

Novel Quinone-Based Couples for Flow Batteries

Brian Huskinson,¹ Saraf Nawar,² Michael R. Gerhardt,¹ and Michael Aziz¹

¹Harvard School of Engineering and Applied Sciences, 29 Oxford Street, Cambridge, MA 02138, USA

²Harvard College, Cambridge, MA 02138, USA

ABSTRACT

Flow batteries are of interest for low-cost grid-scale electrical energy storage in the face of rising electricity production from intermittent renewables like wind and solar. We report on investigations of redox couples based on the reversible protonation of small organic molecules called quinones. These molecules can be very inexpensive and may therefore offer a low cost per kWh of electrical energy storage. Furthermore they are known to rapidly undergo oxidation and reduction with high reversibility under some conditions, suggesting the possibility of high current density operation, which could lead to low cost per kW. We report cyclic voltammetry measurements for 1,4-parabenzoquinone in neutral pH aqueous solution using a three-electrode setup. We report full fuel cell measurements as well, utilizing p-benzoquinone in an acidic solution as a positive electrode material and a hydrogen negative electrode, where current densities in excess of 240 mA cm^{-2} have been achieved to date. These initial results indicate that the quinone/hydroquinone redox couple is a promising candidate for use in redox flow batteries.

INTRODUCTION

Flow batteries have received much attention for the purpose of grid-scale storage, largely due to the ability to decouple energy and power capacities in their design, thereby allowing for the optimal sizing of each capability independently [1,2]. Nevertheless, it remains a challenge to design a scalable energy storage system with low cost per kWh. For example, the vanadium redox flow battery system, which has perhaps received the most attention, suffers from a relatively high market price for the cost of vanadium, setting a floor on the ultimate capital cost per kWh [3]. Small organic molecule based systems could function as cost-effective alternatives, as they do not necessarily have this same cost limitation. Quinones and their derivatives appear to be promising candidates as they offer low cost, low toxicity, and high reversibility. Quinones are ubiquitous in the natural world, playing an active role in oxygen-evolving photosynthesis as part of the electron-transport chain in photosystem II [4]. Figure 1 highlights one redox reaction of interest: the interconversion of 1,4-parabenzoquinone and hydroquinone. These are the simplest quinones being explored here, and, although their equilibrium potentials are relatively low for a battery application (values in excess of 1 V would be better), it is worth noting that open sites on the carbon ring allow for introduction of electron-withdrawing groups that could raise this potential and actually allow for specific tuning of the potential. In this report, we demonstrate a highly reversible p-benzoquinone couple in a neutral

pH solution using cyclic voltammetry and also present preliminary studies of a fuel cell with one electrode composed of a quinone/hydroquinone couple. The present studies show that quinone chemistries constitute a promising approach to stationary energy storage.

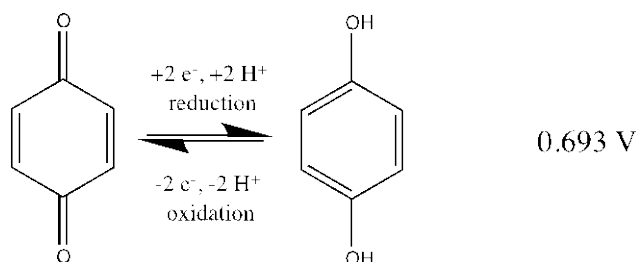


Figure 1: Reduction-oxidation couples for 1,4-parabenzoquinone. The equilibrium potential vs. SHE is indicated as well.

EXPERIMENTAL

Cyclic voltammetry experiments were done using a three-electrode cell. A platinum wire was used as the working electrode, with a platinum foil as a counter electrode and a Ag/AgCl reference electrode (0.210 V vs. SHE). A 1 mM p-benzoquinone solution, with 1 M KCl as a supporting electrolyte, (DI-H₂O, Millipore) was used near pH 7, with sweeps done at 100 mV/s.

Full cell measurements were done using a test bench originally constructed by Sustainable Innovations, LLC and modified in our lab. Figure 2 shows a schematic of the cell operation (left) and an image of the cell used (right). The cell featured aluminum endplates, pyrolytic graphite current collectors with serpentine flow channels, a 25 μm thick Nafion 211 proton exchange membrane (pretreated using methods previously described in Ref. [5]), and PTFE/Viton tubing and gasketing throughout. On both sides of the cell, a commercial Pt-Ru/C carbon paper commercial electrode was used.

