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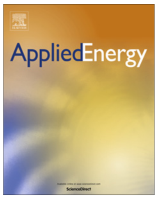

Cyclohexanedione as the negative electrode reaction for aqueous organic redox flow batteries

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HIGHLIGHTS

- One of the most negative electrode potentials in neutral/acidic systems.
- Highly soluble (>2.0 mol dm^{-3}) in both reduced and oxidized forms.
- Large theoretical specific capacities (>474 A h kg^{-1}).
- Up to 4 electron-transfers are theoretically possible in this group.
- Reaction mechanisms have been proposed for both acidic and alkaline routes.

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ABSTRACT

The electrochemical reduction and oxidation of cyclohexanedione is evaluated for the first time as the negative electrode reaction in an organic redox flow battery. Electrochemical characterization indicates that the redox reaction of cyclohexanedione is a proton-coupled electron transfer process with quasi-reversible behavior in acidic media (pH < 3). Among three isomeric compounds (1,2-, 1,3- and 1,4-cyclohexanedione), the reduction of 1,3-cyclohexanedione exhibits the most negative electrode potential (*c.a.* −0.6 V *vs.* Ag|AgCl (*c.a.* −0.4 V *vs.* NHE)) as well as the widest pH operating range (pH 1–5) for relatively reversible reactions. The resulting electrode potential is the most negative of those to have been reported in neutral/acidic electrolytes. 1,3-cyclohexanedione is subsequently used as the active species in the negative electrode of a parallel plate flow cell, which is charge-discharge cycled at 3.4 mA cm^{-2} for 100 cycles, yielding half-cell coulombic efficiencies of *c.a.* 99%. The organic molecules derived from this group are observed to have high solubilities (>2 M) and exhibit reduction process with up to 4 electrons transferred.

1. Introduction

The European Union commission has set a target of a 43% reduction in greenhouse gas emissions from all sectors by 2030 (from the 2005 level) [1]. Achieving this and similar targets adopted in other regions of the world will require the wide-scale deployment of renewable power sources in grid-scale and transport applications [2]. In order to facilitate the penetration of intermittent renewables into power grids (provide flexible and stable energy outputs to end-users), it is commonly accepted that efficient and competitively priced energy storage systems will play a major role [3–10].

In the past few decades, a number of energy storage technologies have been developed and successfully demonstrated. Among these technologies, electrochemical devices are considered to be attractive since they can be installed in any location (not terrain dependent in contrast to pumped-hydro and compressed air), do not involve any disruption to the environment and do not involve

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very high capital costs [5,6]. To ensure that energy storage devices are economically viable in long term, the Department of Energy of the United States (DoE) has set a system capital cost target of USD$ 150 kW h by 2023, to match with the operating costs of existing physical energy storage technologies [7–11].

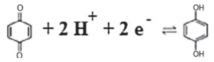
Considering their potential economic and safety advantages, redox flow batteries are recognized as the most realistic candidates for storage in the range of a few kW/kW h up to tens of MW/MW h. In contrast to conventional rechargeable batteries, redox flow batteries store energy in the form of reduced and oxidized electroactive species in flowing electrolytes and/or on the electrode surfaces, while conventional batteries (e.g., lead acid and lithium-ion batteries) contain static electrolytes and store energy within the electrode structures [5]. For flow batteries, the power output and energy capacity can be adjusted readily by increasing the electrode size or/and the electrolyte volume.

Since the invention of the redox flow battery concept, various chemistries based on metallic active materials (i.e. all-vanadium [12], zinc-cerium [13], vanadium-cerium [14] and all-copper [15]) have been proposed. The all-vanadium redox flow battery is the most developed and widely studied system due to its high reversibility and relatively large power output. In relation to the DoE target (USD$ 150 kW h), the capital costs of vanadium systems are, however, still too high (USD$ 200–750 kW h) for extensive market penetration [16]. For example, the electrolyte cost of the vanadium redox flow batteries exceeds USD$ 80 kW h [17].

In order to reduce costs (especially those of the electrolytes), recent investigations have proposed the use of organic active materials. In general, organic molecules are abundant and can be extracted readily from various sources. Even in the early stage of development, the electrolyte cost of the organic flow battery has been demonstrated to be lower than USD$ 35 kW h (half-/full-cell estimations for the redox couples of anthraquinone/benzoquinone or anthraquinone/bromine) [18,19].

