Electronic Supplementary Material (ESI) for Digital Discovery.

Supplementary Information

ExpFlow: a graphical user interface for automated reproducible electrochemistry

Rebekah Duke,[1,2] Siamak Mahmoudi,[2] Aman Preet Kaur, [1,2] Vinayak Bhat, [1,2] Ian Dingle,[2] Nathan C. Stumme,[3] Scott K. Shaw,[3] David Eaton,[2] Asmund Vego,[2] Chad Risko[1,2]

[1]Department of Chemistry,
University of Kentucky
Lexington, Kentucky 40506 USA

[2]Center for Applied Energy Research
University of Kentucky
Lexington, Kentucky 40511 USA

[3]Department of Chemistry
University of Iowa
Iowa City, Iowa 52242 USA

Contents

1. Software

Technology Stack

ExpFlow is available via the D^{3}TaLES website (https://d3tales.as.uky.edu/) which is built and hosted through Django[1] and WSGI.[2] The databases and website are located on OpenStack Virtual Machines at the University of Kentucky. The data are stored in databases implemented with MongoDB[3] using JSON Schema[4] style schema that are publicly available.[5] These packages upon which ExpFlow is built are widely-used open sources packages. The underlying code for ExpFlow calculations utilizes the D^{3}TaLES API,[6] and this code is available at https://github.com/D3TaLES/d3tales_api. As noted in the D^{3}TaLES API documentation, parsed data is formatted using the D^{3}TaLES Schema (found at https://github.com/D3TaLES/schema). Additionally, the ExpFlow operating details (next section) can be found on the ExpFlow Docs page at https://d3tales.as.uky.edu/expflow/docs.

ExpFlow: Operating Details

A user first builds a T*emplate* that lists the reagent types, apparatus items, and workflow actions. For example, in a basic cyclic voltammetry (CV) experiment to determine diffusion coefficient, the reagents would include a `redox_molecule` and solvent. Likewise, the apparatus list might include a beaker, `electrode_working`, `electrode_reference`, `electrode_counter`, and `electrochemical_cell`. Then, the user must list the workflow actions for the experiment: `transfer_liquid` to measure solvent and transfer it to the beaker, `transfer_solid` to measure the redox-active molecule and transfer it to the beaker, `heat_stir` the solution, `measure_surface_area_of_working_electrode`, and `collect_cv_data`. There may be multiple data collection actions. For example, in this example, the user might add five `collect_cv_data` actions because the experiment includes five CVs, each run at a different scan rate. Each action incorporates a standard action type, starting and ending positions, and a brief description. Although these T*emplates* take time and effort to produce, they can be reused for all related experiments. Additionally, any existing T*emplate* can be cloned and modified, limiting the amount of time needed to construct new T*emplates*. T*emplates* can also be shared among ExpFlow users and with the broader scientific community (e.g., through publications) (**Figure S1**).

Workflow:

Sequence	Name	Description	Start Position	End Position
1	transfer_liquid	measure solvent	Acetonitrile	solution beaker 1
2	transfer_solid	measure redox molecule	TEMPO	solution beaker 1
3	heat_stir	measure temperature of e...	solution beaker 1	solution beaker 1
4	measure_working_electrode_area	measure surface area of ...	Polycrystalline platinum electrode	Polycrystalline platinum electrode
5	collect_cv_data	collect cv 1	electrochemical cell	electrochemical cell
6	collect_cv_data	collect cv 2	electrochemical cell	electrochemical cell
7	collect_cv_data	collect cv 3	electrochemical cell	electrochemical cell
8	collect_cv_data	collect cv 4	electrochemical cell	electrochemical cell
9	collect_cv_data	collect cv 5	electrochemical cell	electrochemical cell

Figure S1. Screenshot of an ExpFlow Template.

One T*emplate* can be used for many experiments with the same procedure. An *Experiment* specifies the T*emplate* reagents. For example, the T*emplate* described above might be used to create four E*xperiments*: Two for quinone in water then in acetonitrile, and two for anthraquinone in water then in acetonitrile (**Figure S2**).

