



# Molecular Engineering of an Alkaline Naphthoquinone Flow Battery

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3 **Molecular Engineering of an Alkaline Naphthoquinone Flow Battery**  
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24  
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35 **Abstract:** Aqueous organic redox flow batteries (AORFBs) have recently gained significant  
36 attention as a potential candidate for grid-scale electrical energy storage. Successful  
37 implementation of this technology will require redox-active organic molecules with many  
38 desired properties. Here we introduce a naphthoquinone dimer, bislawsone, as the redox-  
39 active material in a negative potential electrolyte (negolyte) for an AORFB. This novel  
40 dimerization strategy substantially improves the performance of the electrolyte vs. that of the  
41 lawsone monomer in terms of solubility, stability, reversible capacity, permeability and cell  
42 voltage. An AORFB pairing bislawsone with a ferri/ferrocyanide positive electrolyte delivers  
43 an open-circuit voltage of 1.05 V and cycles at a current density of 300 mA/cm<sup>2</sup> with a  
44 negolyte concentration of 2 M electrons in alkaline solution. We determined the degradation  
45 mechanism for the naphthoquinone-based electrolyte using chemical analysis, and predict  
46 theoretically electrolytes based on naphthoquinones that will be even more stable.

## 47 48 **1. Introduction**

49 The cost of renewable solar and wind electricity has dropped so much that the greatest  
50 barrier to their widespread adoption is their intrinsic intermittency. A cost-effective, long  
51 discharge duration electrical energy storage solution could solve the problem of unbalanced  
52 supply and demand. Among the various proposed technologies, redox-flow batteries<sup>1</sup> are  
53 particularly attractive for long discharge duration because liquid redox-active electrolytes can  
54 be stored in external tanks that are separated from the power generating stack. With this  
55 design, energy capacity can be scaled independently of power capacity by simply changing  
56 the volume of electrolyte.

57 Recent years have seen a great deal of research into developing organic redox-active  
58 species for aqueous flow battery electrolytes. These redox-active materials are based on earth-  
59 abundant elements such as carbon, nitrogen, oxygen and sulfur, and usually utilize well-  
60 known redox-active compounds such as quinones,<sup>2-9</sup> viologens,<sup>10-13</sup> ferrocenes,<sup>14-15</sup> aza-

61 aromatics,<sup>16-18</sup> and nitroxide radicals<sup>10-11, 19</sup>. Organic-based aqueous flow batteries offer  
62 several advantages over vanadium and non-aqueous based flow batteries in cost, scalability  
63 and safety. In addition, the use of organic molecules in flow batteries opens a vast chemical  
64 space for tailoring the properties of redox-active electrolytes, including solubility, reduction  
65 potential, rate capacity, and stability. Within the quinone family, benzoquinones<sup>6</sup> and  
66 anthraquinones<sup>2, 4, 7, 9</sup> have been explored extensively as redox-active electrolytes in aqueous  
67 organic flow batteries. To date, however, there are limited reports on using naphthoquinone as  
68 an active electrolyte due not only to stability and solubility concerns but also because  
69 naphthoquinone reduction potentials tend to be intermediate between those of benzoquinones  
70 and anthraquinones, making them unsuitable for either terminal of an aqueous flow battery. 2-  
71 hydroxynaphthoquinone, commonly known as lawsone, is a natural product extracted from  
72 the leaves of the henna plant and the flower of the water hyacinth, which makes its use or  
73 derivatives of it particularly appealing from a cost and scalability perspective.<sup>20</sup> Lawsone has  
74 been explored as a candidate for alkaline flow batteries,<sup>21-22</sup> however, poor cycling stability  
75 has limited further investigation into this class of molecules. It is hypothesized that the C-H  
76 position next to the quinone functional group in the molecule is prone to Michael addition,  
77 particularly in alkaline media, and subsequent degradation from hydroxide or other  
78 nucleophiles during cycling<sup>6, 23-24</sup>. Efforts to modify the molecule have been made by  
79 installing a carboxyl group onto the open aromatic C-H position. Despite the increased  
80 solubility of this derivative, capacity utilization, cycling stability, and permeability remain as  
81 issues.<sup>25</sup>

82         Here, we report a naphthoquinone dimer 2,2'-bis(3-hydroxy-1,4-naphthoquinone), or  
83 bislawsone, as a high capacity, reversible electrolyte material for aqueous organic flow batteries.  
84 Bislawsone was constructed by taking advantage of the reactive open site and linking two  
85 lawsone units via their 3-position. We demonstrate that this dimerization strategy improves  
86 solubility, stability, reduction potential, and permeability without compromising the capacity

87 per molecular weight. We also elucidate the degradation mechanism of bislawsone and  
88 propose strategies to further stabilize the molecule based on theoretical calculations. We draw  
89 important implications for the synthetic strategy and rational design of stable quinone  
90 molecules for AORFBs.

