**Fig (2): Thermal charge test for Aluminum-Graphite cells with different electrolytes.**



**Fig(3): Thermal discharge test for Aluminum-Graphite cells with different electrolytes**

Where the cells were fully charged for 5 minutes at 3 (DC) volts and the temperature was measured, Fig(2), then the cells were discharged for 5 minutes at 0.5 amperes, the temperature was measured also coinciding with time, Fig(3), it was noted that the temperature did not exceed 15 degrees allowed within the approved charging and discharging of the batteries [28].

**3. Internal Resistant Test**

The concept of internal resistance, which is the amount of impediment to the flow of current inside the batteries, gives a broad idea of the validity of the battery cells and their ability to supply energy. The internal resistance of the four aluminum cells was measured by using a digital internal resistant tester, and the amount of current for each cell was calculated (without any external load) using Ohm's law (equation 3).

Ohm's law:  $R= V/I...3$

Where *R*resistance, *V* volte, *I* current.

From the recorded results in Table (2), it was noted that the internal resistance is affected by the quality, concentration of the electrolyte and, the distance between the electrodes, etc. Where the better cell efficiency, the lower value of internal resistance[29].

**Table (2): Voltage, Internal Resistance and Current measurements for Aluminum-Graphite cells with different electrolytes.**

Aluminum-Graphite cells with:	Volte (V unit)	Internal Resistance (Ohm unit)	Current (A unit)
<b>IL</b>	1.21	18	0.067
<b>IL+DCM</b>	1.73	9	0.192
<b>DES</b>	0.64	43	0.015
<b>DES+ DI water</b>	1.27	22	0.058

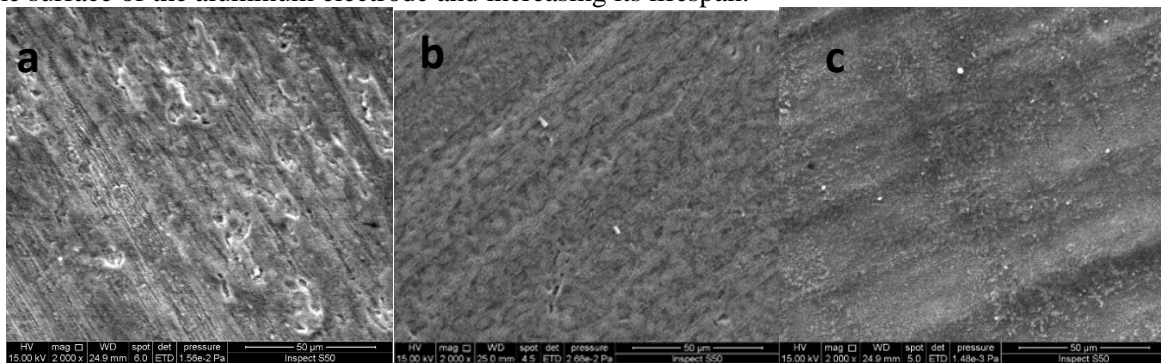
**4. Scanning Electron Microscope (SEM) and Energy dispersive X-ray analysis (EDXA) examination results**

Initially, the surface of the aluminum electrode was examined before and after its treatment with Two electrolytes (IL+DCM and DES+ DI water) that were used in this research, by Scanning Electron Microscope (SEM), Fig(4a, 4b, 4c). Where the results showed a significant effect of electrolytes on the aluminum surface. It is likely that, a layer of an oxide ( $Al_2O_3$ ) was formed over the aluminum

electrode when the electrode is exposed to the DES+ DI water Fig (4b), What helped to form that layer of an oxide could be the presence of water in the DES+ DI water composition [30].

