Perfunctionalized Dodecaborate Clusters as Stable Metal-Free Active Materials for Charge Storage

John L. Barton,†‡,†,§ Alex I. Wixtrom,†,§ Jeffrey A. Kowalski,†,§ Fikile R. Brushett,‡,§,‖ Alexander M. Spokony.†,*‡,§

†Joint Center for Energy Storage Research, Argonne National Laboratory, 9700 South Ave Bldg. 200, Argonne, Illinois, USA
‡Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, Massachusetts 02139, USA
†Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Drive East, Los Angeles, California 90095-1569, USA
§California NanoSystems Institute, University of California, Los Angeles, 570 Westwood Plaza, Los Angeles, California 90095-1569, USA

Supporting Information Placeholder

ABSTRACT: We report a class of perfunctionalized dodecaborate clusters that exhibit high stability towards high concentration electrochemical cycling. These boron clusters afford several degrees of freedom in material design to tailor properties including solubility and redox potential. The exceptional stability of these clusters was demonstrated using a symmetric flow cell setup for electrochemical cycling between two oxidation states for 45 days, with post-run analysis showing negligible decomposition of the active species (<0.1%). To further probe the limits of this system, a prototype redox flow battery with two different cluster materials was used to determine mutual compatibility. This work effectively illustrates the potential of bespoke boron clusters as robust material platform for electrochemical energy conversion and storage.

The ability to reversibly shuttle electrons over a range of timescales is a ubiquitous feature found in both natural and synthetic molecules, and is essential for energy conversion and storage applications.1–10 Energy storage systems often utilize redox active metal cations as stable salts or coordination complexes, though inherent limitations hinder the degree to which solubility and redox potential of these species can be modified.11 Metal-free species can also undergo well-defined redox processes, though decomposition due to innate reactivity of radical intermediates formed during single electron shuttling is a common pitfall.12,13 To mitigate this undesired reactivity, molecular systems have been designed to delocalize radical density throughout neighboring bonds and/or to sterically protect the site of the unpaired electron (Figure 1a), which can lead to dramatic improvements in the cycle stability of these compounds.11,12,14

Perfunctionalized dodecaborate clusters (B₁₂(OR)₁₂, R = H, alkyl, benzyl) are a promising new class of redox materials, which have demonstrated reversible redox activity when modified with different substituents (Figure 1b).15–17 Many of these clusters are extremely robust molecules, displaying remarkable thermal stability and resistance to harsh chemical environments.18 Over a dozen B₁₂(OR)₁₂ clusters have been synthesized and electrochemically characterized by cyclic voltammetry (CV), exhibiting redox transitions that are reversibly accessible via sequential one-electron oxidation or reduction.15,16

Figure 1. (a) Decomposition pathway of a prototypical redox-active organic radical (TEMPO) via a radical coupling. (b) Redox-active B₁₂(OR)₁₂ clusters do not undergo decomposition via radical coupling due to the 3D delocalization of the radical spin density.
In addition, the solubility and size of functionalized boron clusters can be modified to incorporate specific properties desirable for particular applications.\textsuperscript{16,19-21} Importantly, B\textsubscript{12}(OR)\textsubscript{12} species can be isolated in a monoradical form (1) and have shown unprecedented stability due to the complete delocalization of the radical spin density across the boron cluster cage (Figure 1b). Extending beyond voltammetric studies and ex-situ evaluation of stability, here we demonstrate the viability of these perfunctionalized boron clusters in complex electrolyte environments found in modern and emerging electrochemical systems. Specifically, we show several of these B\textsubscript{12}(OR)\textsubscript{12} compounds can be electrochemically charged and discharged multiple times over 1000 hours without any apparent chemical degradation. Leveraging these attractive electrochemical properties, we have furthermore assembled a proof-of-concept redox flow battery, where performance of this metal-free cluster system was further demonstrated.

While voltammetric analysis of molecular compounds can be useful for initial analysis of redox processes, during these tests the materials are only charged for short durations, with only a small fraction of the active material charged at any given time. In order to better evaluate and understand the stability of the B\textsubscript{12}(OR)\textsubscript{12} system to electrochemical cycling associated with bulk charge storage, we decided to test these molecules further under controlled conditions that more closely mimic energy storage applications. We started by identifying two model B\textsubscript{12}(OR)\textsubscript{12} cluster systems with high (1) and low (2) redox potentials relative to each other (Figure 2). The high-potential cluster 1 features 12 benzyl substituents with perfluorinated aryl groups, which, due to their inherent inductive electron-withdrawing nature, increase the redox potential for the 2-/1- redox couple.\textsuperscript{16} For a cluster system exhibiting redox properties at lower potential, we designed 2, which contains 12 inductively electron-donating alkyl groups with terminating OMe moieties that improve solubility in polar solvents. Both species have a solubility $>$0.1 M in MeCN in all relevant states-of-charge.