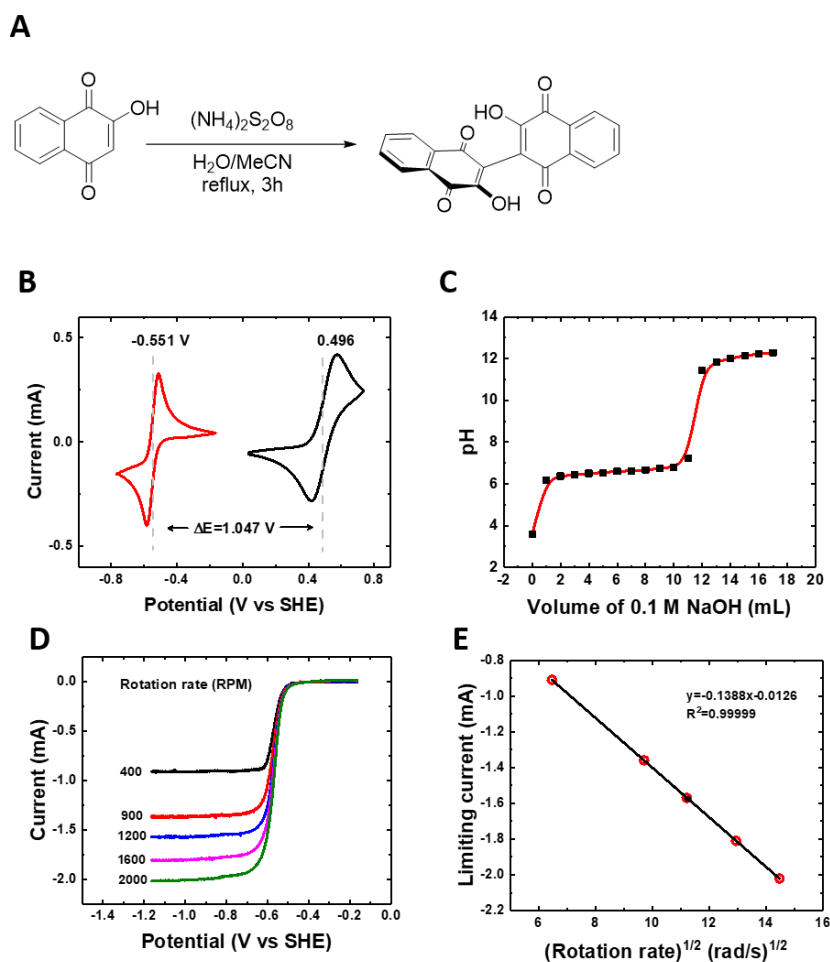
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92

## 93 **2. Results and Discussion**

94 **Synthesis and physical properties study.** Bislawsone was synthesized via a one-step radical  
95 dimerization of the natural product lawsone using inexpensive chemicals and solvents (**Figure**  
96 **1A**, Figure S1, S2). No further steps were necessary to purify this yellow powder. Its physical  
97 and electrochemical properties were evaluated. Cyclic voltammetry of bislawsone in 1M  
98 KOH showed a reduction potential of -0.551 V vs. standard hydrogen electrode (SHE) with a  
99 peak separation ( $\Delta E$ ) of 71 mV for 4 electrons. The reduction potential is 50 mV more  
100 negative than that of the lawsone monomer with overlapping peaks for the two subunits  
101 (Figure S3A), indicating higher cell voltage, and improved reversibility despite the doubling  
102 of the molecular size and the number of electrons transferred. Pairing this electrolyte with  
103 potassium ferrocyanide should yield an equilibrium cell potential of 1.05 V (**Figure 1B**).  
104 Based on the sharpness of the CV peaks, the two redox centers in the molecule do not appear  
105 to interact with each other; this conclusion is also supported by theoretical calculations  
106 (Figure 4). The pKa values ( $\sim 6.5$ ) for each of the hydroxyl groups in the molecule are  
107 indistinguishable by titration and are slightly higher than that of lawsone (**Figure 1C**, Figure  
108 S3B, Table S1). The two low pKa phenols in bislawsone serve as the solubilizing groups in  
109 alkaline solution. To our surprise, the solubility of bislawsone reached 0.56 M (2.24 M  
110 electrons or 60.0 Ah/L) in pH 14 solution, as compared to the 0.48 M (0.96 M electrons)  
111 solubility of lawsone in pH 14 solution. The origin of this increased solubility is hypothesized  
112 to be from the non-planar nature of the dimer along the 3,3'-single bond. The non-planar

113 feature may disrupt crystal packing, which would raise the solubility of the whole molecule  
114 compared to that of the planar monomer. The increased solubility of the dimer is in contrasted  
115 with the usually decreased solubility of many extended polymers compared to their parent  
116 monomers.<sup>26</sup>