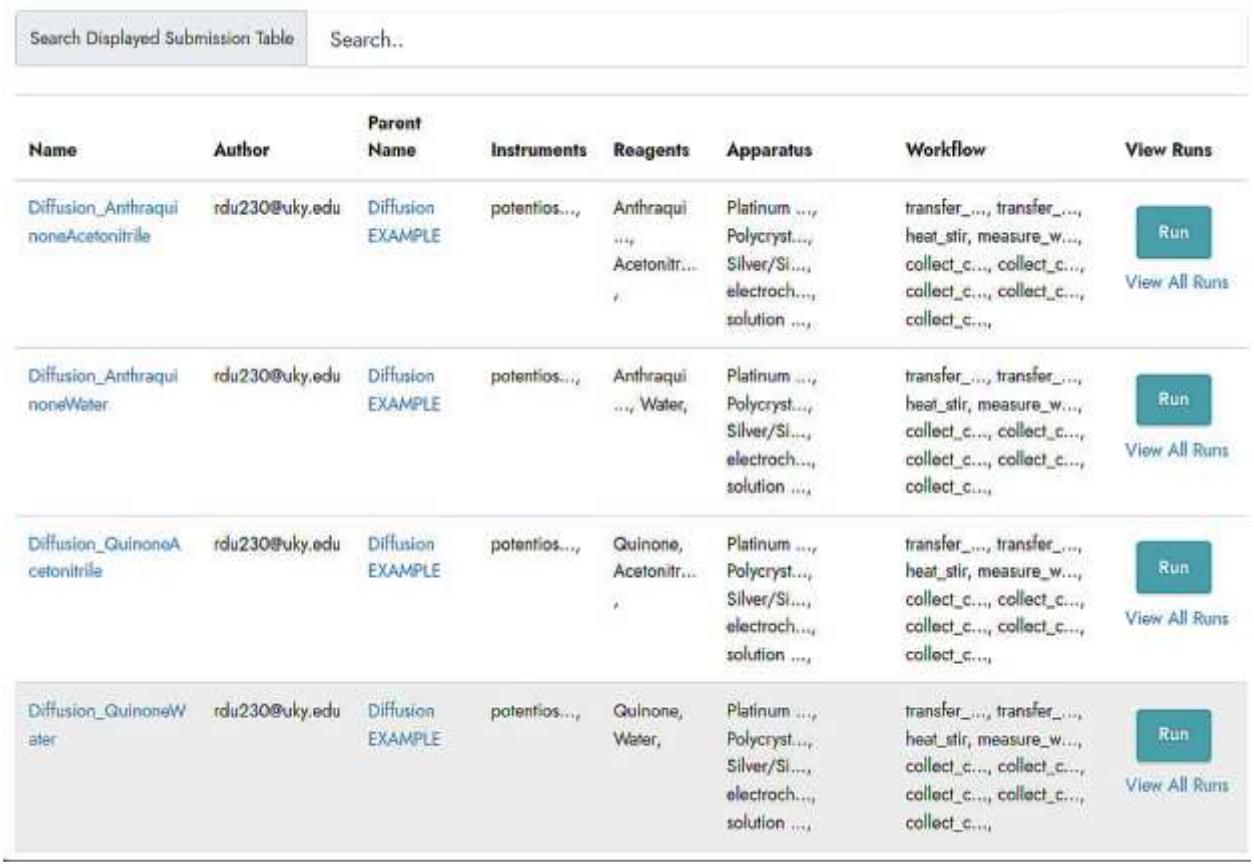


Figure S2. Screenshot of an ExpFlow *Experiment*.

Once a user constructs an *Experiment*, they may run that experiment any number of times. Experiment *Runs* record specific values such as times, weights, temperature, and raw data files. Each action type (specified in the *Template*-building step) includes a series of built-in run parameters. During a *Run*, the user is prompted to fill in each of these run parameters. For example, the `transfer_liquid` action type prompts the user to record the liquid's exact volume, while the `heat_stir` action type prompts the user to record the temperature and the time of stirring. Data collection action types such as `collect_cv_data` prompts the user to upload a raw data file, in this case, the potentiostat output file (**Figure S3**).

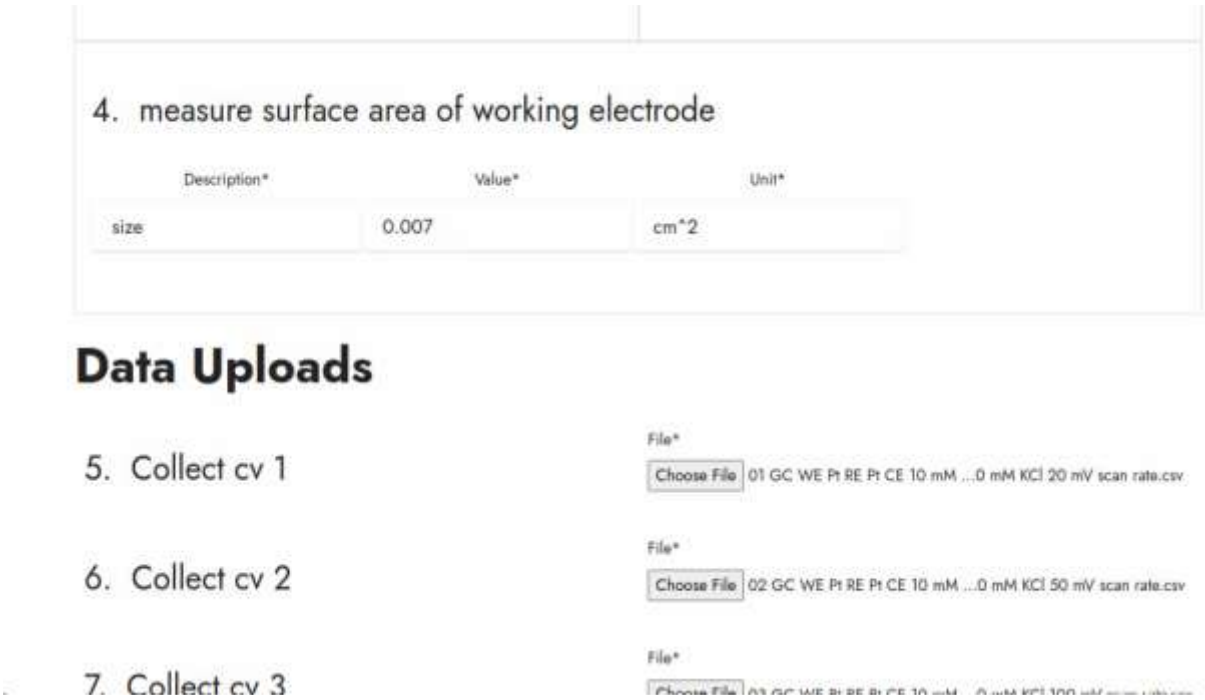


Figure S3. Screenshot of an ExpFlow Experiment Run.

After an *Experiment* is run, ExpFlow uses the D^{3}TaLES data parsers to extract data from the uploaded experiment files. ExpFlow also extracts key metadata from experiment run parameter data. For example, ExpFlow extracts the solution temperature from the `heat_stir` action and it calculates the solution concentration from the `transfer_solid` and `transfer_liquid` actions. All extracted data are displayed on a user interface where the user can inspect and approve the *Run* data. This user interface also hosts the ExpFlow calculators for experiment runs with relevant data. For example, in the diffusion coefficient experiment example, the user can calculate the diffusion coefficient from a run with the push of a button (**Figure S4**). Currently, ExpFlow contains data parsing for only cyclic voltammetry experiments, and it hosts only calculators for diffusion coefficient and charge transfer rate. However, work is ongoing to include parsing for IR and UV-Vis spectroscopy experiments, etc., and to build more processors.

