Recent Advances in the Use of Carbonyl Compounds as Active Components in Organic-Based Batteries


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Keywords: Carbonyl Compounds Battery Energy

1. Introduction

The world’s increasing energy demand has led to the exploitation of non-renewable energy supplies such as coal, oil, natural gas etc., [1, 2] which has led to the emergency problems of climate change, smog, impeding exhaustion of fossil fuels, and constant threats of global warming. These have therefore resulted to a quest for a low-carbon society where intensive research efforts have been channelled towards the field of renewable energy. Several renewable energy options such as the solar, wind, biomass, hydropower and tidal energies were proposed and investigated with the hope that they can prove solutions to mitigate the aforementioned crisis [3-6]. The efficient utilization of such intermittent energy sources requires effective and flexible storage systems [7-13]. On the other hand, battery systems (with a long battery life of > 10,000 cycles, high current density and fast charging) are identified as a viable solution [7, 8], while on the other hand, the cost of production of a conventional battery is far from ideal, owing to the fact that the fabrication of electrodes from limited ores increases battery cost and similarly the life cycle of the batteries are far from the stated value because their operations are driven by redox reaction of the metal elements [14, 15].

Furthermore, there are safety concerns with respect to the currently available types of batteries because they contain toxic and/or environmentally unfriendly components, such as toxic non-aqueous electrolyte in current Li-ion batteries, acid/alkaline electrolyte in Ni-MH or lead-acid batteries, and toxic electrode materials such as Pb in lead-acid batteries, Cd in Ni-Cd batteries, VOx in vanadium flow batteries, and Br in Zn-Br2 flow batteries. It is therefore essential that these toxic materials be replaced with non-toxic, biodegradable materials so that they can become more sustainable and less hazardous to the environment. Similarly, the growing markets for thin, small and lightweight portable devices also require battery systems of similar properties by adjusting their structural flexibility, redox stability, renewability and structural diversity. Interestingly, organic compounds of carbonyl functionality have been identified as potential candidates to proffer solutions to the above-mentioned challenges. This review therefore discusses various classes of carbonyl compounds as active components in some rechargeable batteries, highlighting their major strengths and drawbacks.
1. Those that employ vicinal carbonyls to form stable enolates e.g. 1,2-diones which can be further stabilized by neighbouring aromatic systems as in phenanthraquinones.

\[ \text{N} - \text{N} - \text{N} \rightarrow +2e^- +2Li^+ \rightarrow -2e^- -2Li^+ \]

2. Those that contain aromatic carbonyl derivatives directly connected to an aromatic core, dispersing the negative charge by delocalization.

\[ \text{NH} - \text{NH} \rightarrow +2e^- +2Li^+ \rightarrow -2e^- -2Li^+ \]

3. Those that contain quinonestructures whose stabilizing force is the formation of additional aromatic system upon reduction.

\[ \text{N} - \text{O} \rightarrow +4e^- +4Li^+ \rightarrow -4e^- -4Li^+ \]

1.1 Operating Principles of a Battery

Batteries, regardless of their chemistry (aqueous, non-aqueous, Li or Na-based) store energy within the electrode structure through charge transfer reactions. Such device architecture consists of several electrochemical cells that are connected in series and/or in parallel in order to provide the required voltage and capacity, respectively. Each cell is composed of a positive electrode referred to as the cathode which is usually contained within the battery and a negative electrode known as the anode which usually forms the outer case of the battery. These are terminals where the redox reactions take place i.e. oxidation takes place at the anode while reduction takes place at the cathode. The electrodes are separated by an electrolyte, usually a solution containing dissociated salts so as to enable ion transfer between the two electrodes i.e. cations which are positively charged ions move from the anode to the cathode and anions which are negatively charged ions move from the cathode to the anode. Once these electrodes are connected externally, the chemical reactions proceed in tandem at electrodes, liberating electrons and providing the current to be tapped by the user.

Fig. 1 Schematic illustration of (A) cell structure and (B) electrode reactions

2.1 Factors Affecting the Electrochemical Performance of Organic Carbonyl-based Batteries

Certain parameters of interest namely cell voltage and charge/discharge cycling stability of batteries are used performance indicators of a battery systems. However, the aforementioned parameters are influenced by some factors which reduce the theoretical efficiency of the battery. It can be recalled that the architecture of a battery requires two electrodes with different redox potentials; carbonyl compounds can have their redox potentials improved or lowered by adding substituents which can either have electron donating or withdrawal effect. These substituents that are not directly involved in the redox process decrease the theoretical capacity of the compound since it is a function of the molar mass of the compound and the number of electrons utilized during the reaction [43]. Also, charge/discharge cycling of the battery is dependent on several factors, some of which includes; solubility of the active materials in solution resulting to decrease in capacity, side reactions and/or instabilities of anions formed, structural modification during the charge/discharge leading to capacity loss on cycling. Finally, low conductivity of organic materials is also a limiting factor and this should be addressed by using conductive additive materials such as carbon nanotubes [44] and graphene [45, 46] in order to improve electron transport within the electrode.