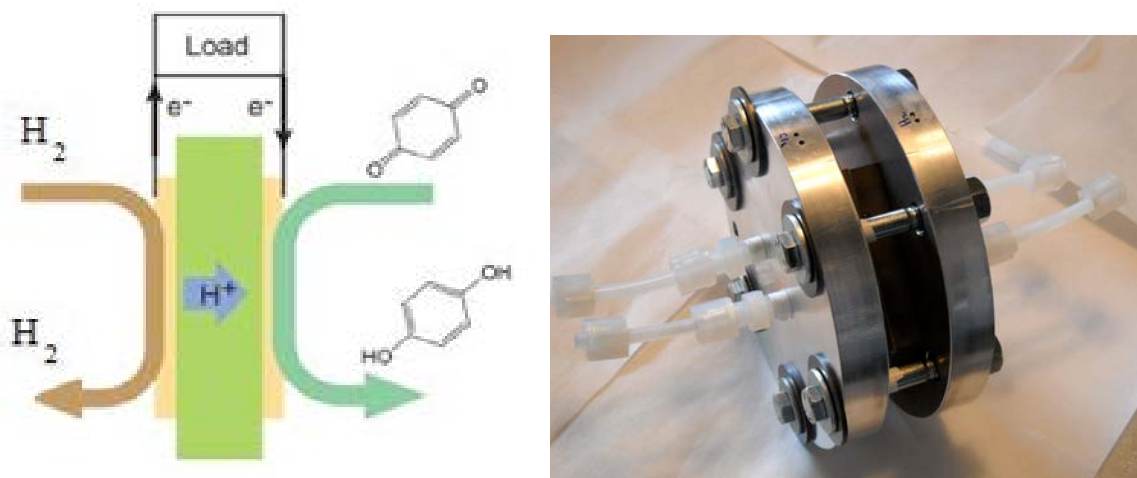


Figure 2: Cell schematic (left) and an image of the actual cell used (right).

The cell was operated in galvanic mode using previously described methods [5], with high-purity hydrogen gas flowed through the negative side of the cell near 5 psig and a 0.1 M p-benzoquinone solution in 1 N H₂SO₄ flowed through the positive side using a Cole Parmer

Masterflex peristaltic pump. This reaction is spontaneous and drives electrons through an external load. Before each set of measurements, an N₂ purge was performed to remove any remaining O₂ and to ensure there were no leaks in the assembly. A DC electronic load was used to draw incrementally higher currents from the cell, and, once the voltage stabilized (typically within a few seconds), its value was recorded. Each measurement was done five times at every current density, and the results were averaged.

RESULTS AND DISCUSSION

Figure 3 shows cyclic voltammetry curves for a 1 mM p-benzoquinone at pH 7 and 20°C. Prominent reduction and oxidation peaks are visible with little separation between them, indicative of high reversibility. These curves corroborate data reported by Quan et al [6]. The equilibrium potential is consistent with previously reported values as well [7]. There appear to be minimal differences in the reaction kinetics between glassy carbon and platinum surfaces, as indicated by the similar shape of the curves in Figure 3.

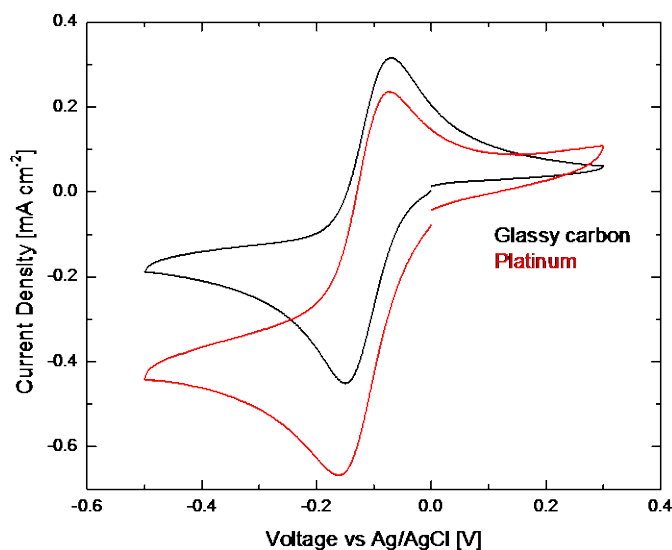


Figure 3: Cyclic voltammetry of a 1 mM p-benzoquinone solution at pH 7 using a Pt working electrode (red) and a glassy carbon electrode (black).

Figure 4 shows the cell potential vs. current density and the power density vs. current density for the p-benzoquinone/H₂ cell described above. The cell reached current densities of about 240 mA/cm² and power densities near 50 mW/cm², which are higher than values previously reported using soluble quinones for the positive electrode in a full cell configuration [8]. The I-V curves exhibit no demonstrable activation loss, as indicated by the linearity of the curves at low current densities. Ultimately, the cell performance was restricted by mass transport effects due to the limited solubility of p-benzoquinone in aqueous solutions at low pH. The power density as a function of current density is also shown in Figure 4. As expected, we find that increased flow rates lead to improved cell performance, as we are able to achieve both increased power densities and limiting current densities with increased flow rates. This emphasizes the importance of the mass transport characteristics of the system.