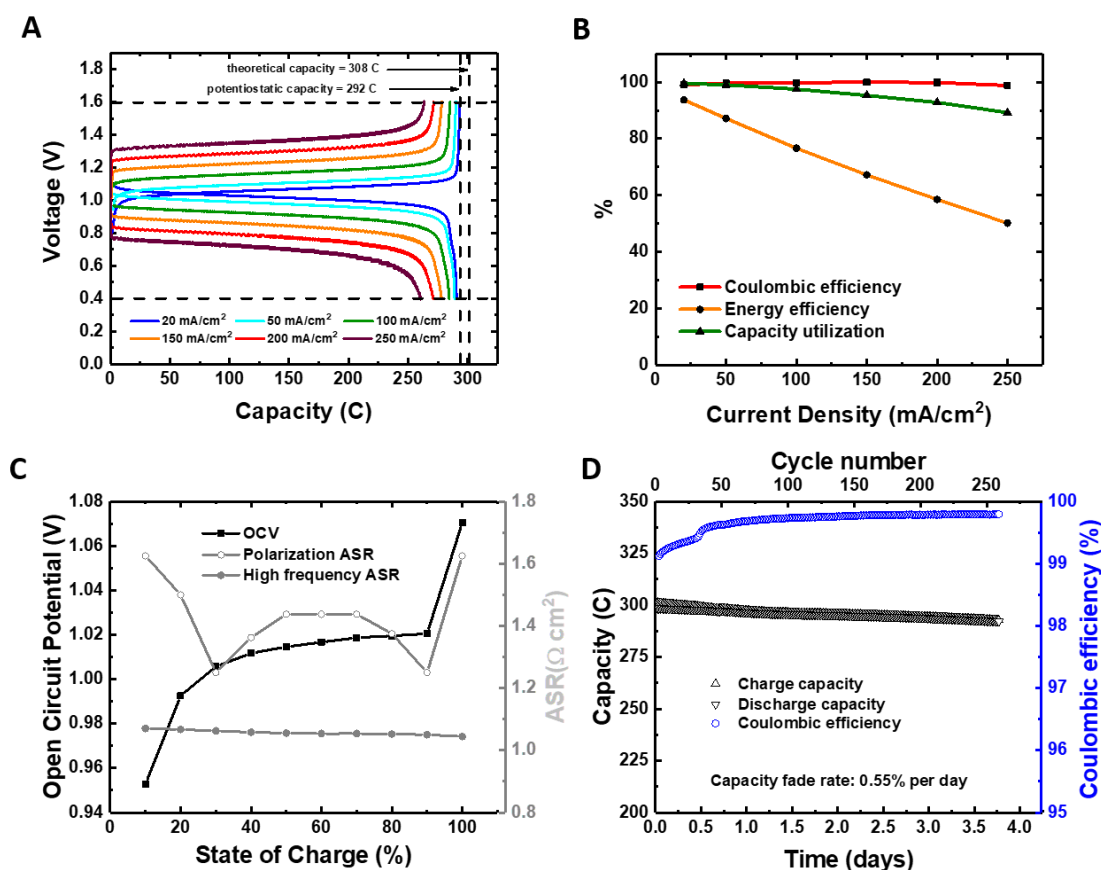


117  
118 **Figure 1.** Synthesis and physical Characterization of bislawsone. (A) Synthetic scheme of  
119 bislawsone. (B) Cyclic voltammograms of 5 mM bislawsone (red), and 10 mM potassium  
120 ferrocyanide (black) in 1M KOH at a scan rate of 50 mV/s. The redox potential vs SHE is  
121 indicated. (C) Titration of 10 mL 0.05 M bislawsone using 0.1M NaOH solution. (D) Rotating  
122 disk electrode (RDE) measurements of bislawsone using a glassy carbon electrode in 1 M  
123 KOH at 5 rotation rates. (E) Levich plot of limiting current versus square root of rotation rate  
124 ( $\omega^{1/2}$ )

125  
126 A dimerization strategy, as employed in the case of bislawsone, should offer the  
127 advantage of lowered permeability without significantly compromising the diffusivity or  
128 viscosity. The diffusion coefficient ( $D$ ) of bislawsone was determined by rotating disk

129 electrode measurement and calculated according to the Levich plot of limiting current versus  
130 square root of rotation rate to be  $4.54 \times 10^{-6} \text{ cm}^2/\text{s}$  (**Figure 1D, 1E**), which is in line with those  
131 of most small organic molecules.<sup>2, 4, 6, 9, 25</sup> The viscosity of bislawsone dissolved in 1M KOH  
132 was consistently below 2 cP for concentrations up to the solubility limit (Figure S4), which  
133 bodes well for minimizing energy inefficiency due to pumping loss. The crossover rates of  
134 bislawsone and lawsone through a Fumasep E-620K cation exchange membrane were  
135 measured in a two-compartment rotating cell (Figure S5). The permeability of bislawsone was  
136 determined to be  $1.19 \times 10^{-11} \text{ cm}^2/\text{s}$ , which is an order of magnitude lower than the value of  
137  $1.01 \times 10^{-10} \text{ cm}^2/\text{s}$  for lawsone, as expected.

