

Chapter 10

A Concept Note on Aqueous Type Graphite Dual-ion Battery: A Promising Low-Cost Electrical Energy Storage Technology



Sunny Nandi, Arnab Dutta, and Shyamal K. Das

Abstract Electrical energy storage technologies are an integral part of renewable energy generation infrastructure. The rechargeable battery is a unique example of portable storage technologies. Among various rechargeable batteries, dual-ion batteries are catching the attention recently. Herein, we present a proof-of-concept of a novel and eco-friendly dual-ion battery with electrochemically processed graphite electrodes in aqueous electrolyte. We also take the advantage of the three electrons transfer process of Al^{3+} ion while operating the battery. The battery shows excellent cycling stability over 100 cycles with specific capacity of 10 mAhg^{-1} . The notable part of the work is that it proposes to use exceptionally low-cost and easily available raw materials.

Keywords Energy storage · Dual-ion battery · Graphite

1 Introduction

The global carbon-dioxide emission due to fossil fuel burning for energy generation is estimated to be 33 gigatonnes in 2019 [1]. This massive quantity of carbon footprint is a major cause in bringing certain degree of uncertainty and instability to our environment. In a bid to circumvent this problem, harnessing energy from small- and large-scale renewable sources is gaining unprecedented popularity worldwide. The United Nations also acknowledged this very idea of eco-friendly electricity generation and consumption by pinning ‘Affordable and Clean Energy’ as one of Sustainable Development Goals. However, the unpredictable and intermittent nature of renewable energy sources demand its integration with electrical energy storage devices for a more viable and consumer friendly on-demand consumption. It has unambiguously propelled the research interest in the area of energy storage technologies. In order to tap the vastness of renewables, a wide variety of storage technologies is available. For

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instance, a pumped hydroelectric system is an excellent storage technology capable of storing electricity in gigawatts [2]. These kinds of large-scale systems are permanently installed in desired geographical territories for the delivery of electricity in the grid. However, this option has limited opportunity for portable consumption of electricity. The revolution that has undergone in the last decade in the electronics industry relentlessly demands for more-efficient, long-lasting, lightweight, and small-scale energy storage devices. Hence, rechargeable batteries emerged as the powerhouse for storing and on-demand delivery of portable mode of electricity. The most notable among rechargeable batteries which made remarkable contributions to our modern way of living is lithium-ion battery. These types of batteries possess exceptionally high energy density, long life time, and require low maintenance. In recent times, however, the depleting condition of the essential ingredients for the manufacturing of lithium-ion batteries and a rapid surge in their cost have set off alarm bells both in academia and industry. Consequently, it has a triggering effect to find alternative rechargeable batteries base on inexpensive and naturally abundant resources.

There are several propositions on analogues of lithium-ion batteries based on elements such as Na, K, Zn, and Mg [3]. However, an old concept of dual-ion batteries is resurfaced and gaining immense popularity recently. There is a clear distinction in the operation of dual-ion and lithium-ion batteries as shown in Fig. 1. In lithium-ion