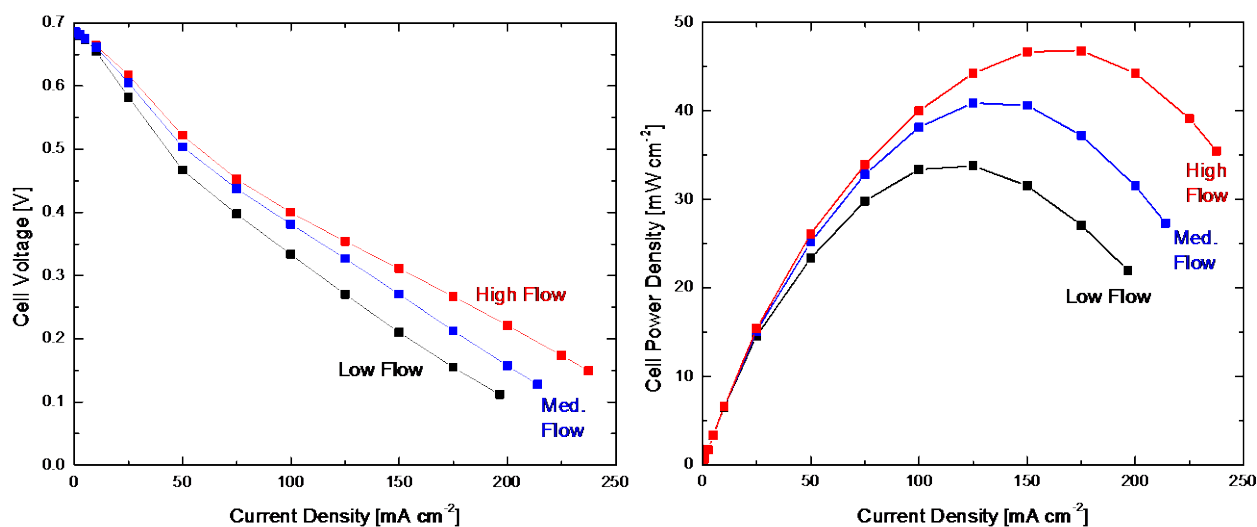


Figure 4: Cell voltage vs. current density (left) and cell power density vs. current density (right) for a p-benzoquinone/H₂ cell operated in galvanic mode at 20 °C. The cathode side consisted of a flowing solution of 0.1 M p-benzoquinone in 1 N H₂SO₄ and the anode side was flowing H₂ gas.

CONCLUSIONS

We have shown preliminary half-cell and full-cell results for aqueous p-benzoquinone solutions. At pH 7, the reaction kinetics were shown to be highly reversible. A lower pH solution was demonstrated to provide power densities near 50 mW/cm² when placed against a hydrogen electrode. The present results appear highly promising for the use of quinones and quinone-like compounds in flow battery applications. Future work will involve tailoring quinones to achieve ideal properties for our intended applications. This could lead to an all-quinone flow battery, which would provide a path towards very inexpensive stationary energy storage.

ACKNOWLEDGMENTS

We thank Prof. Roy Gordon and his group, Prof. Alán Aspuru-Guzik and his group, and Prof. Theodore Betley for helpful discussions. This work was supported by the Dept. of Energy ARPA-E program, the Harvard University Center for the Environment and the Harvard School of Engineering and Applied Sciences. S.N. was supported in part by the Physics Department at Harvard University. B.H. was supported in part by an NSF Graduate Research Fellowship.

REFERENCES

- [1] J. Rugolo and M. J. Aziz, *Energy & Environmental Science* **5**, 7151 (2012).
- [2] J. Eyer and G. Corey, *Energy Storage for the Electricity Grid: Benefits and Market Potential*

- Assessment Guide, 2010.
- [3] T. Nguyen and R.F. Savinell, "Flow Batteries", *Electrochemical Society Interface* **19**, 54 (2010).
 - [4] F. Müh, C. Glöckner, J. Hellmich, and A. Zouni, *Biochimica et Biophysica Acta* **44**, 1817 (2012).
 - [5] B. Huskinson, J. Rugolo, S. Mondal, and M.J. Aziz, *Energy & Environmental Science* **5**, 8690 (2012).
 - [6] M. Quan, D. Sanchez, M.F. Wasylkiw, and D. Smith. *J. Am. Chem. Soc.* **129**, 12847 (2007).
 - [7] H. Nivinskas, S. Staškevičienė, J. Šarlauskas, R. Koder, A. Miller, N. Čėnas, *Arch. Biochem. Biophys.* **403**, 249 (2002).
 - [8] Y. Xu, Y. Wen, J. Cheng, Y. Yanga, Z. Xie, and G. Cao. "Novel Organic Redox Flow Batteries Using Soluble Quinonoid Compounds as Positive Materials," in *World Non-Grid-Connected Wind Power and Energy Conference* (Nanjing, China, 2009).