The electrolyte cost per kW h can be further decreased by selecting the most suitable active materials with regards to the resulting cell voltages or/and multi-electron transfers. At the same time, the selected organic molecules should provide reasonable energy densities ($\mathrm{W\,h\,dm^{-3}}$) by maintaining high solubilities in particular solvents. In the past few years, several organic compounds, including the derivatives of 2,5-di-*tert*-butyl-1,4,bis(2-methoxyethox)benzene (DBBB) [20,21], quinoxaline [22,23] and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) [24], have been evaluated in non-aqueous solvents (i.e. propylene carbonate, acetonitrile). Despite the wider electrochemical stability windows (>1.3 V) and the possibility of higher solubilities, non-aqueous solvents tend to be volatile and moisture sensitive [25]. The ionic conductivities of these pure solvents (e.g., $1 \times 10^{-8}\ \mathrm{S\,cm^{-1}}$ for propylene carbonate; $6 \times 10^{-10}\ \mathrm{S\,cm^{-1}}$ for acetonitrile) are significantly lower than that of water ($6 \times 10^{-8}\ \mathrm{S\,cm^{-1}}$) [25]. Furthermore, the cost of non-aqueous solvents (e.g. USD$ 1.5–1.7 per $\mathrm{dm^{-3}}$ for propylene carbonate [26]) and their salts (particularly, fluorinated salts) can be a factor of several hundred times more expensive than water (<USD$ 0.004 per $\mathrm{dm^{-3}}$ [27]) and the corresponding salts for industrial applications. For these reasons, the aim of this work is to develop organic redox flow batteries based on aqueous electrolytes.

In recent years, a number of aqueous chemistries with high energy contents have been introduced for energy storage applications [28–32]. For the case of redox flow batteries, there have been few studies of the use of organic molecules [33–41], particularly quinone-based molecules, for the electrode reactions. The prototypical member of the quinone molecule is 1,4-benzoquinone, which is also known as cyclohexadienedione. The corresponding redox reactions in aqueous electrolytes are expressed as follow:



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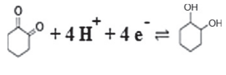
The resulting chemistries involve at least one proton and one electron by forming hydroxyl group(s) (OH—), which result in the transformation of hydroquinone molecules. Such hydroxyl groups not only serve as the liquid carriers of hydrogen for energy conversion [42] but also enhance the solubilities in aqueous electrolytes [43]. The selection of quinone molecules, including benzoquinones, naphthoquinones and anthraquinones, has been facilitated by computational screening within the framework of the density functional theory (DFT), by evaluating the equilibrium potentials and the solubilities of up to 1700 quinone-based redox couples [43]. Unless the functional groups were modified, the equilibrium potentials of the parent isomers of these quinone molecules were between +0.05 and +1.1 V vs. SHE. These previous investigations [43] suggest that the 9-10-anthraquinone (E_0 = +0.1 V *vs.* SHE) is the most suitable redox couple for the negative electrode, whereas the 1,2-benzoquinone, 2,3-naphthoquinones and 2,3-anthraquinone ($E_0 \geq$ +0.7 V *vs.* SHE) are reasonable candidates for the positive electrode reactions.

The resulting quinone-based molecules have been tested experimentally in redox flow batteries by two research groups (Harvard [19,35] and Southern California Universities [33]) in the United States. Both research groups proposed different battery chemistries based on metal-free compounds (Harvard: anthraquinone/bromine; Southern California: anthraquinone/benzoquinone) but used the derivatives of the 9,10-anthraquinone molecules as the negative electrode reactions. The redox potentials of these molecules ($E_0 \geq$ *c.a.* + 0.1 V *vs.* SHE) are still rather too positive, however, to be used as the negative electrode reactions. On the other hand, more than 300 quinones were predicted to have electrode potentials of above 0.7 V *vs.* SHE, which tend to be more positive in neutral/acidic electrolytes, and are therefore suitable for the positive electrode reaction [42].

Furthermore, the reported anthraquinone molecules with sulfonic acid and hydroxyl substituents have solubilities of around $1.0\ \mathrm{mol\,dm^{-3}}$ (9,10-anthraquinone-2,7-disulfonic acid: $1.0\ \mathrm{mol\,dm^{-3}}$ [19]; 9,10-anthraquinone-2,6-disulfonic acid: $0.5\ \mathrm{mol\,dm^{-3}}$ [33], 9,10-anthraquinone-2-sulfonic acid: $0.2\ \mathrm{mol\,dm^{-3}}$ [33]) and even less in the un-substituted forms ($<0.2\ \mathrm{mol\,dm^{-3}}$). For the development of organic redox flow batteries, it is important to search for alternative redox couples that offer negative electrode potentials and reasonable solubilities (i.e. $>0.5\ \mathrm{mol\,dm^{-3}}$). Among the various organic compounds, in this work we investigate the possibility of using cyclohexanedione for the negative electrode reaction in redox flow batteries. The proposed organic compound is a simple molecule (molecular weight: $112\ \mathrm{g\,mol^{-1}}$), similar to benzoquinone in terms of molecular structure, which exhibits two hydroxyl groups for energy conversion. The low molecular weight of this molecule suggests the highest theoretical specific capacities ($474\ \mathrm{A\,h\,kg^{-1}}$ (2 e^- transfers); $948\ \mathrm{A\,h\,kg^{-1}}$ (4 e^- transfers)) among all the organic molecules used in the negative electrolytes (Table S1 in Supplementary Information).

As documented in the field of organic chemistry [44–46], the redox reactions of the three isomeric cyclohexanediones undergo proton-coupled electron transfer, and transform to cyclohexanediol structures:

1,2-cyclohexanedione:



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