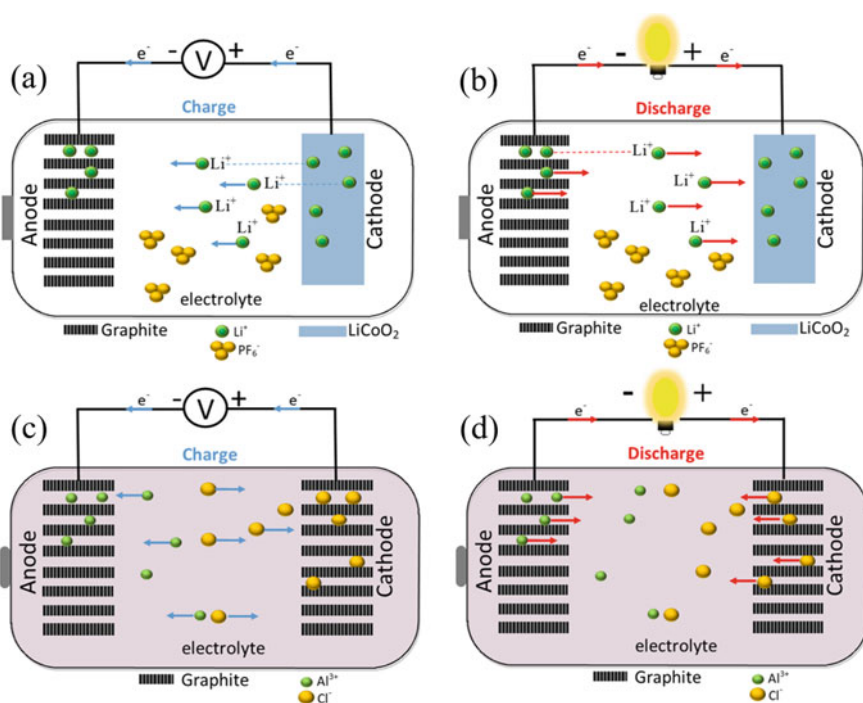


Fig. 1 Schematic of **a, b** Lithium-ion battery and **c, d** Dual-ion battery in charge and discharge conditions

batteries, the cation (i.e., Li^+ ion) shuttles between the cathode and anode through the electrolytic medium (Fig. 1a, b). The direction of Li^+ ion migration depends on the discharge and charge cycles. The source of Li^+ ions is an inorganic lithium salt such as LiPF_6 dissolved in non-aqueous solvent or solvent mixtures. This electrolyte also contains PF_6^- anion, which remains inactive during the operation of the battery. The typical cathode and anode in lithium-ion batteries are lithium cobalt oxide and graphite, respectively. On contrary, in dual-ion battery, both the cation and anion available in the electrolytic medium simultaneously shuttle between the cathode and anode. In the charging process, the cation (e.g., Al^{3+} ion) and anion (e.g., Cl^- ion) intercalate in the anode and cathode, respectively (Fig. 1c). The reverse process occurs during the discharge cycle. The opposite charge transport processes in two opposite directions result in enhanced electron transport in the external circuit and, hence, it boosts the energy and power density of the system. The challenge in dual-ion battery is to find an electrode material which could host anions. The cations such as Li^+ , Na^+ , Mg^{2+} could, in general, be easily diffused in an electrode due to their small ionic radii. However, the large-sized anions encounter steric barrier during the diffusion process in an electrode. Hence, there are very few known electrode materials as anion host [4]. One such promising candidate is graphite. Rüdorff and Hofmann, in 1938, first demonstrated the electrochemical intercalation of HSO_4^- anion from concentrated sulfuric acid electrolyte in graphitic electrode [5]. It is well-known that graphene sheets are stacked in ABAB configuration in graphite. The interplanar spacing in graphite is 0.335 nm and the graphene sheets are held together by weak van der Waals forces. Under suitable electrochemical conditions, certain cations and anions can intercalate in between the graphene sheets overcoming the van-der-Waals force. Some of the examples of anions that intercalate in graphite are PF_6^- , BF_4^- , AlCl_4^- , ClO_4^- , TFSI⁻, etc. [6]. Based on the intercalation of these types of anions, there are demonstrations of the operation of dual-ion batteries in recent times [4]. However, these studies make use of non-aqueous carbonate or ionic liquid-based electrolytes. The demerits of such type of electrolyte are high cost, harmful to environment, and difficulty in handling them in ambient atmosphere. Hence, despite graphite being a low-cost and eco-friendly material, the choice of electrolytes may not make dual-ion batteries a green and sustainable system.

In an effort to build an exceptionally low-cost and sustainable dual-ion battery system, we embark on to investigate the operation feasibility of such system in water based (or aqueous) electrolyte. This type of electrolyte has the merits of being low-cost, ease in processing, and environment friendly. We demonstrate here the proof-of-concept of a dual-ion battery utilizing graphite as electrodes and aqueous electrolyte. The demonstrated battery could be easily assembled in ambient atmosphere unlike lithium-ion battery or non-aqueous dual-ion battery. We note that further studies are essential for improving the performance of the system. It is also noted here that this work draws inspiration from the outcome of our previous work on aqueous aluminum-graphite battery [7].