First, CV on a glassy carbon electrode was conducted to provide in-depth information about the electrochemical and transport metrics for the two cluster systems (Figure 2). The first oxidation of 1 and the first reduction of 2 occur at 0.074 V vs. Fc/Fc\textsuperior and -0.256 V vs. Fc/Fc\textsubior, respectively. Both materials show excellent chemical reversibility on the CV timescale (seconds-minutes) as evidenced by a peak current ratio close to one across all scan rates (1: 0.97 ± 0.03, 2: 1.00 ± 0.02). Additionally, both redox couples show electrochemical reversibility with a peak separation of 61 ± 1 mV (Nernstian is 60 mV at ambient glovebox temperature), which is invariant of scan rate. Lastly, the diffusion coefficients of the starting materials were calculated using Randles-Sevick analysis (Figure S2) with scan rates of 10 to 100 mV s\textsuperscript{-1}, and were determined to be 3.3 x 10\textsuperscript{-6} cm\textsuperscript{2} s\textsuperscript{-1}. As expected based on the borate cluster sizes and the Stokes-Einstein relation (diffusivity is inversely proportional to molecular radius), these diffusion coefficients are about an order of magnitude lower than those of small organic molecules in similar electrolyte solutions, but are still sufficiently large to support a range of electrochemical applications.\textsuperscript{22,23} Importantly, clusters 1 and 2 appear to be non-interacting on the CV timescale as the voltammogram with both materials present represents a superposition of the two independent scans with no changes in original peak shape, height, or position, and no new peaks appearing as a function of cycling.

![Figure 2](image)

We then assembled a symmetric flow cell with 1 (Figure 3). The symmetric flow cell allows for cycling of both the reduced and oxidized species in the cluster redox pairs to determine the active species stability without the convoluting effects of side products generated at the counter electrode or the mass transport enforced concentration limitations, which are both associated with conventional bulk electrolysis apparatus.\textsuperscript{24-26} Figure 3a shows the initial active species distribution within the reservoirs and redox reactions occurring during the charging step. During the discharge step, these reactions occur in reverse. Although it is generally desirable to test at higher active species concentrations (> 0.1 M), to both reduce mass transport resistance and explore more practical electrolyte formulation, we sought to first demonstrate behavior at lower concentrations. Consequently, we have used a low current density of 5 mA cm\textsuperscript{-2}, to mitigate the effect of mass transfer limitations on the accessed capacity (see SI for experimental details). Figure 3b shows capacity and coulombic efficiency as a function of cycle number and illustrates a low fade rate due to high material stability.
The cell retained high coulombic efficiency (> 96%) and 40% of the initial capacity after 1089 h (45 days) of cycling, which exceeds the duration of many published nonaqueous RFB stability studies.\[^{27-30}\] We suspect that a portion of the cell fade at the later stages of this experiment, specifically the decrease in accessed capacity and the increase coulombic efficiency instability, are due to a combination of imperfect sealing and pressure driven crossover. Although compression fittings and expanded PTFE gaskets are used in the cell construction, we inevitably lose some redox active electrolyte via evaporative leaking. Loss of volatile components, specifically the solvent, gradually increases the solution viscosity and promotes further leaks (observed) via an increased pressure within the cell. Dashed gray vertical lines indicate experimental interruptions. The cycling was stopped briefly to rebalance the electrolyte reservoirs at 424 h as the reservoir levels were visibly mismatched (ca. 5 mL vs. 15 mL), which is partially enabled by our use of a non-selective separator (Daramic 175). A second (unintentional) interruption occurred at 632 h when the building lost power. Voltage profiles from select cycles, as indicated by arrowheads in Figure 3b, are shown in Figure 3c, illustrating the appreciable fraction of the theoretical capacity that is repeatedly accessible for select cycles over all uninterrupted segments of the experiment. Note that at least one cycle is shown from each uninterrupted segment of the cycling protocol. The third cycle shown, cycle 200, takes place after the electrolyte rebalancing at 424 h, and the increase in capacity (30%) from cycle 140 is indicative of a crossover imbalance within our experimental setup. We attribute the limited approach to theoretical capacity (80% for cycle 1) to the mass-transfer limitations at extreme states of charge, which are exacerbated by the relatively low total concentration (0.1 M). For the entire experiment the coulombic efficiency remained high (> 96%), indicating high material stability (Figure 3d). Importantly and consistent with our hypothesis, post-mortem analysis of \(\dagger\) via NMR spectroscopy indicates no observable decomposition of the parent molecule (Figure S5).