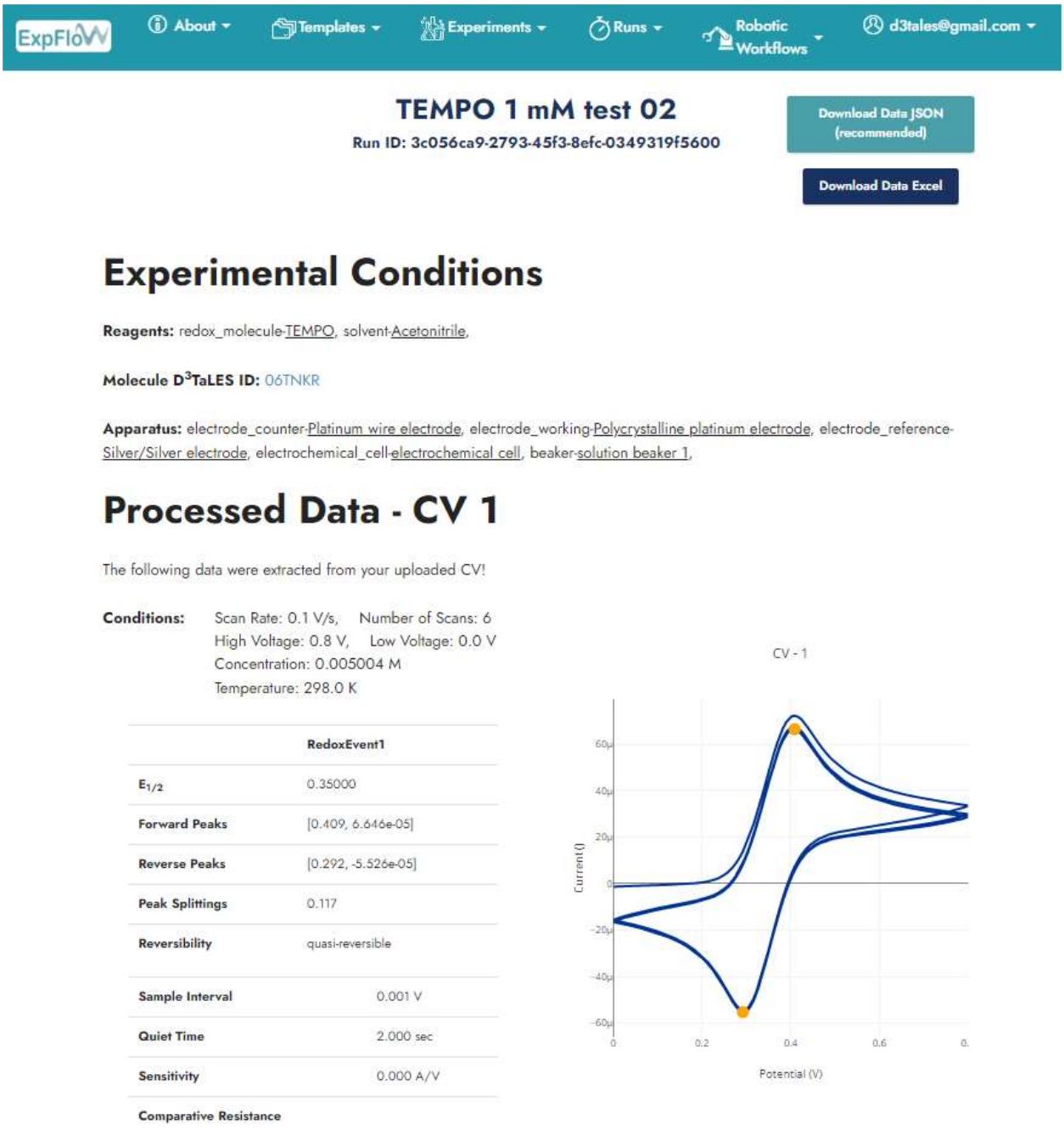


Figure S4. Screenshot of processed ExpFlow CV data.

Example Properties from CV Processing

Table S1. Example extracted and calculated metadata derived by ExpFlow from CV experiments. More detailed lists of properties are found in the D[3]TaLES documentation.[7]

Property	Description	Property Type
`scan_data`	List of scans	CV Prop. (extracted)
`peak_potential`	Highest potential reached	CV Prop. (extracted)
`reversibility`	List of reversibility categorizations for peaks	CV Prop. (extracted)
`e_half`	List of $E_{1/2}$ for peaks	CV Prop. (extracted)
`peak_splittings`	List of peak splittings for peaks	CV Prop. (extracted)
`middle_sweep`	Middle sweep list	CV Prop. (extracted)
`forward`	Data points from forward scan	CV Prop. (extracted)
`reverse`	Data points from reverse scan	CV Prop. (extracted)
`oxidation_potential`	Oxidation potential of the molecule	Molecular Prop. (calculated)
`reduction_potential`	Reduction potential of the molecule	Molecular Prop. (calculated)
`diffusion_coefficient`	Diffusion coefficient using Randles-Sevcik equation, default cm^2/s	Molecular Prop. (calculated)
`charge_transfer_rate`	Rate of charge transfer in solution, default cm/s	Molecular Prop. (calculated)