2 Experimental Section

2.1 Materials

Commercially available graphite foil of thickness 0.5 mm is used in the work. The aqueous electrolyte is prepared by dissolving aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) in 1 M concentration in ambient atmosphere. It is worth to mention here that one should be extremely careful while preparing the electrolyte since AlCl_3 exothermically reacts with water. The electrolyte can be stored for several months without any degradation.

2.2 Processing of Graphite Electrode

An electrochemical process was applied to obtain the functional graphite electrodes for the dual-ion battery. Two pieces of graphite foil of dimension 1 cm \times 1.5 cm (breadth \times length) were submerged in a glass cell containing 1 M AlCl_3 aqueous electrolyte. The separation between the two was maintained at 1 cm. The immersion length of both the electrodes in the electrolyte was 1 cm. A DC potential (or bias) of 3 V was applied between the electrodes using a DC power source for 5 min. The experimental setup is shown in Fig. 2. After the application of the bias, the graphite electrodes were washed with deionized water for several times and dried at 110 °C for 12 h. These dried electrodes were further used for assembling the dual-ion battery.

2.3 Characterization of the Processed Graphite Electrode

The crystallographic phase identification was performed by using powder X-ray diffraction (BRUKER AXS D8 FOCUS; Cu- K_α radiation, $\lambda = 1.5406 \text{ \AA}$). The surface morphology of the electrodes was observed by scanning electron microscopy (SEM, JEOL JSM 6390LV) and transmission electron microscopy (TEM, JOEL JEM 2100).

2.4 Electrochemical Analysis

The dual-ion battery was assembled with two processed graphite electrodes. These two electrodes were dipped in 1M AlCl_3 aqueous electrolyte. Galvanostatic discharge/charge experiments at different current rates were performed to test the feasibility of operation of the battery. All experiments were performed at room temperature and in ambient conditions.

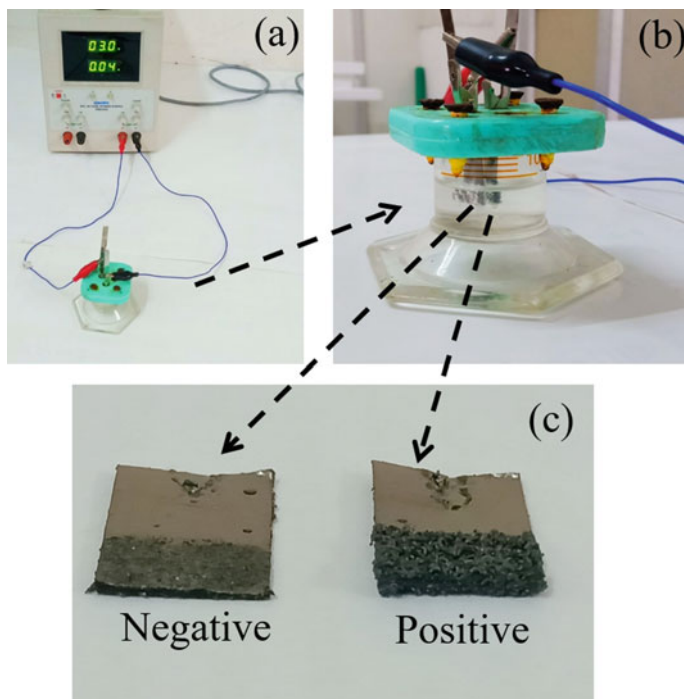


Fig. 2 a Experimental setup for performing the electrochemical processing of the graphite electrode, b enlarged view of the electrochemical cell, and c digital photograph of the graphite electrodes connected to the positive and negative terminals of the electrochemical cell

3 Results and Discussion

As discussed earlier, one of the fundamental criteria for the functioning of a dual-ion battery is the availability of sufficient cation and anion in the electrolyte. It is noted here that the utilized electrolyte contains hydrated Al^{3+} cations and Cl^- anions as charge carriers [7]. Hence, the selection of the electrolyte for the present work is well justified. Another prime reason for using Al^{3+} ion electrolyte is that each Al^{3+} cation pushes three electrons across the load unlike one electron per Li^+ ion. In addition, AlCl_3 electrolyte is extremely cheap and easily available.