3. Classes of Carbonyl-Containing Electrode Materials

This aspect of the review discusses the various classes of carbonyl-containing materials with different active sites depending on the type of functional groups present, which are employed as electrode materials in rechargeable batteries with emphasis placed on material activity and cycling stability.

3.1 Organic Anhydrides

This class of carbonyl compound was first studied as electrode material in rechargeable battery by Han and his co-workers in 2007. They utilized 3,4,9,10-perylenetetracarboxylicdianhydride as a functional material which yielded an initial capacity of 135 mAhg\(^{-1}\) with a cycling stability of 60% loss over 80 cycles due to dissolution in the electrolyte [25]. However, it showed improved performance when employed as cathode material in a sodium-ion battery [47]. The general mechanism for any aromatic anhydride is that it undergoes two-step electron reduction in which the reduced system is stabilized by enolation. Its application as an active component in energy storage systems owes to the fact that the stabilized carbonyl allows for reversible insertion of lithium ions at the oxygen atom of the anhydride functional group.
This class of carbonyl compounds has proven to be an electrode material in energy storage systems because it has a unique ability to undergo two-step redox reactions involving two electrons. This is because stability is achieved on the carbonyl molecules during the first stage of the reaction by inducing the formation of stabilized radical anions on the electrode, which do not conduct to the second step inappropriately because it results in the destruction of the redox system. Aromatic imides have been successfully employed in battery systems because of its high specific theoretical capacity (248 mAh g⁻¹). The first success story with respect to aromatic imides was recorded by Renault and his co-workers in 2011 [48]. They investigated the charge/discharge properties of dilithium pyromellitimide used as an electrode material in a rechargeable battery, they found out that the material exhibited an activity of 220 mAh g⁻¹ which slightly dropped even after 25 charge/discharge cycles to about 200 mAh g⁻¹. Another aromatic diamides employed for the same purpose is naphtalene díamide [49], which exhibited material activity of 140 mAh g⁻¹ but drops to 80 mAh g⁻¹ after 100 cycles.

Even though these classes of carbonyl compound have shown promise, their full cycling stability has not been achieved yet because their practical application as an active component in rechargeable batteries is hampered by their solubility in electrolytes. This can be partly resolved by the formation of metal salts of the corresponding imide which have lower solubility in most of the electrolytes used in rechargeable batteries or alternatively, by using aqueous electrolytes which comes with its own drawbacks.

### 3.3 Polyamides

Similarly, polyamides because of their redox-active properties are also considered as candidates for secondary energy storage systems. These possessed similar two-step redox reaction involving two electrons exhibited by aromatic diamides with the first reversible reaction utilized in storage systems. So, the theoretical capacity of the materials is a function of the size and the aromatic unit between the two β-diketimide molecules. The smaller the aromatic unit, the lower the redox potential and the higher the theoretical capacity of the material. To this end, several polyamides have been intensively studied as electrode materials in both lithium and sodium batteries, some of which include: polyimides synthesized by polycondensation of 1,4-phenylenediamine with pyromellitic anhydride 6 and 4,4'-oxydipthalic anhydride [50], polyimides synthesized by polycondensation reactions of pyromellitic anhydride and 1,4,5,8-naphthalenetetracarboxylic dianhydride with 1,4-phenylenediamine and 1,2-benzenediamine were investigated [51]. Dense polyamide networks were obtained by polycondensation of 1,2,5-tris(4-aminophenyl)benzene with pyromellitidianhydride 1,4,4,5,8-naphthalenetetracarboxylic dihydride and 3,4,9,10-perylene tetracarboxylic dihydride, respectively [52]. These materials showed varying degree of success in terms of material activity, redox potential and charge/discharge cycling stability. However, the application of polyamides as cathode materials in both lithium and sodium batteries is still hampered by two major drawbacks which are; low operating voltage, usually 1.5 to 2.3 V vs. Li/Li⁺ and deep discharging can lead to the destruction of the active material through irreversible reactions because the polyamide system has little protection against the second reduction of the β-diketimide system.

### 3.4 Conjugated Carboxylates

Organic conjugated carboxylic acids undergo a reversible two electron redox reaction, whereby the resulting diamin is stabilized by a conjugated, preferably aromatic system. The loss of resonance or aromaticity in the core of the molecule stabilizes the redox reaction to very low potential. The first example of carboxylates in organic sodium-ion batteries (OSIBs) was disodium terephthalate (Na₂TAP) which was simultaneously reported by two research groups [53, 54]. Na₂TAP contains two carboxyl groups that allow inserting or extracting Na-ions, corresponding to a theoretical capacity of 255 mAh g⁻¹. Similarly, organic lithium batteries based on dilithium terephthalate electrodes displayed an extraordinary performance. At a cell potential of 0.5 V a capacity of 300 mAh g⁻¹ (100% active material) was observed at the first charge/discharge cycle. Upon cycling over 50 charge/discharge cycles, the battery still exhibited a capacity of 234 mAh g⁻¹ (78% material activity) [55]. Several other carboxylates have been tested positive as electrode materials in a rechargeable battery which include 4,4'-oxalenedicarboxylate [56], (2,5-dilithium-oxyl)terephthalate [57] and 2,5-pyrazinedicarboxylate [58].