Robotic Data Flow

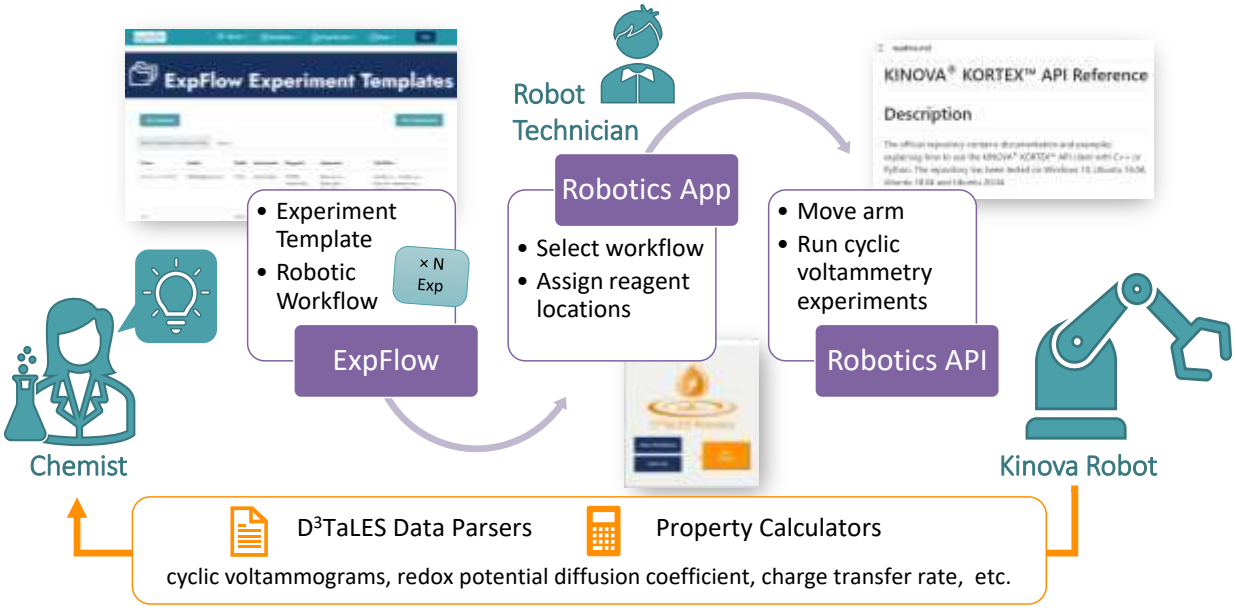


Figure S5. Schematic illustrating the data cycle for translating human-conceptualized experimental procedures to robotic actions and translating resulting experiment data to human-readable information.

2. Hardware

We implemented the robotic arm model "Gen3" from Kinova in our setup.[8] The Gen3 Kinova arm has six degrees of freedom. The maximum reach is 89cm and it holds a maximum payload of 2kg. The Kinova arm interfaces with the computer through ethernet port and can be integrated in several software environments, including python, which was the language of choice in this work.

We used a Biologic[9] "SP-50e" potentiostat, a single channel unit that is capable of interfacing with python via available APIs via a USB connection.

Grid vial stand consists of 12 individual vial holders designed in a way the robotic arm can access each vial without colliding with other vials. Hence, each row of vials has its own unique height.

The vial elevator has a platform that receives the vials carried by the robotic arm. This platform rises so that the electrodes (connected to potentiostat) dip into the solution and then lowers after data are acquired. A centering mechanism also centers the vial during its rise to meet the tight precision requirement between the printed electrode and the rim of the vials. The vial elevator serves two main purposes: (1) it provides the precision needed for moving the vials and (2) eliminates mechanical disturbances that would otherwise degrade the quality of the CV data.

3. Robotic Experiments

ExpFlow Template

The ExpFlow Template depicted in **Figure S6** was used for the robotic experiments. It can also be found at https://d3tales.as.uky.edu/expflow/exper_temp/661d6628-e83a-452d-943a-b880cd2ab12a/. The workflow first selects a vial of a blank solvent/supporting electrolyte solution and runs one CV scan at 100 mV/s to record the state of the electrodes (`collect_electrode_test` action, sequence **1**). Then it selects the appropriate vial of redox-active molecule/solvent/supporting electrolyte solution and prepares to run the experiment CV (sequences **2**-**5**). (Note that, while the solution preparation sequences include `transfer_solid`, `transfer_liquid`, and `heat_stir` actions, these are not yet implemented in our current robotic setup. The code simply selects the appropriate pre-mixed solutions and skips over these preparation actions.) The workflow then runs one CV at a pre-specified voltage interval (sequence **6**), then a processing action finds the CV peaks and institutes a new voltage interval 0.3V before and after the CV peaks (`process_cv_benchmark` action, sequence **7**). Finally, eight CV scans are run, each at a different scan rate, (sequences **8**-**15**) and data processing is performed to plot data and determine meta properties (sequence **16**).

Workflow:

Sequence	Name	Description	Start Position	End Position
1	collect_electrode_test	test electrode with blan...	Acetonitrile	potentiostat__test
2	measure_working_electrode_area	measure surface area of ...	Polycrystalline platinum electrode	Platinum wire electrode
3	transfer_solid	measure redox-active mol...	TEMPO	solution beaker
4	transfer_liquid	measure solvent	Acetonitrile	solution beaker
5	heat_stir	heat and stir solution t...	solution beaker	solution beaker
6	collect_cv_data	Run CV benchmarking	potentiostat__test	potentiostat__test
7	process_cv_benchmarking	process test_electrode d...	potentiostat__test	potentiostat__test
8	collect_cv_data	collect cv 1	solution beaker	potentiostat__test
9	collect_cv_data	collect cv 2	solution beaker	potentiostat__test
10	collect_cv_data	collect cv 3	solution beaker	potentiostat__test
11	collect_cv_data	collect cv 4	solution beaker	potentiostat__test
12	collect_cv_data	collect cv 5	solution beaker	potentiostat__test
13	collect_cv_data	collect cv 6	solution beaker	potentiostat__test
14	collect_cv_data	collect cv 7	solution beaker	potentiostat__test
15	collect_cv_data	collect cv 8	solution beaker	potentiostat__test
16	process_cv_data	process all CV data	potentiostat__test	potentiostat__test

Figure S6. ExpFlow Template workflow used for robotic experiments.

Figure S7. Variable properties for the ExpFlow Robotic Workflow used for the robotic experiments.