Our previous reported work on aqueous Al-graphite battery evidenced that pristine graphite electrode is not suitable for Al^{3+} ion storage in aqueous electrolyte. It is because the intercalation process of Al^{3+} ions between the graphene layers in pristine graphite electrode is extremely slow due to the large dimension of the electrode. Hence, it is important to process the pristine graphite electrode to obtain graphene like nanostructures so that the diffusion process could be reasonably enhanced. This is the reason for the electrochemical processing of the graphite electrode prior to the assembly of a dual-ion battery. It is worth to note here that only the graphite electrode

connected to the positive terminal of the DC power source shows expansion (Fig. 2c) and, hence, only this processed electrode is used in the dual-ion battery.

Figure 3 compares the surface morphology of pristine graphite and the processed graphite electrode. It is clearly evident that the surface of the processed graphite electrode is covered with nanoflakes (Fig. 3b), whereas the pristine graphite surface is smooth (Fig. 3a). The digital photograph, as shown in Fig. 2c, shows an expansion of the processed electrode. Thickness measurement by Vernier calipers indicates 200–250% expansion of the graphite electrode after processing. TEM images (Fig. 3c, d) show few layers of graphene nanoflakes.

The phenomenon of Cl^- anion intercalation in graphene like electrode is evidenced from the ex situ XRD investigations conducted on the charged and discharged state graphene electrodes derived from an aqueous Al-graphite cell. Figure 4 shows the normalized ex situ patterns. The charged state electrode shows the disappearance of (002) graphitic peak usually observed at $2\theta = 26.33^\circ$. In fact, this peak is prominently observed for the pristine electrode. Now, there is emergence of two new peaks at 25.03° and 27.52° . This splitting of the (002) peak during charging cycle indicates an additional intercalation process with Al^{3+} ion intercalation in the graphene electrode. Since the only other available charged species is Cl^- anion, it gives an indirect evidence of Cl^- anion intercalation in the graphene electrode during the electrochemical process and this process is reversible. Hence, both Al^{3+} cation and Cl^- anion can participate in the redox process when a graphitic electrode is used

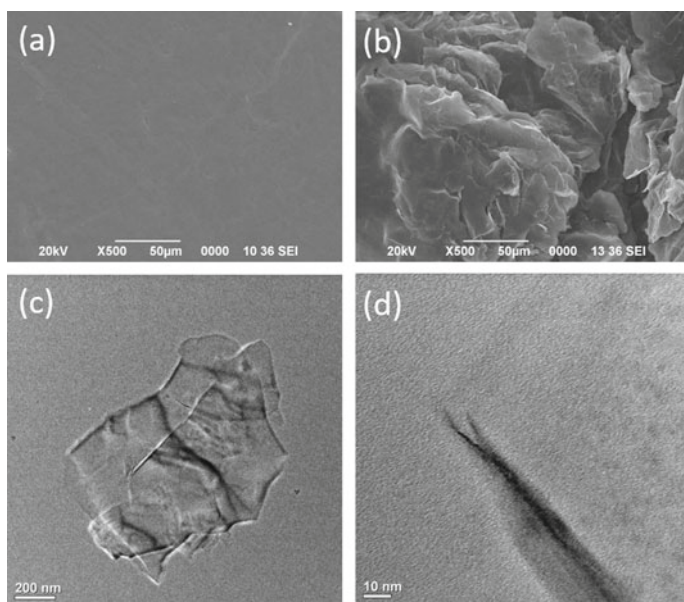
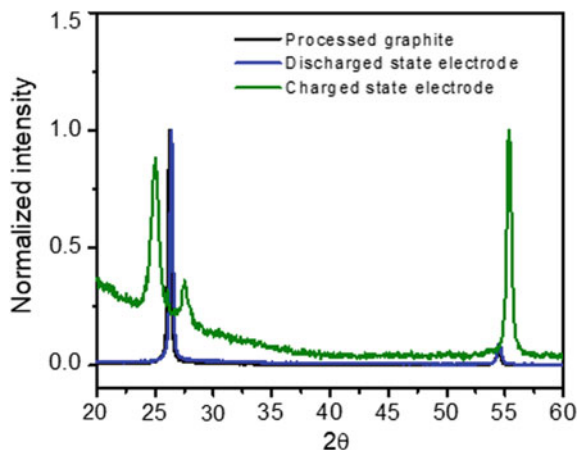