### 3.5 Ketones

Ketones can be electrochemically reduced to the corresponding alcohols and reoxidized to their original state, realizing a one-electron redox reaction. Several compounds of ketones have been tested positive as an electrode material some of which included isodium salt of rhodizonate [59], which has a theoretical capacity of approximately 500 mAh g⁻¹ and has been extensively studied in sodium ion battery. It yielded a capacity of 150 mAh g⁻¹ which drops to 18 mAh g⁻¹ after 40 cycles. Similarly, tri-carbonyl-based tri-N-salicylidenenanthranilic (TSAAn) and tri-N-salicylideneanthraquinonic (TSAQ) showed irreversible transformation between C=O and C-ONa because the reactivity of the α-carbon radical intermediates was largely suppressed by an electronic resonance effect and steric hindrance from the substitution groups [60]. TSAQ delivered capacities of 370 and 220 mAh g⁻¹ at 50 mAh g⁻¹ and 1 Ag⁻¹, respectively, and showed no obvious capacity degradation after more than 2500 cycles at 1 Ag⁻¹.

### 3.6 Quinones

The quinone materials are regarded as the most important electrode materials in the carbonyl electrode materials for secondary batteries owing to their higher redox potentials and higher theoretical capacities compared with other imides and conjugated carboxylate-based electrodes. This is because they are resource abundant and have environmental benignity. They can be extracted or refined from many plants. The quinone electrode materials can be categorized into two different groups: small molecule quinone electrodes (e.g. multi-carbon quinone fused heteroaromatic, quinone polymers, and, quinone derivatives as oxo-carbon salts and carboxylic quinones) and quinone polymer electrodes. Small molecule quinones with high theoretical capacities, such as benzoquinone, anthraquinone and phenanthrene quinone [61, 62], can generate multi-electron transfer reversible reaction. With the benzoquinone as the base compound, and polymeric, form multivalent charged anions, leading to a high theoretical capacity for the quinone materials. Taking benzoquinone as an example, during the discharge process, one of the carbonyl groups accepts one electron and forms a free radical anion, and the other carbonyl group continues to obtain more electrons, producing divalent anions. The redox mechanism of the quinone electrode materials is based on electron transfer reaction therefore they can only be applied in Lithium ion batteries/sodium ion batteries but also can be extended to magnesium, zinc batteries and supercapacitors. The first example of quinone in a battery system was reported by Williams in 1970 [36] where they used dichloroisocyanuric acid (DCA) as the active component. The DCA electrode showed an irreversible electrochemical redox reaction in an organic non-aqueous electrolyte. Chloranil as an electroactive material reported by Alt et al. was used in the first secondary battery [65]. The quinone electrode displayed 95% retention of capacity after 50 cycles at a current rate of 0.5 C in both aqueous acid and organic electrolytes. In general, the quinone electrode materials showed the advantages of high theoretical capacity and high resource availability. Although the three main challenges of the organic materials such as the dissolution of the quinone electrodes in organic electrolytes, poor electronic conductivity and low discharge plateaus need to be solved before practical application in secondary batteries. One approach to overcome the dissolution problem of small molecule quinoid structures in the electrolyte and the consequent capacity loss is the incorporation of the quinone structure into a polymeric moiety. This approach is accompanied with challenges. The choice of the appropriate polymerization technique is difficult because of both the radical scavenging properties of quinones and their electrophilic and nucleophilic moiety. Generally speaking, high yield polymers depend on polymerization techniques.

### 4. Conclusion and Future Perspective

Application of carbonyl compounds as active components in rechargeable batteries over the last three decades have come a long way owing to their environmental benignity and resource availability. This study reveals that various classes of carbonyl compounds can be employed...
as electrode materials with high theoretical capacity but their electrochemical performance is dependent on the functionality of the carbonyl compounds themselves. Of all the classes of carbonyls considered, quinone structures in our opinion, are the most promising class of carbonyls to be explored in this regard but the progress achieved hitherto is far from ideal, owing to the fact that quinone just like most other organic compounds, is soluble in the system electrolyte, has low electrochemical stability and discharge potential. However, these challenges could be addressed by modifying their structures with carbon-based materials such as graphene, carbon nanotubes and porous carbon. This can not only improve the conductivity but will also inhibit dissolution of the quinone themselves.

From a sustainable point of view, carbonyl compounds can be obtained from a wide range of renewable sources including plants, and various extraction techniques have been revealed on how to utilize this important class of organic compounds in energy storage-gt still remains a major challenge for carbonyl compounds to achieve high energy, power density and material activity. There are still many possibilities to improve the electrode kinetics and the capacity of organic carbonyl compounds to discover even more efficient electroactive structures.

References