Materials

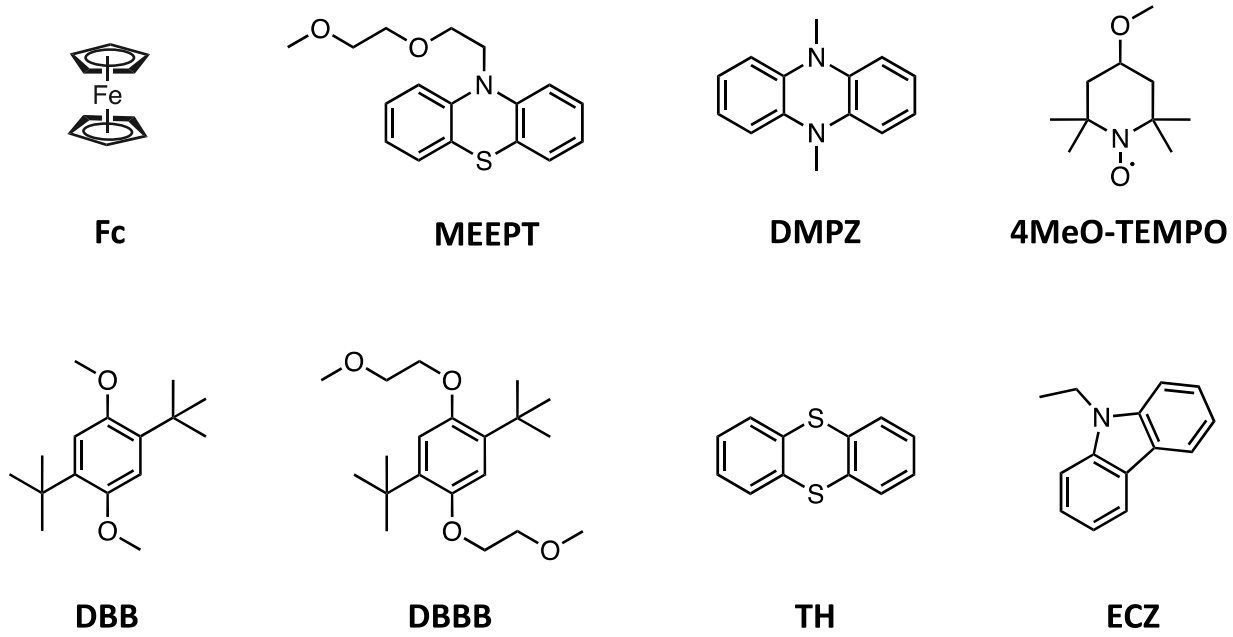


Figure S8. Chemical structures of various electro-active molecules used in the study.

Acetonitrile (ACN, anhydrous ≥99.8%, ChemSeal) was purchased from Thermo Scientific through VWR. Tetraethylammonium tetrafluoroborate ($TEABF_4$, > 99.9%, Gotion), silver tetrafluoroborate ($AgBF_4$, 99%, Matrix Scientific), ferrocene (Fc, 98%, Aldrich), *N*-[2-(2-methoxyethoxy)ethyl]phenothiazine (MEEPT, >98%, TCI America), 5,10-dimethyl-5,10-dihydrophenazine (DMPZ, 99%, A2B Chem LLC), 4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy (4MeO-TEMPO, 97%, Aldrich), 1,4-di-tert-butyl-2,5-dimethoxybenzene (DBB, 3M), 1,4-di-tert-butyl-2,5-bis(2-methoxyethoxy)benzene (DBBB, >99%, Strem Chemicals), thianthrene (TH, 97%, Aldrich) and 9-ethylcarbazole (ECZ, >99%, TCI America) were used as purchased.

Experimental Data

Oxidation Potentials

Table S2. Comparison of values produced during robotic experimentation and literature-reported oxidation potentials. All values are reported in V. The robotics/ExpFlow values relative to Fc/Fc^+ use the potential gathered for Fc in the robotic experiments as the standard.

		Robotic/ExpFlow						**Literature Reported vs. Ag/Ag+**		**Literature Reported vs. Fc/Fc+**	
Exp.	ROM	Trial 1	Trial 2	Trial 3	Avg. (vs. Ag/Ag^+)	Std. Dev.	vs. $Fc/Fc^{+\,\alpha}$	Value	Ref.	Value	Ref.
Exp1	Fc	0.081	0.082	0.082	0.082	0.001	0.000	0.086	Ref.[10]		
Exp2	MEEPT	0.396	0.396	0.396	0.396	0.000	0.314	0.410*	Ref.[11]	0.310	Ref.[12]
Exp3	DMPZ	-0.156	-0.156	-0.156	-0.156	0.000	-0.238	-0.150	Ref.[13]		
Exp4	4-MeO TEMPO	0.371	0.376	0.375	0.374	0.003	0.292	0.68^{++}	Ref.[14]		
Exp5	DBB	0.773	0.773	0.773	0.773	0.000	0.691	0.710	Ref.[15]		
Exp6	DBBB	0.773	0.768	0.773	0.771	0.003	0.690			$0.60^{‡}$	Ref.[16]
Exp7	TH	0.910	0.910	0.910	0.910	0.000	0.828	0.900	Ref.[17]	0.840	Ref.[18]
Exp8	ECZ**	0.678	0.678	0.672	0.676	0.003	0.594				

α Oxidation potential vs. Fc/Fc^+ is estimated using the oxidation potential of Fc redox couple obtained from our robotics measurements.

* Literature reported E_{ox} is for MPT.

$^{++}$ Literature reported E_{ox} is for TEMPO. Consequently, this point is not included in **Figure 6**.

** The first oxidation of ECZ is irreversible, so no oxidation potential value is reported in the literature. The D^3TaLES processing code flagged this as irreversible.

‡ E_{ox} estimated based on E_{cell} potential provided in Reference 10

Diffusion Coefficients

Table S3. Comparison of values produced during robotic experimentation and literature-reported values for diffusion coefficient. All values are reported in 10^{-5} cm^2/s.

