Towards Reproducible and Automated Electrochemistry

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Abstract

Ensuring scientific reproducibility holds increasing importance in chemistry as it underpins the credibility and integrity of research findings. However, reproducing experiments and measurements is often hindered by incomplete or ambiguous procedural data in scientific literature. Additionally, the time-consuming process of data generation limits the scale of reproducing experiments. Growing efforts towards automation will contribute to enhancing reproducibility. Nevertheless, both manual reproducibility efforts and the development of automated experiments and measurements will require improved methods for recording and sharing experimental procedures in machine-readable formats. Here we develop ExpFlow, a data sharing and reporting software that currently targets electrochemistry. The ExpFlow software allows researchers to systematically encode laboratory procedures through a graphical user interface that operates like a fill-in-the-blank lab notebook. Built-in calculators derive properties such as diffusion coefficient and charge-transfer rate constant. Additionally, ExpFlow's machine-readable experimental workflows enable the easy translation of human-developed laboratory procedures to robotic experimentation. We deploy ExpFlow procedures with a robotic system to perform cyclic voltammetry measurements, reproducing several literature-reported electrochemical results. Ultimately, these tools enable automated cyclic voltammetry experiments and measurements that will facilitate high-throughput experimentation, reproducibility, and eventually data-driven discovery in electrochemistry.

Introduction

Chemistry has seen a growing emphasis on reproducibility, driven by the recognition that the credibility and integrity of scientific findings heavily rely on the ability to reproduce experimental results.[1-4] However, producing reproducible results is not always straightforward. Procedures described in scientific literature are often incomplete or ambiguous and may unintentionally lack critical details. This lack of comprehensive and standardized documentation hampers the reproducibility of experiments and measurements. Additionally, experimental data can be tedious and time consuming to produce, limiting the number of data points available for ensuring reproducibility and drawing robust scientific conclusions.

Automation has emerged as a pivotal component in enhancing reproducibility while enabling the generation of vast quantities of data.[5-9] Not only does automation increase the quantity of experiments and measurements that can be performed, but also it replaces manual, error-prone processes with automated systems that enable greater precision, accuracy, and consistency. Furthermore, the automated generation of large quantities of experimental data will allow for more big data analysis. Rapid advances in the availability and scale of big data in chemistry have generated exciting results already,[10-13] and when applied to experimental data, big data approaches such as machine learning (ML) and trend analysis can be even more promising.[6, 14-17]

Achieving scientific reproducibility and advancing automation will require the convergence of data, software, domain knowledge, and the development of effective data management frameworks.[14, 18] Specifically, it is essential to develop improved methods for recording and sharing experimental procedures, permitting researchers to reproduce and validate results more effectively. Moreover, these captured experimental procedures should be machine-readable, allowing for the translation of human ideas into machine actions. The integration of human-readable protocols with machine automation will promote both reproducibility and automation, accelerating scientific progress.

Many research efforts to capture experiment procedural data[19-23] and automate experiments and measurements[5-8, 24] exist. However, only a few efforts exist to systematically capture electrochemistry procedural data and/or automate electrochemistry experiments.[17, 25] Yet electrochemistry, and especially cyclic voltammetry (CV), holds a crucial role in chemical research. Fields ranging across drug discovery,[26, 27] energy and materials research,[28-30] process engineering,[31, 32] and environmental chemistry[33] use CV for characterization and analysis. Thus, software to capture electrochemical procedural data and subsequent software and hardware to translate these data into automated CV experimentation and measurements can have broad impact across science.

Here, we present ExpFlow, a data sharing and reporting software where electrochemists can systematically encode their laboratory workflows through an intuitive graphical user interface. We then demonstrate the use of ExpFlow in directing basic electrochemistry experiments with a robotic system. By creating standardized experimental workflows, we facilitate the translation of human-developed laboratory procedures to robotic experimentation, and the resulting data reproduce well literature-reported results.