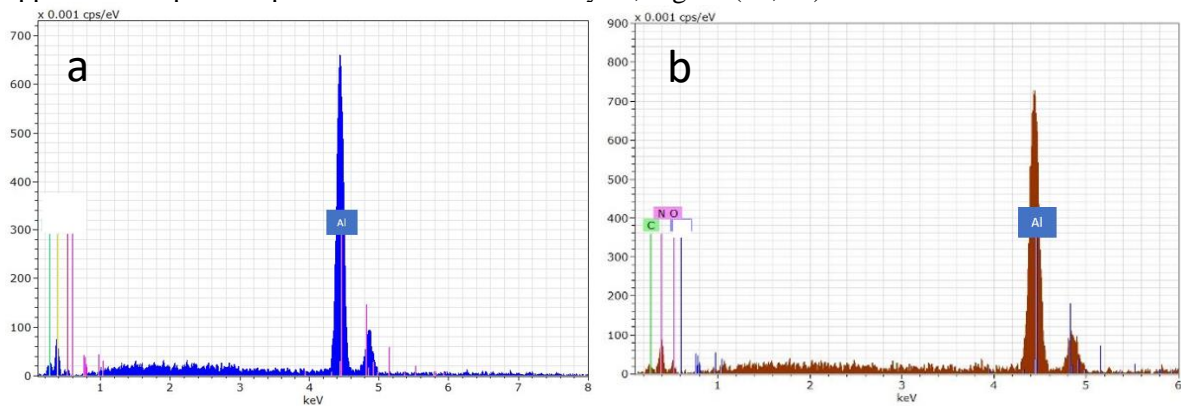
When using the IL+DCM, it also suffers from the formation of an oxide layer (Al<sub>2</sub>O<sub>3</sub>) due to the electrochemical reaction in the presence of corrosive Al<sub>2</sub>O<sub>7</sub><sup>-</sup> ion, which is part of the components of the ionic liquid Fig (4c) [31].

It is certain that the repetition of the charging and discharging process will increase the formation of that layer depending on the time and the thickness of the aluminum electrode, which may affect the efficiency of the cell. But it is worth noting that the ionic liquid maybe can act as a coating material during the charging process [32], and this leads to another benefit that can be achieved by preserving the surface of the aluminum electrode and increasing its lifespan.

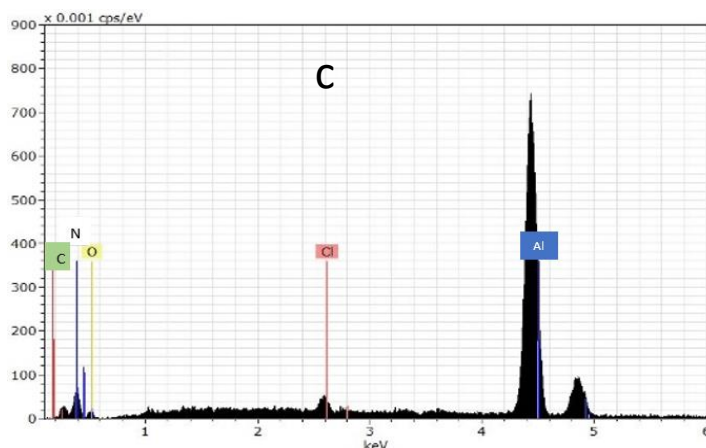


**Fig (4):SEM images of Al-electrode before (4a) and after immersion in DES+ DI water(4b), IL+DCM(4c).**

On the other hand, the EDXA test was conducted to find out the surface components of the aluminum electrode after exposure to the two electrolytes, where Figure(5a) Shows the aluminum electrode before immersion in the electrolyte as it contains only the element aluminum, but when it is immersed in the electrolytes(IL+DCM or DES+ DI water), the elements nitrogen, oxygen, carbon and chlorine appear as components present in the used electrolytes, Figure (5b, 5c).







**Fig (5): EDXA images of Al-electrode before (5a) and after immersion inDES+ DI water(5b), IL+DCM(5c).**

Note that all samples that were examined for the aluminum electrode with the two electrolytes was taken after 7 days of charging and discharging the aluminum –Graphite cell.

### Conclusion

In this article, models of batteryaluminum-graphite electrodes cellsbased on electrolytes consisting of  $\text{AlCl}_3$ - chloroacetamideionic liquid (enhanced withDCM) and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ - Acetamide DES(enhanced with deionized water), were established with a 1 cmelectrodes immersion inside the electrolytes and a rate of Charging 3 DC volts for 5 minutes, as the cells formed from the ionic liquid gave an open circuit Potential (OCP) of (1.73) volts, an internal resistance of (9.0) ohms, and a current of (0.192) amperes without using an external resistance, compared withcells based on DES that gave an open circuit Potential (OCP)of (1.27) and an internal resistance (22.0) ohms and the amount of current (0.058) amperes without using an external resistance too. All cells showed thermal stability when charging and discharging and gave similar behavior to all electrochemical cells in terms of surface oxidation and the role of theionic species and their concentration in the electrolytes, and this is proven by measurements and images For SCM and EDXA.