		Robotics / ExpFlow					**Literature Reported**	
Exp.	ROM	Trial 1	Trial 2	Trial 3	Avg.	Std. Dev.	Value	Ref.
Exp1	Fc	1.70	1.70	1.80	1.73	0.06	2.10	Ref.[19]
Exp2	MEEPT	0.93	0.87	0.99	0.93	0.06	1.16	Ref.[12]
Exp3	DMPZ	1.50	1.30	1.50	1.43	0.12	1.58	Ref.[13]
Exp4	4-MeOTEMPO	1.20	1.10	1.30	1.20	0.10	2.60^{++}	Ref.[14]
Exp5	DBB	0.90	1.00	0.86	0.92	0.07	1.00*	Ref.[15]
Exp6	DBBB	0.77	0.81	0.86	0.81	0.05		
Exp7	TH	1.70	1.70	1.80	1.73	0.06	2.01	Ref.[20]
Exp8	ECZ**	3.50	4.20	5.60	4.43	1.07		

$^{++}$ Literature reported diffusion coefficient is for TEMPO. Consequently, this point is not included in **Figure 6**.

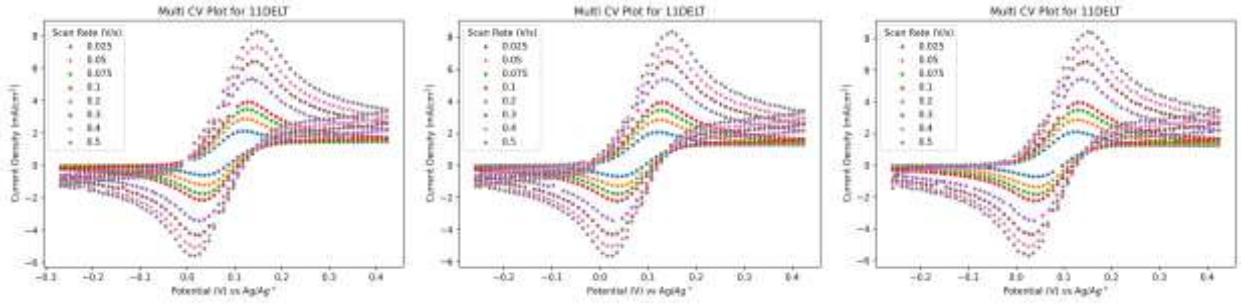
* Diffusion reported 0.77×10^{-5} to 1.23×10^{-5} cm^2/s

** The first oxidation of ECZ is irreversible, so no diffusion coefficient value is reported in the literature. The D^3TaLES processing code flagged this as irreversible.

All Cyclic Voltammograms

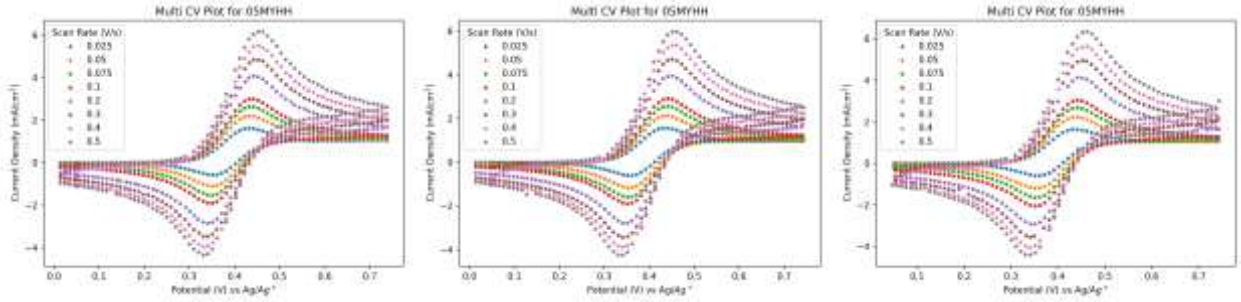
Exp 1: Ferrocene (**Fc**) CVs

Trail 1 | Trial 2 | Trial 3



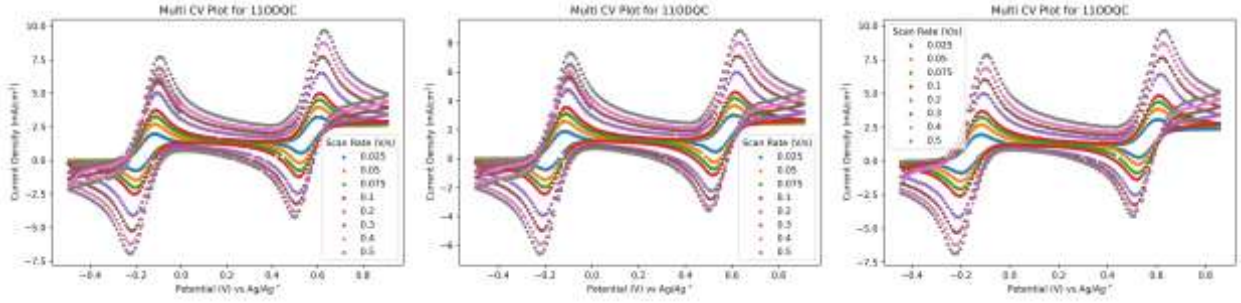
Exp 2: N-[2-(2-Methoxyethoxy)ethyl]-phenothiazine (**MEEPT**) CVs