Methods

ExpFlow and Robotic Software

The software ecosystem consists of an experiment data management software with a Python-based web-interface (ExpFlow) and an interface between ExpFlow and the automation hardware with a desktop application. ExpFlow uses Django[34] web-framework with a MongoDB[35] database to store the experimental information and is hosted on an Apache[36] web server. The interface to the automation hardware uses the Kinova API[37] and Fireworks[38] Python packages and is packaged into a desktop app with Tkinter.[39]

Automated System Hardware

The automated CV hardware consists of a Kinova[40] Gen 3 robotic arm with six degrees of freedom. A grid vial stand and vial elevator were designed, 3D-printed, and assembled in-house. A BioLogic SP-50e potentiostat is integrated into the system for cyclic voltammetry measurements. More information on the hardware can be found in SI Section 2.

CV Experiments

The electrolyte used for CV experiments contained 0.25 M $TEABF_4$ in ACN. Ferrocene (Fc), *N*-[2-(2-methoxyethoxy)ethyl]-phenothiazine (MEEPT), dimethylphenazine (DMPZ), 4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy (4-MeOTEMPO), 1,4-di-tert-butyl-2,5-dimethoxybenzene (DBB), 1,4-di-tert-butyl-2,5-bis (2-methoxyethoxy)benzene (DBBB), thianthrene (TH) and N-ethylcarbazole (ECZ) (**Figure S7**) were individually dissolved at 10 mM in 0.25 M $TEABF_4$/ACN (10 mL) in screw capped scintillation glass vials. All solutions were freshly prepared for each trial.

CV experiments were performed on electro-active solutions using a three-electrode system under ambient conditions. The cell is comprised of a screen-printed electrode fabricated on ceramic substrate (Pine Research[41]) with a 2 mm diameter Au working electrode, and a large surface area U-shaped Au counter electrode and an Ag pseudo-reference electrode (Pine Research[41]). The reference electrode was freshly prepared by immersing silver wire in a fritted tube (Pine Research[41]) containing 10 mM $AgBF_4$ dissolved in 0.25 M $TEABF_4$/ACN. The electrodes were held in place using a grip mount (Pine Research[41]) and a cell cap (Pine Research,[41] fits scintillation vial and grip mount), and connected to the potentiostat using a universal specialty cell connection kit (Pine Research[41]). The electrodes were used as received. A new screen-printed electrode and glass frit as a reference electrode were used for each trial of the eight experiments. CV measurements were performed, and data were collected using the Bio Logic SP-50e potentiostat. The voltammograms were recorded at scan rates of 25, 50, 75, 100, 200, 300, 400 and 500 mV/s. No solution resistance compensation (iR correction) was applied.

Results and Discussion

ExpFlow: Encoding Experimental Procedures

To tackle the challenges of collecting and analyzing experimental electrochemical data, we created ExpFlow, a data sharing and reporting software targeting electrochemistry that enhances data reusability and facilitates analysis. The procedural and experimental data are divided into three categories for organization and reuse: *Template*, *Experiment*, and *Run* (**Figure 1**). The customizable *Template* allows researchers to document experimental steps, *Experiment* specifies experiment reagents and apparatus, and *Run* works like a fill-in-the-blank lab notebook, where researchers record measurements and attach data files. Built-in calculators perform calculations (e.g., peak splitting, peak potentials, reversibility, diffusion coefficient, charge transfer rate, etc.) (**Table S1**). Additionally, an existing *Template* can be cloned, modified, and shared (either among ExpFlow users or via download). All of this is hosted on a web user interface.[42] Procedural and experimental data stored in ExpFlow are comprehensive and machine-readable, which increases reproducibility and enables translation of experiment procedures to robotic experiments.