138  
139 **Synthesis and physical properties study.** We assembled an alkaline flow battery with a  
140 positive electrolyte (posolyte) comprising 44 mL 0.2 M potassium ferrocyanide and 0.02 M  
141 potassium ferricyanide and a negative electrolyte (negolyte) comprising 8 mL 0.1 M (0.4 M  
142 electrons) bislawsone in 1M KOH solution (see “Full Cell Measurement” in the supporting  
143 information), separated by a Fumasep E620K cation-exchange membrane. This non-  
144 fluorinated membrane has been shown to provide very low permeability to ferro/ferricyanide  
145 and to anthraquinones.<sup>9</sup> These solutions were pumped through a flow cell constructed from  
146 graphite flow plates and carbon paper electrodes. During charging, the negolyte biquinone  
147 was reduced into bihydroquinone while the ferrocyanide was oxidized into ferricyanide. An  
148 excess amount of ferrocyanide was used in the cell testing in order to isolate the negolyte as  
149 the capacity limiting side.



150  
151

152 **Figure 2.** Full cell characterization of low concentration 0.1 M bislawsone. The negolyte  
 153 comprised 8 mL of 0.1 M bislawsone in 1 M KOH while the non-limiting posolyte comprised  
 154 45 mL of 0.2 M potassium ferrocyanide and 0.02 M potassium ferricyanide in 1 M KOH  
 155 solution. (A) Galvanostatic charge and discharge curves from 20 to 250 mA/cm<sup>2</sup>. The vertical  
 156 dashed lines indicate the maximum capacity realized with potentiostatic charge and discharge  
 157 at the voltage cutoffs (1.6 and 0.4 V, respectively), as well as the theoretical capacity. (B)  
 158 Coulombic efficiency, round-trip energy efficiency, and capacity utilization as a percentage of  
 159 potentiostatic capacity versus current density. (C) OCV, high-frequency ASR, and polarization  
 160 ASR versus SOC. (D) Coulombic efficiency (circle) and charge (upward-pointing triangles)  
 161 and discharge (downward-pointing triangles) capacity versus time and cycle number for a  
 162 negolyte-limited bislawsone cell. The cell was cycled galvanostatically at 100 mA/cm<sup>2</sup> for  
 163 3.8 days. The cell was cycled between 1.4 and 0.5 V, and each half cycle ended with a  
 164 potentiostatic hold until the magnitude of the current density fell below 2 mA/cm<sup>2</sup>.

165

166 To confirm that all four electrons in bislawsone can be accessed reversibly, the cell  
 167 was cycled at different current densities ranging from 20 mA/cm<sup>2</sup> to 250 mA/cm<sup>2</sup> (**Figure 2A**).  
 168 For each current density tested, a > 99% coulombic efficiency and > 90% capacity utilization  
 169 were achieved based on the four-electron experimental potentiostatic capacity. A capacity  
 170 utilization of 97.5% and round-trip energy efficiency of 77% was reached at 100 mA/cm<sup>2</sup>

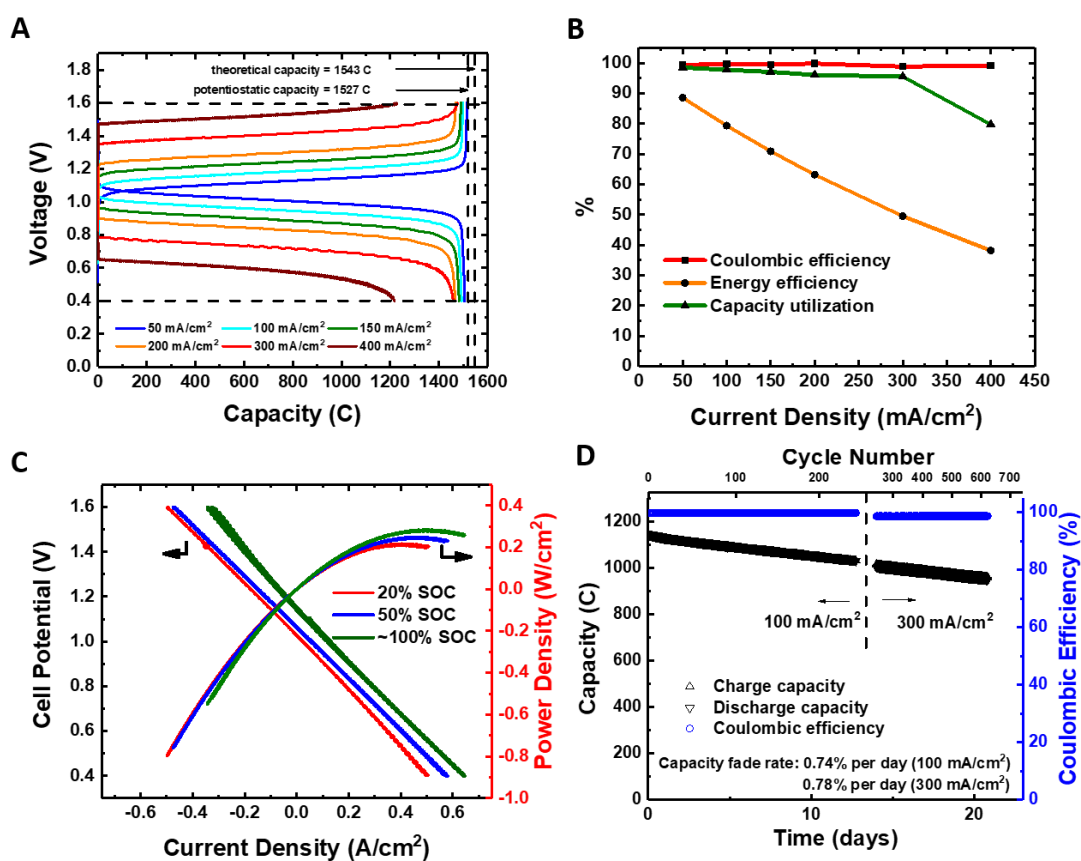
171 **(Figure 2B)**. The nuclear magnetic resonance (NMR) spectrum of a charged negolyte showed  
172 a clean conversion to the fully reduced bislawsone (Figure S6). The high capacity utilization  
173 at high current density demonstrated that the dimerization strategy does not negatively affect  
174 the kinetics and accessed capacity.