It should be noted that all done cells are experimental models to prove the ability of ionic liquids and DESs to be applied as electrolytes, as they need an industrial application in a manner that contributes to develop these cells into batteries with high energy and storage capacity that can be used at all levels because they are environmentally friendly batteries.

### References

1. Annette E.; Vladimir S.; Tim J.; “Assessment of utility energy storage options for increased renewable energy penetration” *Renewable and Sustainable Energy Reviews*, 16 /4141– 4147, 2012.
2. Vazquez S, Lukic SM, Galvan E, Franquelo LG, Carrasco JM. Energy storage systems for transport and grid applications. *IEEE Trans Ind Electron*, 57:3881–95, 2010.
3. Shukla AK, Venugopalan S, Hariprakash B. Nickel-based rechargeable batteries. *J Power Sources*, 100:125–48, 2001.
4. Walawalkar R, Apt J. Market analysis of emerging electric energy storage systems. Carnegie Mellon Electricity Industry Center, National Energy Technology Laboratory;DOE/NETL-1330, 2008.
5. Michael M. T.; Sun-Ho K.; Christopher S. J.; John T. V.; *et al.*; “Li<sub>2</sub> MnO<sub>3</sub>-stabilized LiMO<sub>2</sub> (M= Mn, Ni, Co) electrodes for lithium-ion batteries” *Journal of Materials chemistry*, 17, 30, 3112-3125, 2007.

6. Jos F. O.; Loïc B.; Peter H. N.; “All-solid-state lithium-ion microbatteries: a review of various three-dimensional concepts” *Advanced Energy Materials*, 1, 1, 10-33, 2011.
7. Do Kyung Kim, P Muralidharan, Hyun-Wook Lee.; *et al.*; “Spinel LiMn<sub>2</sub>O<sub>4</sub> Nanorods as Lithium Ion Battery Cathodes”, *Nano letters*, 8, 11, 3948-3952, 2008.
8. Wang D.; Wei C.; Lin M.; “Advanced rechargeable aluminium ion battery with a high-quality natural graphite cathode” *Nat. Commun*, 8, 14283, 2017.
9. Lin M.; Gong M.; Lu B.; *et al.*; “An ultrafast rechargeable aluminium-ion battery” *Nature*, 520, 324, 2015.
10. Kerman K.; Luntz A.; Viswanathan V.; *et al.*; “Review—Practical Challenges Hindering the Development of Solid-State Li Ion Batteries”, *J. Electrochem. Soc.* 164, A1731, 2017.
11. Yang H.; Li H.; Li J.; *et al.*, “The rechargeable aluminum battery: opportunities and challenges,” *Angewandte Chemie International Edition*, vol. 58, no. 35, pp. 11978–11996, 2019.
12. Elia G. A.; Marquardt K.; Hoeppe K.; *et al.*; “An overview and future perspectives of aluminum batteries,” *Advanced Materials*, vol. 28, no. 35, pp. 7564–7579, 2016.
13. Dong X.; Xu H.; Chen H.; *et al.*; “Commercial expanded graphite as high-performance cathode for low-cost aluminum-ion battery,” *Carbon*, vol. 148, pp. 134–140, 2019.
14. Zhang C.; He R.; Zhang J.; *et al.*; “Amorphous carbon-derived nanosheet-bricked porous graphite as high-performance cathode for aluminum-ion batteries,” *ACS applied materials & interfaces*, vol. 10, no. 31, pp. 26510–26516, 2018.
15. Wei J.; Chen W.; Chen D.; and Yang K.; “An amorphous carbon-graphite composite cathode for long cycle life rechargeable aluminum ion batteries,” *Journal of Materials Science & Technology*, vol. 34, no. 6, pp. 983–989, 2018.
16. Wang D. Y.; Wei C. Y.; Lin M. C.; *et al.*; “Advanced rechargeable aluminum ion battery with a high-quality natural graphite cathode,” *Nature communications*, vol. 8, p. 14283, 2017.
17. Kravchuk K. V.; Wang S.; Piveteau L.; and Kovalenko M. V.; “Efficient aluminum chloride–natural graphite battery,” *Chemistry of Materials*, vol. 29, no. 10, pp. 4484–4492, 2017.
18. Choi S.; Go H.; Lee G.; and Tak Y.; “Electrochemical properties of aluminum anode in ionic liquid electrolyte for rechargeable aluminum-ion battery,” *Physical Chemistry Chemical Physics*, vol. 19, no. 13, pp. 8653–8656, 2013.
19. Lee D.; Lee G.; and Tak Y.; “Hypostatic instability of aluminum anode in acidic ionic liquid for aluminum-ion battery,” *Nanotechnology*, vol. 29, no. 36, article 36LT01, 2018.
20. Wu F.; Zhu N.; Bai Y.; Gao Y.; and Wu C.; “An interfacial reconstruction effect for rechargeable aluminum battery in ionic liquid electrolyte to enhance cycling performances,” *Green Energy & Environment*, vol. 3, no. 1, pp. 71–77, 2018.
21. Wang H.; Gu S.; Bai Y.; *et al.*; “A high voltage and non-corrosive ionic liquid electrolyte used in rechargeable aluminum battery,” *ACS applied materials & interfaces*, vol. 8, pp. 27444–27448, 2016.
22. Hasan BB.; Abood MA.; Mohamed SN.; “Preparation and characterization of deep eutectic solvent: Physical properties and electrochemical studies” *AIP Conference Proceedings* 2398, 030009/10.1063/5.0095413, 2022.
23. Hasan BB.; Abood MA.; Mohamed SN.; “Effect of Some Aluminum Salts - Amine Ionic Liquids on Several Serum Human Parameters and Bacterial Growth of *Klebsiella pneumoniae* and *Staphylococcus aureus*” *Journal of Al-Nahrain University* 21(1):14-22/10.22401/JUNS.21.1.03, 2018.
24. Abood H.; Abbott A.; Ballantyne A. and Ryder K.; “Do all ionic liquids need organic cations? Characterization of [AlCl<sub>2</sub>.nAmide] + AlCl<sub>4</sub><sup>-</sup> and comparison with imidazolium-based system”; *Chem. Commun.*; 47; 3523-3525; 2011.
25. Zhu N.; Zhang K.; Wu F.; “Ionic Liquid-Based Electrolytes for Aluminum/Magnesium/Sodium-Ion Batteries”, *Energy Material Advances*, 10.34133/9204217, 2021.