We then sought to evaluate the use of \(\dagger\) and \(\ddagger\) in a full redox flow battery (RFB).\[^{35}\] A flow cell containing \(\dagger^{2+/1}\) (high potential) and \(\ddagger^{0/1}\) (low potential) was cycled at 5 mA cm\(^{-2}\) (Figure 4 and S1). Both reservoirs initially contained 10 mL of 0.05 M \(\ddagger^{2+} / 0.05 \ M \ d^{1+/0.5 \ M \ TBAPF_6}\) in MeCN. Utilizing the two materials together leads to a cell voltage of 0.33 V. Indeed, this is lower than desirable for a RFB, but full cell cycling can highlight the stability of the highly tunable borate clusters.\[^{36}\]
Specifically, this borate cluster pairing was selected based on preliminary assessments of stability, solubility, and simplicity of synthesis in spite of the low average discharge voltage, 0.258 V. The cell configuration, which used pre-mixed electrolytes, similar to an Fe-Cr RFB, to mitigate crossover-driven capacity fade, is shown in Figure 4a. Detailed experimental conditions and electrochemical impedance spectra are included in the SI (Figure S4). Figure 4b shows the charge and discharge profiles for cycles 1, 50, 100, 150, and 200, spanning 248 h of experiment time. Figure 4c shows the capacity as a function of cycle number, which remains relatively stable and has a mean value of 0.366 Ah L⁻¹ (55% of theoretical) based on discharge. Energy, coulombic, and voltage efficiencies are shown in Figure 4d. The low average voltage efficiency, 66%, can be primarily attributed to the low cell voltage, as well as significant contributions from ohmic and mass-transfer overpotentials due to low active species concentration. Specifically, the voltage losses within the cell are not atypically large as compared to prior non-aqueous flow battery literature, however, they constitute a larger fraction of the total cell voltage, thus significantly impacting the voltaic efficiency. The ohmic resistance, as determined through impedance analysis, was 3.6 Ω cm⁻², and contributes 23% of the voltage losses (i.e., 8% of the average charging voltage). The combination of stable capacity along with moderate average coulombic efficiency (87%) suggests that the cell experiences significant yet non-destructive parasitic charge-transfer pathways, presumably crossover coupled to self-discharge. These losses may be greatly diminished through ongoing membrane research for RFBs. In particular, these clusters appear sufficiently large (ca. 2.3 nm) as compared to smaller redox-active organic molecules (ca. 0.6 nm), to enable the use of nanoporous size-selective separators for crossover mitigation. This, in turn, would obviate the need for functionalized membranes, reducing both component cost and research time.

In summary, we have demonstrated the design versatility and bulk electrochemical stability and cyclability of several perfunctionalized dodecaborate clusters, B₁₂(OR)₁₂. This work expands upon the repertoire of cluster-based materials amenable to electrochemical cycling with flow cell cycling validating the exceptional stability of this material class as it is cycled between two oxidation states for 45 days showing no apparent chemical degradation. Given the favorable and tunable properties of perfunctionalized boron clusters, we envision further optimization of this system to enable more practical energy storage uses.

**ASSOCIATED CONTENT**

**Supporting Information**

NMR spectra, elemental analysis, and mass spectra of the dodecaborate clusters along with additional flow cell and bulk electrolysis data is provided.

**AUTHOR INFORMATION**

**Corresponding Authors**

*brushett@mit.edu

*spokony@chem.ucla.edu

**Author Contributions**

† J.L.B, A.I.W, and J.A.K contributed equally.

**Notes**

The authors declare no competing financial interests.

**ORCID:**

John L. Barton - https://orcid.org/0000-0002-2572-9127

Jeffrey A. Kowalski: https://orcid.org/0000-0001-7334-0936

Fikile R. Brushett – https://orcid.org/0000-0002-7361-6637

Alex I. Wixtrom – https://orcid.org/0000-0002-0622-4633
ACKNOWLEDGMENT

J. L. B., J. A. K., and F. R. B. gratefully acknowledge support from the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. J. L. B. acknowledges additional funding from the ExxonMobil-MIT Energy Fellowship (2017-2018). A. M. S. acknowledges the University of California, Los Angeles (UCLA) Department of Chemistry and Biochemistry for start-up funds, 3M for a Non-Tenured Faculty Award, the Alfred P. Sloan Foundation for a research fellowship in chemistry, Research Corporation for Science Advancement for a Cottrell Scholar Award and the NIGMS for the Maximizing Investigators Research Award (MIRA, R35GM124746). The authors thank the MRI program of the National Science Foundation (NSF grant no. 1532232 and 1625776). We thank UCLA Molecular Instrumentation Center for mass spectrometry and NMR spectroscopy (NIH grant 1S10OD016387-01).

REFERENCES


TOC draft

metal-free boron clusters stable to >1000 hrs bulk cycling

tunable redox & solubility via R group