175 A charging current of 100 mA/cm<sup>2</sup> was applied to charge the cell, and polarization  
176 curves were measured at 20, 50, and 100% states of quinone charge (SOC). The open circuit  
177 voltage (OCV) is 1.01 V at 50% SOC and 1.07 V at 100% SOC **(Figure 2C)**, consistent with  
178 CV measurement. The membrane resistance contributed the largest fraction of the overall  
179 resistance; it can possibly be decreased in the future by manipulating the electrolyte  
180 composition and by decreasing the membrane thickness. The polarization curve (Figure S7)  
181 shows no sign of redox kinetic limitations and exhibits a peak galvanic power density  
182 exceeding 0.20 W cm<sup>-2</sup>.

183 The viability of a flow battery hinges on the long-term stability of the system.  
184 Molecular stability has been a major concern for organic-based flow battery systems as there  
185 are many potential degradation pathways for organic molecules. Capacity fade may have both  
186 temporal or electrochemical cycling contributions, with the former dominating the lifetimes of  
187 the organic molecules that have been carefully studied to date.<sup>27</sup> To investigate the long-term  
188 stability of bislawsone, prolonged galvanostatic cycling of the 0.1 M bislawsone cell was  
189 performed at 100 mA/cm<sup>2</sup>. In order to avoid temporal variations in accessed capacity and to  
190 ensure that 100% of the redox-active material was cycled, potential holds at 1.4 V and 0.5 V  
191 were applied until the magnitude of the current density fell below 2 mA/cm<sup>2</sup>. 95% of  
192 theoretical capacity was accessed. The 5% discrepancy may be due to material transfer and  
193 residual water in the synthesized bislawsone powder. Over a 3.8-day period of cycling, a 2%  
194 capacity loss was observed, which corresponds to a capacity fade rate of 0.55% per day, or  
195 0.008% per cycle. The cell maintained an average of 99.5% coulombic efficiency, and  
196 membrane resistance remained unchanged before and after the cycling. The capacity fade rate

197 indicates that the lifetime is approximately an order of magnitude longer than that of  
198 unprotected lawsone,<sup>21-22</sup> demonstrating the protective effect of the dimerization strategy  
199 employed

200 To investigate the performance at high concentration, a 0.5 M bislawsone cell (2 M  
201 electrons, 53.6 Ah/L) was constructed. All four electrons per molecule were accessed at high  
202 concentration, as shown in **Figure 3A**, leading to a 95.5% capacity utilization even at 300 mA  
203 cm<sup>-2</sup> (**Figure 3B**). This near-quantitative capacity utilization at high current density has not  
204 been reported before to our knowledge in alkaline organic flow battery systems, which are  
205 usually limited by cell resistance and molecular diffusion. At 400 mA/cm<sup>2</sup>, a lower capacity  
206 (80.0%) was accessed because membrane resistance dominated the voltage profile and the cell  
207 voltage quickly reached the 1.6 V and 0.4 V voltage cutoffs. At 100 mA/cm<sup>2</sup>, 97.7% of the  
208 capacity was reversibly accessed with a Coulombic efficiency of 99.7% and round-trip energy  
209 efficiency of 79.3%, representing a significant improvement over a lawsone flow battery  
210 which had 70% accessed capacity and 68% round-trip energy efficiency.<sup>25</sup> The OCV of the  
211 0.5 M bislawsone cell displayed typical Nernstian behavior with respect to SOC (Figure S8).  
212 A peak galvanic power density of 0.28 W/cm<sup>2</sup> was achieved as determined by the polarization  
213 curve at near 100% SOC (**Figure 3C**). The power density is mainly limited by high frequency  
214 area specific resistance. This is dominated by the membrane resistance (Figure S8), which is  
215 above 1 Ω·cm<sup>2</sup>; it can possibly be decreased in the future by manipulating the electrolyte  
216 composition and by using a membrane with better conductivity.