26. Hasan, B. B; Salman, T. A; New ionic liquids constructed on complexation of Aluminum chloride anhydrous and Chloroacetamide, chemrxiv-2022, 10.26434.
27. Wenjing Li, Zhaofu Zhang, Buxing Han, Suqin Hu, Ye Xie, and Guanying Yang, "Effect of Water and Organic Solvents on the Ionic Dissociation of Ionic Liquids" J. Phys. Chem. B 2007, 111, 6452-6456.
28. Annika Stein, Daniel Kehl, Cedric Jackmann, Stefan Essmann, Frank Lieneschand Michael Kurrat "Thermal Electrical Tests for Battery Safety Standardization" Energies 2022, 15, 7930. <https://doi.org/10.3390/en15217930>
29. Cristina Gonzalez Moral, Diego Fernández Laborda, Lidia Sánchez Alonso, Juan Manuel Guerrero, Daniel Fernandez, Carlos Rivas and David Díaz Reigosa, "Battery internal resistance estimation using a batterybalancing system based on switched capacitors" IEEE, 56, 5, 5363 – 5374, 2020, DOI: 10.1109/TIA.2020.3005382
30. Dries De Sloovere, Danny E. P. Vanpoucke, Andreas Paulus, Bjorn Joos, Lavinia Calvi; *et al.*; "Deep Eutectic Solvents as Nonflammable Electrolytes for Durable Sodium-Ion Batteries" Adv. Energy Sustainability Res. 2022, 3, 2100159.
31. Michael Angell, Guanzhou Zhu, Meng-Chang Lin, Youmin Rong, and Hongjie Dai, "Ionic Liquid Analogs of AlCl<sub>3</sub> with Urea Derivatives as Electrolytes for Aluminum Batteries" Adv. Funct. Mater. 2019, 1901928
32. Andrew P. Abbott, Fulian Qiu, Hadi M. A. Abood, M. Rostom Aliac and Karl S. Ryder "Double layer, diluent and anode effects upon the electrodeposition of aluminium from chloroaluminate based ionic liquids" Phys. Chem. Chem. Phys., 2010, 12, 1862–1872.