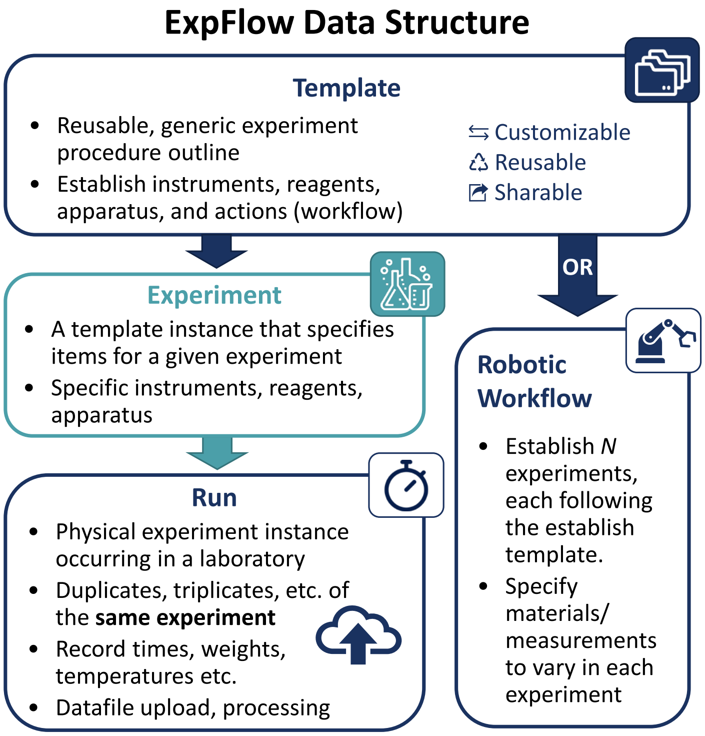


Figure 1. Schematic showing ExpFlow data organizational structure.

An ExpFlow *Template* converts experimental procedures into graphs that contain data provenances. The *Template* has categories for *reagent* (e.g., redox material, solvent), *apparatus* (e.g., beaker, electrode) and *instrument* (e.g., potentiostat, spectrometer). In a *Template* graph, nodes (the reagent, apparatus, and instrument categories) are connected by edges that correspond to *actions* (e.g., dispense, heat). Each action contains a start position, an end position, and action parameters (e.g., volume for dispensing liquid, temperature for heating, etc.). As the actions are sequenced, ExpFlow graphs capture the action provenances.

For example, a CV experiment to determine the diffusion coefficient might include redox-active molecule and solvent reagents, a beaker/vial apparatus, and a potentiostat instrument (**Figure 2**). Workflow actions might include transferring the liquid solvent and solid solute to the beaker, heating and stirring the solution, measuring the working electrode surface area, and collecting CV data. In this example, the user might add five collect-CV-data actions because the experiment includes five CV scans, each performed at a different scan rate. Although the *Template* can take time and effort to produce, it can be reused for all related and subsequent experiments.