Trail 1 | Trial 2 | Trial 3



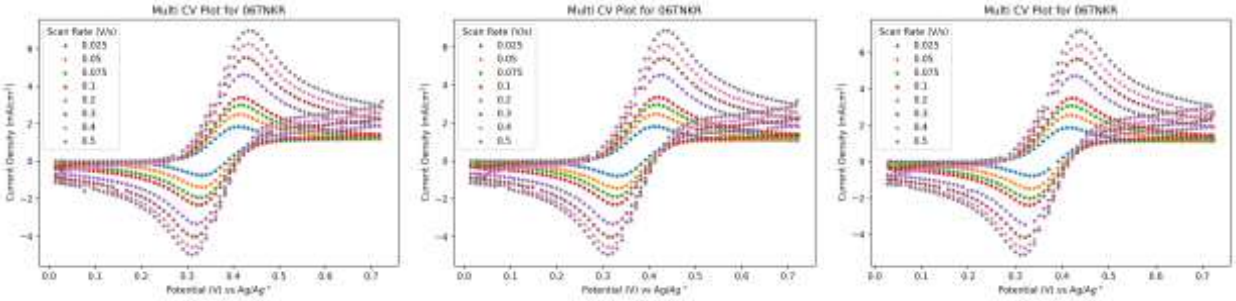
Exp 3: Dimethylphenazine (**DMPZ**) CVs

Trail 1 | Trial 2 | Trial 3



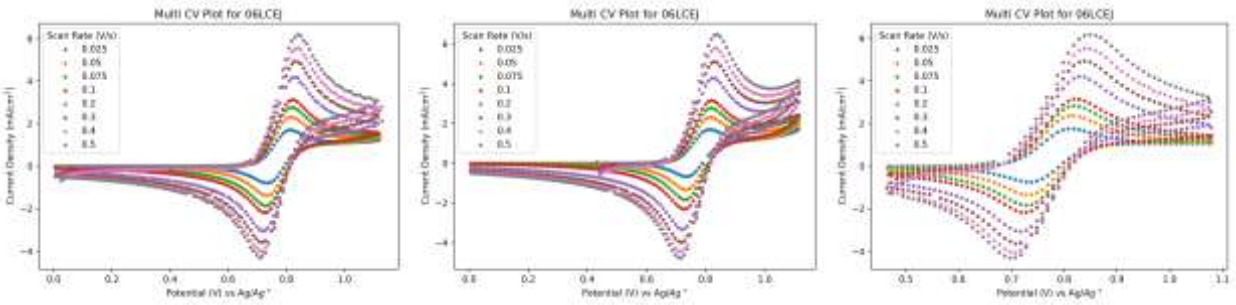
Exp 4: 4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy (**4-MeOTEMPO**) CVs

Trail 1 Trial 2 Trial 3



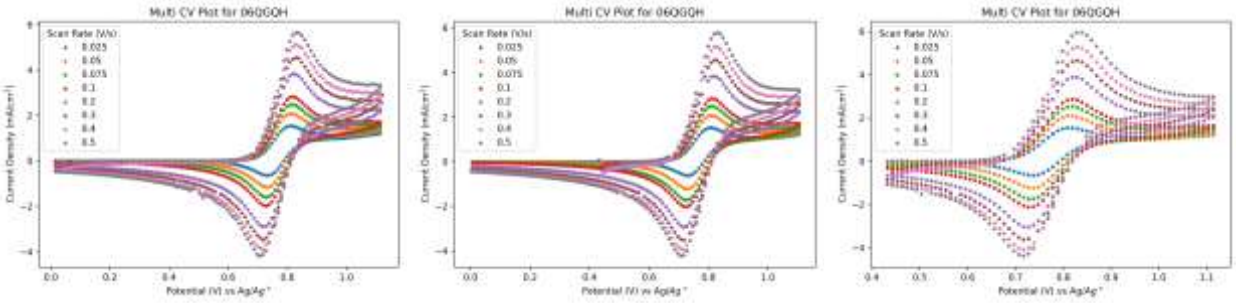
Exp 5: 1,4-Di-tert-butyl-2,5-dimethoxybenzene (**DBB**) CVs

Trail 1 Trial 2 Trial 3



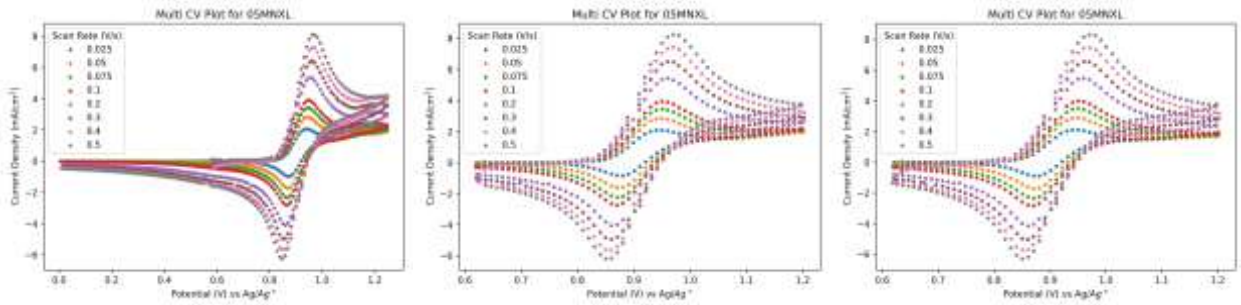
Exp 6: 1,4-Di-tert-butyl-2,5-bis (2-methoxyethoxy)benzene (**DBBB**) CVs

