Current Applied Physics 16 (2016) 939–943

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Computational screening of organic molecules as redox active species in redox flow batteries

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ARTICLE INFO

Article history:
Received 22 April 2016
Accepted 16 May 2016
Available online 17 May 2016

Keywords:
Redox flow battery
Computational screening
First-principles calculation
Redox active material
Organic molecule
Solvent effect

ABSTRACT

In general, redox active species with a wide redox window and high solubility are necessary to increase the energy density of redox flow batteries. We employed the following three screening factors aimed at identifying such new redox active materials: oxidation potential, reduction potential, and solvation energy. Of the 106 organic molecule candidates, we managed to obtain five molecules that satisfy the screening criteria, namely, trifluoromethoxy-trifluoromethoxybenzylbenzene, bromo-methoxybenzonitrile, dimethoxy-octafluorobiphenyl, chloro-methoxypyridine, and dimethoxyphenyl-ethanone. The characteristics of each molecule are then examined, which enable us to suggest two promising redox active materials for redox flow batteries: fluoro-methoxybenzonitrile and dimethoxy-octafluorobiphenyl.

1. Introduction

In light of the rapid growth of renewable energy sources such as wind and solar energy, the development of an energy storage system is becoming increasingly urgent, since supplies of renewable energy are somewhat irregular. Of the various energy storage systems available, the redox flow battery is one of the most viable options [1–5]. In particular, compared to the conventional transition metal-based active materials, the organic redox active materials in redox flow batteries are considered more suitable for high-capacity energy storage systems due to their superior electrochemical performance, low cost, and design flexibility [6–20].

These redox active molecules store energy through a reversible oxidation–reduction process. A redox active material with a wide redox window and high solubility is required to increase the energy density of redox flow batteries [21,22]. The redox active molecules that have been widely researched in recent years include quinone and quinoxaline compounds with a small molecular weight and high solubility [23–27]. Curtiss et al. [21] reported three screening criteria, namely, oxidation potential > 5.00 V, reduction potential < 1.43 V, and solvation energy < −4.2 kcal/mol. These criteria were devised by calculating the oxidation potential, reduction potential, and solvation energy of quinoxaline derivatives.

We selected 106 organic molecules [28] as candidates for redox active materials, calculated their oxidation potential, reduction potential, and solvation energy, and, based on these results, identified appropriate candidates that satisfy the criteria of a wide redox window and high solubility. Furthermore, we will present two examples of a new material design that takes account of the characteristics specified in the screening criteria.

We believe that computational screening of this type will enable researchers to pinpoint new materials more effectively. Moreover, the suggestion of promising materials may be beneficial for reducing trial and error during the development of high-performance materials in redox flow batteries [29–32].

2. Computational details

For this calculation, we used the methods applied in the previous study [21]. Specifically, 106 molecular structures of all neutral and charged species were optimized using the B3LYP density functional [33] in conjunction with the 6-31+G(d) basis set, and these were confirmed as minimum structures by means of vibrational frequency calculations at the same level of theory. Solvation free energies were calculated using the polarizable continuum model (PCM) [34] at the geometries optimized in the gas phase. The dielectric constant of water (78.36) was used for solvation energy

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http://dx.doi.org/10.1016/j.cap.2016.05.012
1567-1739/

calculation to assess the effect of the dielectric constant on solvation energy. The oxidation potential of the molecule was calculated as ionization potential (IP) + solvation free energy difference [$\Delta G_{solv}(M^+) - \Delta G_{solv}(M)$]. Similarly, the reduction potential was calculated as electron affinity (EA) + [$\Delta G_{solv}(M) - \Delta G_{solv}(M^-)$]. All of the density functional theory (DFT) and PCM calculations were performed using the Gaussian 09 program [35].

3. Results and discussion

Of the 106 molecules, those that satisfy the three screening criteria (oxidation potential > 5.00 V, reduction potential < 1.43 V, and solvation energy < −4.2 kcal/mol) are screened and the characteristics of each molecule are examined. The calculated values for the 106 molecules are listed in Table S1 (see Supplementary data).

Fig. 1 shows the structures, oxidation potential, reduction potential, and solvation energy values of five molecules of the 106 molecules that satisfy the three screening criteria. In this study, we will examine the structures and characteristics of these five molecules and suggest promising candidate materials for redox active species in redox flow batteries.

Fig. 2 shows a graph presenting the oxidation potential, reduction potential, and solvation energy values of the screened molecule **2** and the diphenylmethane-based candidates (**48** and **100**). For additional comparison, the calculated results for diphenylmethane are also listed in Fig. 2. The oxidation potential and reduction potential of diphenylmethane satisfy the screening criteria, but the solvation energy value of −3.19 kcal/mol does not. However, when both ends of diphenylmethane are substituted with the polar functional group $-OCF_3$, the solvation energy become −4.69 kcal/mol, which satisfies the criterion. On the other hand, when electron-donating groups (EDGs) such as −OR and $-NR_2$ are introduced, structures **48** and **100** fail to satisfy the criterion for oxidation potential, but satisfy the solvation energy criterion.