217

218 **Figure 3.** Full cell characterization of high concentration 0.5 M bislawsone. The negolyte  
 219 comprised 8 mL of 0.5 M bislawsone in 1 M KOH while the non-limiting posolyte comprised  
 220 95 mL of 0.3 M potassium ferrocyanide and 0.1 M potassium ferricyanide in 1 M KOH  
 221 solution. (A) Galvanostatic charge-discharge voltage profiles from 50 to 400 mA/cm<sup>2</sup>. The  
 222 vertical dashed lines indicate the maximum capacity realized with potentiostatic charge and  
 223 discharge at the voltage cutoffs (1.6 and 0.4 V, respectively), as well as the theoretical  
 224 capacity. (B) Coulombic efficiency, round-trip energy efficiency, and capacity utilization as a  
 225 percentage of potentiostatic capacity versus current density. (C) Cell voltage versus discharge  
 226 current density at room temperature at 10%, 30%, 50%, 70%, 90%, and 100% SOC. (D)  
 227 Coulombic efficiency (circles), charge (upward-pointing triangles) and discharge (downward  
 228 pointing triangles) capacity versus time and cycle number for a negolyte-limited bislawsone  
 229 cell. The cell was cycled galvanostatically at 100 mA/cm<sup>2</sup> for 12.8 days and then rested for  
 230 1.2 days before switching to 300 mA/cm<sup>2</sup> for 6.8 days. The cell was cycled between 1.4 and  
 231 0.5 V, and each half cycle ended with a potentiostatic hold until the magnitude of the current  
 232 density fell below 2 mA/cm<sup>2</sup>. The volume of negolyte with same composition used was 6 mL  
 233 in (D).

234

235 Long-term galvanostatic cycling of the 0.5 M bislawsone cell was performed at 100  
 236 mA cm<sup>-2</sup> with potential holds at 1.4 V for charging and 0.5 V for discharging until the current  
 237 density dropped to 2 mA/cm<sup>2</sup> (**Figure 3D**). 98.3% of the theoretical capacity was accessed.  
 238 After 12.8 days of cycling, the capacity had faded by 9.5%, which corresponds to a temporal

239 capacity fade of 0.74% per day, or 0.038% per cycle. Because an excess amount of polysolite  
240 ferrocyanide and ferricyanide were used in the cycling, we attribute the slow capacity fade to  
241 the bislawsone negolyte. The per cycle capacity fade in the high concentration cell was  
242 superficially higher compared to low concentration cell due to longer per cycle cycling time  
243 in high concentration cell. The per day capacity fade rate is similar to that of low  
244 concentration cell (0.74% vs 0.55% per day), indicating that the stability of bislawsone is time  
245 dependent rather than cycle dependent.

246 Encouraged by our high capacity utilization at high current density, we cycled the 0.5  
247 M bislawsone cell at a higher current density of 300 mA/cm<sup>2</sup>. The cell maintained high  
248 capacity rate and stable charging/discharging plateau during the 6.8 days of continuous  
249 cycling with 98.8% coulombic efficiency. The cell lost 5.3% of its capacity, which  
250 corresponds to 0.78% loss per day. This rate is almost identical to the 0.74%/day loss rate  
251 when cycled at 100 mA/cm<sup>2</sup>, demonstrating that bislawsone can be cycled at high current  
252 density under alkaline conditions without compromising its stability.