Trail 1 Trial 2 Trial 3



Exp 7: Thianthrene (**TH**) CVs

Trail 1 Trial 2 Trial 3



Exp 8: N-Ethylcarbazole (**ECZ**) CVs

Trail 1 Trial 2 Trial 3

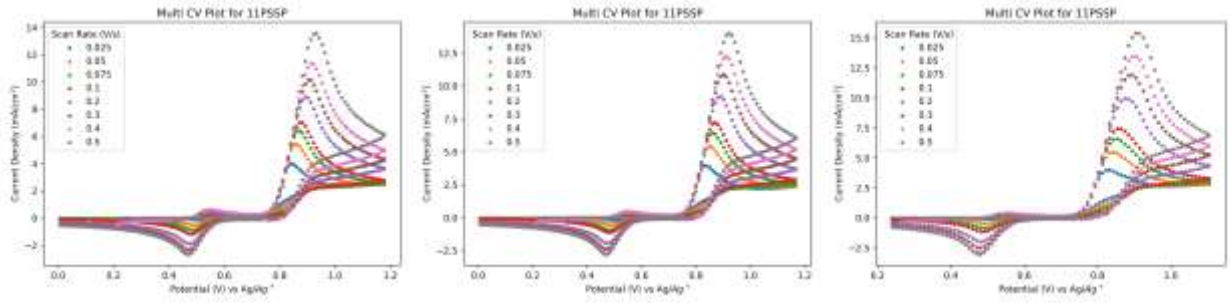


Figure S9. CV gathered for all eight redox-active systems, for all three trials. All redox-active species were dissolved at 0.01 M in 0.25 M $TEABF_4$/acetonitrile electrolyte. Voltammograms are collected at room temperature under ambient conditions and are reported using IUPAC convention. More information about experimental conditions in the previous section.

4. References

(1) Django Software Foundation. Django 2.2. 2019. https://djangoproject.com.

(2) WSGI. https://wsgi.readthedocs.io/.

(3) MongoDB. https://www.mongodb.com/.

(4) JSONSchema. https://json-schema.org/.

(5) D3TaLES Schema. https://github.com/D3TaLES/schema.

(6) Duke, R.; Bhat, V.; Sornberger, P.; Odom, S. A.; Risko, C. Towards a comprehensive data infrastructure for redox-active organic molecules targeting non-aqueous redox flow batteries. *Digital Discovery* **2023**. DOI: 10.1039/d3dd00081h.

(7) D3TaLES Database Documentation. https://d3tales.as.uky.edu/docs/.

(8) Kinova. https://www.kinovarobotics.com/.

(9) BioLogic. https://www.biologic.net/.

(10) Wang, Y.; Rogers, E. I.; Compton, R. G. The measurement of the diffusion coefficients of ferrocene and ferrocenium and their temperature dependence in acetonitrile using double potential step microdisk electrode chronoamperometry. *Journal of Electroanalytical Chemistry* **2010**, *648* (1), 15-19. DOI: https://doi.org/10.1016/j.jelechem.2010.07.006.

(11) Tegegne, B. G.; Kabtamu, D. M.; Li, Y.-Z.; Ou, Y.-T.; Huang, Z.-J.; Hsu, N.-Y.; Ku, H.-H.; Wang, Y.-M.; Wang, C.-H. N-methylphenothiazine as stable and low-cost catholyte for nonaqueous organic redox flow battery. *Journal of Energy Storage* **2023**, *61*, 106753. DOI: https://doi.org/10.1016/j.est.2023.106753.

(12) Milshtein, J. D.; Kaur, A. P.; Casselman, M. D.; Kowalski, J. A.; Modekrutti, S.; Zhang, P. L.; Harsha Attanayake, N.; Elliott, C. F.; Parkin, S. R.; Risko, C.; et al. High current density, long duration cycling of soluble organic active species for non-aqueous redox flow batteries. *Energy & Environmental Science* **2016**, *9* (11), 3531-3543. DOI: 10.1039/c6ee02027e.

(13) Kwon, G.; Lee, S.; Hwang, J.; Shim, H.-S.; Lee, B.; Lee, M. H.; Ko, Y.; Jung, S.-K.; Ku, K.; Hong, J.; et al. Multi-redox Molecule for High-Energy Redox Flow Batteries. *Joule* **2018**, *2* (9), 1771-1782. DOI: 10.1016/j.joule.2018.05.014.

(14) Nihon, K. Electron-Transfer Kinetics of Nitroxide Radicals as an Electrode-Active Material. *Bulletin of the Chemical Society of Japan.* **2004**, *77* (12), 2203-2204. DOI: 10.1246/bcsj.77.2203.

(15) Huo, Y.; Xing, X.; Zhang, C.; Wang, X.; Li, Y. An all organic redox flow battery with high cell voltage. *RSC Advances* **2019**, *9* (23), 13128-13132. DOI: 10.1039/c9ra01514k.

(16) De La Garza, G. D.; Kaur, A. P.; Shkrob, I. A.; Robertson, L. A.; Odom, S. A.; Mcneil, A. J. Soluble and stable symmetric tetrazines as anolytes in redox flow batteries. *Journal of Materials Chemistry A* **2022**, *10* (36), 18745-18752. DOI: 10.1039/d2ta04515j.

(17) Kim, J.; Kim, H.; Lee, S.; Kwon, G.; Kang, T.; Park, H.; Tamwattana, O.; Ko, Y.; Lee, D.; Kang, K. A p–n fusion strategy to design bipolar organic materials for high-energy-density symmetric batteries. *Journal of Materials Chemistry A* **2021**, *9* (25), 14485-14494. DOI: 10.1039/d1ta02059e.

(18) Speer, M. E.; Kolek, M.; Jassoy, J. J.; Heine, J.; Winter, M.; Bieker, P. M.; Esser, B. Thianthrene-functionalized polynorbornenes as high-voltage materials for organic cathode-based dual-ion batteries. *Chemical Communications* **2015**, *51* (83), 15261-15264. DOI: 10.1039/c5cc04932f.

(19) Armstrong, C. G.; Hogue, R. W.; Toghill, K. E. Characterisation of the ferrocene/ferrocenium ion redox couple as a model chemistry for non-aqueous redox flow battery research. *Journal of Electroanalytical Chemistry* **2020**, *872*, 114241. DOI: 10.1016/j.jelechem.2020.114241.

(20) Peerce, P. J.; Bard, A. J. Polymer films on electrodes: Part II. Film structure and mechanism of electron transfer with electrodeposited poly(vinylferrocene). *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1980**, *112* (1), 97-115. DOI: https://doi.org/10.1016/S0022-0728(80)80011-8.