Fig. 3 SEM images of **a** pristine graphite electrode and **b** processed graphite electrode. **c, d** TEM images of the processed graphite electrode

Fig. 4 Ex-situ XRD patterns of discharged and charged state electrodes to verify Cl^- anion intercalation in graphene like electrode. Adapted with permission from Ref. [7], Copyright (2019) American Chemical Society



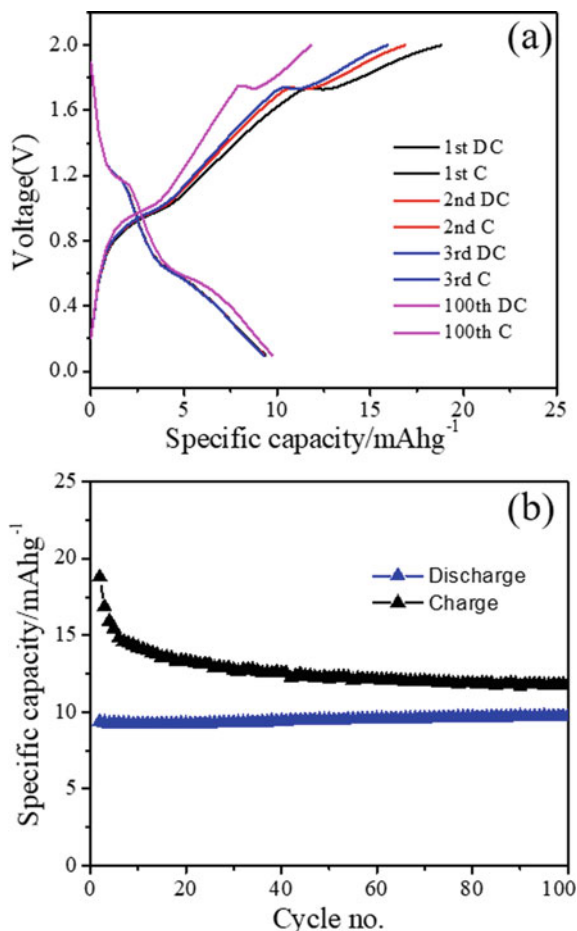
in a battery. Based on this outcome, we explore the feasibility of a dual-ion battery with the processed graphite as both cathode and anode in AlCl_3 aqueous electrolyte.

Galvanostatic charge–discharge experiments were performed to test the viability of a graphite–graphite dual-ion battery in the AlCl_3 aqueous electrolyte. Figure 5a shows the charge–discharge curves obtained at a current rate of 3 Ag^{-1} in the voltage range of 0.01–2 V. The discharge capacity is observed to be 10 mAhg^{-1} . The battery shows excellent durability test. It could show sustainability over 100 cycles without loss of any specific capacity as shown in Fig. 5b. The energy density of the investigated dual-ion battery is lower in comparison to commercially available lead-acid battery. The low energy density is attributed to the higher weight of the graphite electrodes. There exists tremendous opportunity to improve it by utilizing low-mass and thin processed graphite electrodes. The operating reactions in the battery could be summarized as follows: (a) graphite anode: $\text{C}_x + \text{Al}^{3+} + 3\text{e}^- \leftrightarrow [\text{Al}]\text{C}_x$, (b) graphite cathode: $\text{C}_y + \text{Cl}^- \leftrightarrow [\text{Cl}]\text{C}_y + \text{e}^-$ (x and y are, respectively, the molar ratios of carbon atoms to intercalated Al^{3+} and Cl^- ions in the graphite electrode).

4 Conclusions

In summary, a concept note on rechargeable aqueous dual-ion battery is proposed with processed graphite electrode. The battery utilizes raw materials which are locally available in high abundance, low-priced, and eco-friendly. It is noted here that the energy density is quite low in comparison to lithium-ion or lead-acid battery. However, this kind of concept is an important basis for future studies and further improvements in energy storage technologies.

Fig. 5 **a** Galvanostatic charge–discharge curves of graphite–graphite dual-ion battery, **b** variation of charge–discharge capacities with cycle number



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