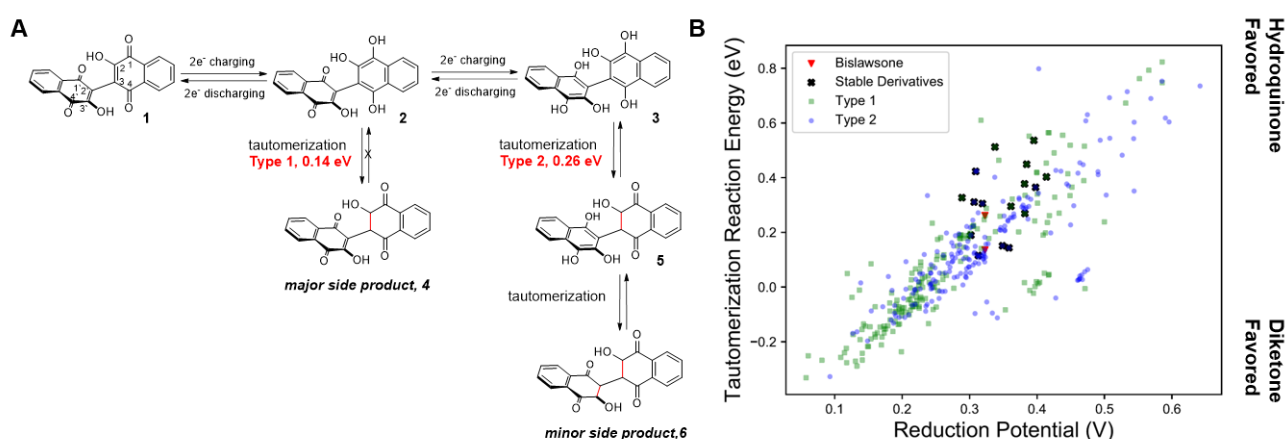
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254 **Investigation and potential mitigation of chemical degradation.** Different strategies have  
255 been made in the field to synthesize more stable derivatives based on various redox-active  
256 scaffolds. However, the chemical space available for organic molecules is huge. Therefore, it  
257 is important to understand how a scaffold molecule degrades in order to rationally design the  
258 next generation of molecules with better performance. Despite the fact that bislawsone can  
259 inhibit Michael-addition decomposition pathway as compared to lawsone, capacity loss in our  
260 system was still observed. We have recently elucidated the molecular degradation mechanism  
261 of anthraquinones in flow batteries using 2,6-dihydroxyanthraquinone as a model system.<sup>28</sup>  
262 We therefore studied the degradation of naphthoquinones using bislawsone as a model system.  
263 A sample was taken from the above cycled discharged 0.5 M cell and subjected to NMR  
264 analysis. One major side product was observed which accounts for 14.2% of total NMR active

265 material (Figure S9). High-resolution liquid chromatography mass spectrometry (LC-MS)  
266 analysis found only one major side product with the mass to charge ratio of 347.0559 in  
267 negative ionization mode (Figure S10). Back calculation of the neutral mass gives  $C_{20}H_{12}O_6$   
268 as the molecular formula, which coincides in mass with a partial (2-electron) reduction of  
269 bislawsone starting material  $C_{20}H_{10}O_6$ .

270 In order to elucidate the chemical structure, the degradation product was isolated by  
271 preparative-scale high performance liquid chromatography (pHPLC, Figure S11).  $^1H$ ,  $^{13}C$ ,  
272 and 2D NMR analysis on the purified degradation product showed the asymmetry between  
273 two monomer units, and the presence of two aliphatic proton peaks with doublet splitting  
274 patterns (Figure S12-S14) indicated a disruption in the conjugated system. Together, the  
275 NMR and LC-MS analyses are consistent with the structure where the bond between C2 and  
276 C3 of the bislawsone is reduced to a carbon-carbon single bond, locking the quinone unit into  
277 a di-ketone molecule, 2,3-dihydrobislawsone **4** (Figure 4A, type 1 tautomerization).  
278 Electrochemical reduction of a ketone into an alcohol and re-oxidation of the alcohol back to  
279 the ketone have high overpotentials and usually require a metal or organic catalyst<sup>29-32</sup>;  
280 therefore this side product should generally be considered as redox-inactive in a catalyst-free  
281 flow battery system using a carbon-based electrode. Because the similar degradation rate  
282 suggests a concentration and rate-independent degradation mechanism, the production of 2,3-  
283 dihydrobislawsone is not due to the direct reduction or oxidization by the electrode, but rather  
284 by the enol-ketone tautomerization of the partially reduced quinone-hydroquinone molecule,  
285 which is a process governed by kinetics and thermal equilibrium. The degradation of  
286 bislawsone into 2,3-dihydrobislawsone may be a general degradation mechanism for  
287 naphthoquinones. This conclusion is backed by some earlier studies,<sup>33-34</sup> which documented  
288 the tautomerization of reduced naphthoquinone. While this tautomerization was observed in  
289 many different naphthoquinone derivatives in earlier studies, the equilibrium and kinetics  
290 were heavily influenced by the substitution groups on the naphthoquinone ring. In this work,

291 the 2,3-dihydrobislawsone did not tautomerize back to the half-reduced hydroquinone form **2**,  
 292 as the isolated 2,3-dihydrobislawsone was stable in air and alkaline solution. Given this  
 293 general phenomenon, we expect that the tautomerization should also occur for the fully  
 294 reduced bislawsone **3** at a different rate (Figure 4A, type 2), that can eventually result in a 4-  
 295 electron reduction 2,2',3,3'-tetrahydrobislawsone form **6** (tetra-ketone instead of bi-quinone)  
 296 that is completely redox inactive). Indeed, careful LC-MS analysis of a discharged sample  
 297 also found a molecule at a much lower concentration with an atomic mass that corresponds to  
 298 a 4-electron reduction product after cycling (Figure S15). This molecule cannot be fully  
 299 reduced bislawsone **3** because the sample was taken at the fully discharged state and exposed  
 300 to air prior to analysis, and therefore is expected to be the redox-inactive tetra-ketone form.