Fig. 3 shows a graph presenting the oxidation potential, reduction potential, and solvation energy values of the screened molecule **3** and the methoxybenzene-based candidates (**11**, **16**, and **58**). For comparison, the calculated results for methoxybenzene are also listed in Fig. 3. All the calculated methoxybenzene derivatives satisfy the reduction potential criterion. However, the oxidation potential and solvation energy values of the molecules do not

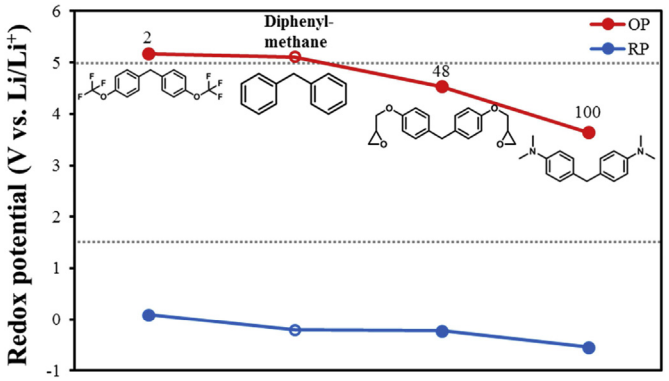


Fig. 2. Graph presenting the oxidation potential, reduction potential, and solvation energy values of the diphenylmethane derivative molecules (red: oxidation potential, blue: reduction potential, filled circle: solvation energy < −4.2 kcal/mol, empty circle: solvation energy > −4.2 kcal/mol). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

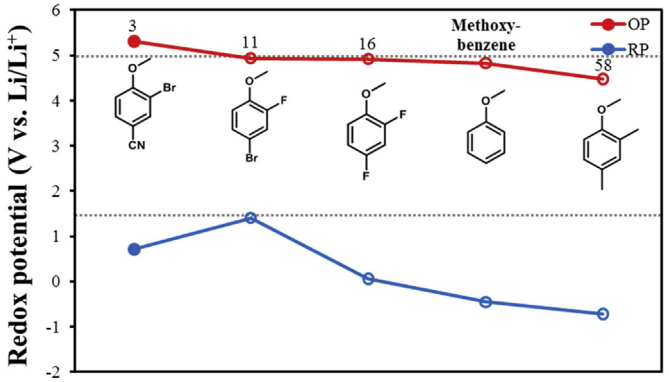
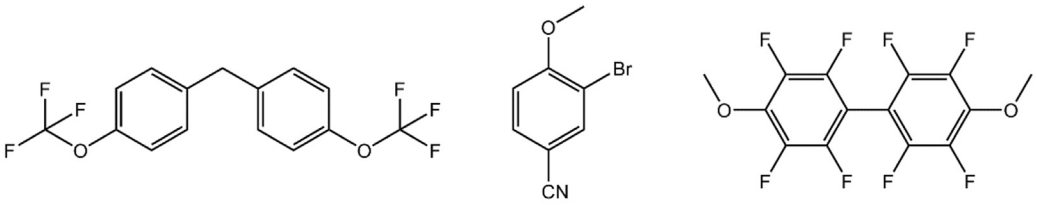
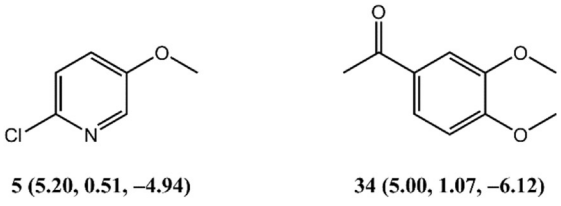


Fig. 3. Graph presenting the oxidation potential, reduction potential, and solvation energy values of the methoxybenzene derivative molecules (red: oxidation potential, blue: reduction potential, filled circle: solvation energy < −4.2 kcal/mol, empty circle: solvation energy > −4.2 kcal/mol). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



2 (5.18, 0.10, −4.69) **3 (5.31, 0.71, −7.16)** **4 (5.09, 0.93, −6.26)**



5 (5.20, 0.51, −4.94) **34 (5.00, 1.07, −6.12)**

Fig. 1. Five molecules are identified, as follows: **2**: 1-trifluoromethoxy)-4-[4-(trifluoromethoxy)benzyl]benzene, **3**: 3-bromo-4-methoxybenzonitrile, **4**: 2,2′,3,3′,5,5′,6,6′-octafluoro-4,4′-dimethoxy-1,1′-biphenyl, **5**: 2-chloro-5-methoxypyridine, and **34**: 1-(3,4-dimethoxyphenyl)-ethanone. These are selected from among 106 molecules to be screened through the calculations of oxidation potential, reduction potential, and solvation energy values.