301  
 302 **Figure 4.** Decomposition study and theoretical calculations. (A) Scheme of decomposition  
 303 pathway. The red text shows the calculated reaction energies of the reduced forms  
 304 tautomerizing as calculated at the B3LYP/6-311+G(d,p) (PCM) level of theory. (B) Calculated  
 305 tautomerization reaction energies plotted against calculated reduction potential of the couple.  
 306 Type 1 and Type 2 refer to the nature of the intermediate: a “half-reduced” molecule (Type 1)  
 307 or a fully reduced molecule (Type 2). Bislawsone is labeled with red triangle and 8 stable  
 308 derivatives within 0.1 V of bislawsone reduction potential are labeled with black squares.

309  
 310 Based on the structure of degradation product, the degradation of bislawsone into the  
 311 di-ketone form **4** should disrupt only half of the redox activity, as the other lawsone monomer  
 312 unit stayed intact. Therefore, 2,3-dihydrobislawsone **4**, which accounts for 14.2% of total  
 313 NMR active material, should only impact 7.1% of total capacity. However, 14.8% of the

314 capacity was lost in 21 days of cycling. There are several possibilities to account for the 7.7%  
315 difference. First, once reduced naphthoquinone **2** tautomerized into diketone form **4**, the 2-  
316 hydroxy group changed from a low-pKa phenol group into a high-pKa alcohol group, and  
317 would stay protonated in alkaline solution. Therefore, the solubility of 2,3-dihydrobislawsone  
318 molecule is expected to drop drastically and precipitate out of the solution, making it  
319 practically redox-inactive. Precipitate was indeed observed in electrolyte that has been cycled  
320 for a long-time. Second, the tetra-ketone form, 2,2',3,3'-tetrahydrobislawsone **6**, accounts for  
321 1% of the degradation product as detected by LC-MS, but its concentration is too low to be  
322 detected in NMR, and is expected to have even lower solubility due to the transformation of  
323 two solubilizing phenol groups into two alcohol groups. Other minor degradation products or  
324 NMR silent species and cell leakage may also contribute to the remaining capacity fade.

325         The equilibrium of hydroquinone-diketone is heavily influenced by the substituents on  
326 the naphthoquinone core; therefore, this presents an opportunity for a next generation  
327 naphthoquinone with a rationally designed substituent group. We have calculated (see the  
328 “Theoretical Calculation” section in Supporting Information) the stability and reduction  
329 potentials of 637 lawsone redox couples, which include 193 bislawsone derivatives. **Figure**  
330 **4B** shows the correlation between the tautomer reaction energies and the predicted standard  
331 reduction potentials of redox couples. In general, lower reduction potentials are more likely to  
332 be subject to tautomerization than higher reduction potentials. Interestingly, despite the fact  
333 that the predicted standard reduction potentials of each of the two reductions of bislawsone  
334 are within 0.01 V of each other, the “type 1” decomposition is more thermodynamically  
335 favored than the “type 2” decomposition.

336         Of these, we predict that 8 bislawsone derivatives with reduction potentials within 0.1  
337 V of bislawsone potentially have higher stability than bislawsone (Figure S16). One common  
338 motif in these stabilized molecules are oxy-alkyl substitutions, which have previously been  
339 shown to stabilize anthraquinone molecules against other decomposition mechanisms.<sup>35</sup> Our

340 calculations also indicate that the increased stability of bislawsone can be at least partially  
341 attributed to its protection against a tautomerization reaction relative to lawsone. Efforts to  
342 synthesize a more stable naphthoquinone are underway.

343

### 344 **3. Conclusion**

345 In summary, we demonstrate that dimerization is a promising synthetic strategy to  
346 improve the performance of quinone-based flow batteries. The bislawsone flow battery  
347 reported in this work delivered a high negolyte volumetric capacity, theoretically 53.6 Ah/L  
348 (2 M electrons), with peak power density of 0.28 W/cm<sup>2</sup>. It reversibly accessed > 95.5% of  
349 theoretical capacity at a current density of 300 mA/cm<sup>2</sup> with significantly improved  
350 permeability and stability, making naphthoquinone a more practical redox-active negolyte in  
351 AORFBs. We identified tautomerization of the reduced naphthoquinone to the redox-inactive  
352 ketone form as a degradation mechanism of naphthoquinone in flow batteries. This  
353 mechanistic insight allowed us to propose more stable naphthoquinones and rationally design  
354 next generation organics for AORFB which could accelerate the use of wind and photovoltaic  
355 electricity.

356

### 357 **Author Contributions**

358 L.T. conceived the idea, developed the synthesis, and performed molecular characterization.  
359 E.M.F. and L.T. performed rotating disk electrode characterization. E.F.K. performed  
360 additional synthesis and measured solubility and viscosity. D.D.P performed permeability  
361 measurements. D.P.T. developed the molecular library and performed the theoretical stability  
362 calculations. Cell performance and electrolyte analysis were performed by L.T. and M.-A.G.  
363 The chemical degradation study was performed by L.T. The manuscript was drafted by L.T.  
364 and D.P.T. and revised by all authors. R.G.G. and M.J.A. supervised the experimental  
365 research and A.A.-G. supervised the theoretical research.

366

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