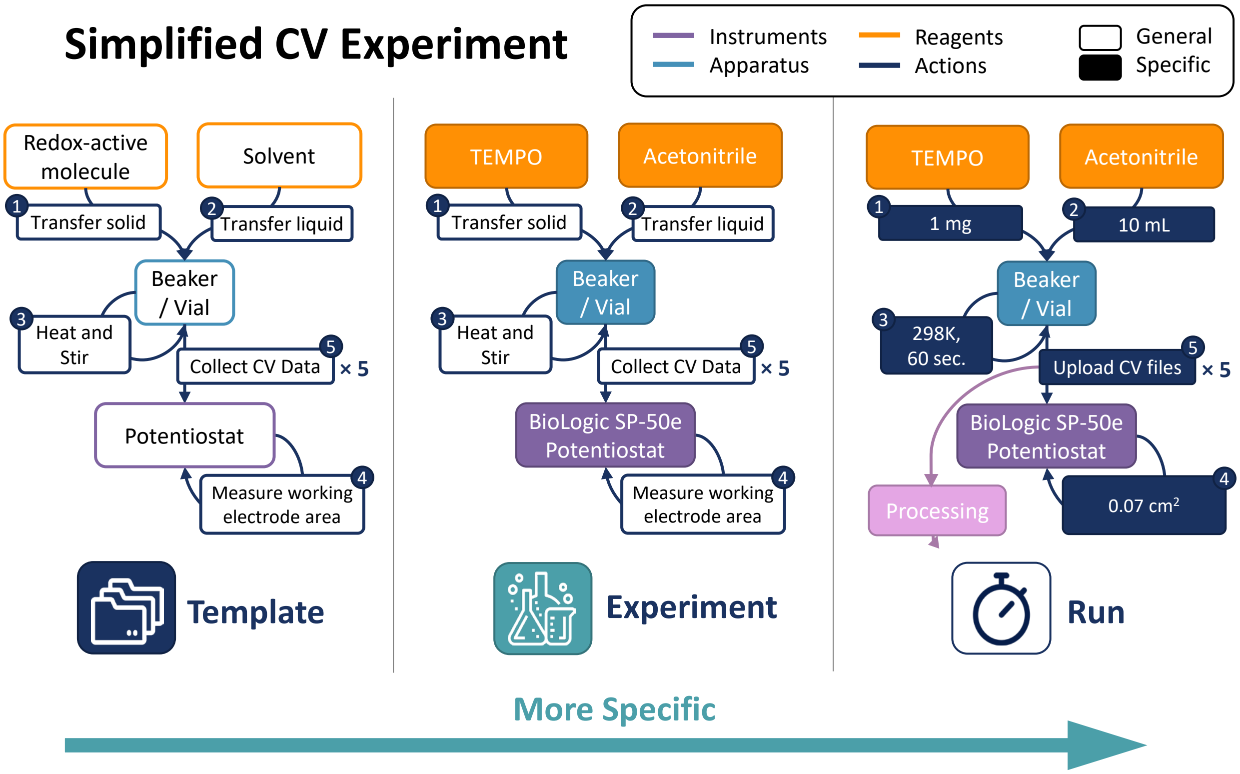


Figure 2. Schematic demonstrating a simplified CV experiment graph as an ExpFlow *Template*, *Experiment*, and *Run*.

A single *Template* can be used for multiple *Experiments* where materials (reagents, instruments, etc.) are specified. For instance, the aforementioned *Template* could parent three *Experiments*, each using a different solvent (e.g., water, acetonitrile, and propylene carbonate). When collecting data, a user runs a given experiment any number of times. During an experiment *Run*, the researcher is prompted to fill in built-in run parameters for each action. For example, the liquid-transfer action type prompts the researcher to record the liquid's exact volume, while the heat-and-stir action type prompts the researcher to record the temperature and the stirring time. Data collection action types prompt the researcher to upload a raw data file, in this case, the potentiostat output file. For more information about the ExpFlow data structure, see SI Section 1.

A *Template* can also be adapted to a *Robotic Workflow*. After selecting a *Template*, the researcher indicates default measurements for all preparation steps and specifies parameters for all data collection steps. Then, the researcher selects one or more parameters to vary. These variable parameters become the columns of a table with *n* rows, where the researcher specifies the variable parameter values for each of *n* experiments (**Figure S7**). ExpFlow then produces a machine-readable workflow for *n* identically structured experiments where one or more measurement parameters varies for each experiment. These machine-readable workflows can be downloaded for use in robotic experimentation (more details in the next section).

After an experiment is run in ExpFlow, data parsers from the D^{3}TaLES API[43] extract data from the uploaded experiment files (**Table S1**). Additionally, key metadata are extracted from the *Run* parameter data. For example, the solution temperature is extracted from the heat-and-stir action, and the solution concentration is calculated from the solid-transfer and liquid-transfer actions. All extracted data are displayed on the web user interface where the researcher can inspect and approve the *Run* data. This user interface also contains the ExpFlow calculators (e.g., diffusion coefficient and charge transfer rate constant) for *Runs* with relevant data.

Proof of Concept: Automated Cyclic Voltammetry

ExpFlow provides a platform for researchers to encode the procedure for their electrochemical experiments and measurements, and we demonstrate the utility of these machine-readable procedures by translating them into automated CV measurements. First, we assembled the robotic hardware infrastructure needed to run a CV measurement from a pre-mixed solution (**Figure 3**). More details about all hardware are provided in SI Section 2. We also built the software infrastructure necessary to connect the researcher-created ExpFlow experiment procedures to robotic actions and then communicate collected data back to the researcher (**Figure S5**). Once a researcher creates an ExpFlow *Template* and converts it into a *Robotic Workflow*, the researcher downloads the *Robotic Workflow* to the local robotics computer. Here, through a desktop application, the researcher loads the workflow and assigns reagent locations in the robot space. This step requires human actions as a safety measure to ensure that robotic experiments have human supervision. Finally, a robotics API translates the loaded workflow into robotic actions. Through the local robotics app, the researcher may launch robotic actions to perform the electrochemistry experiment and complete subsequent data processing.

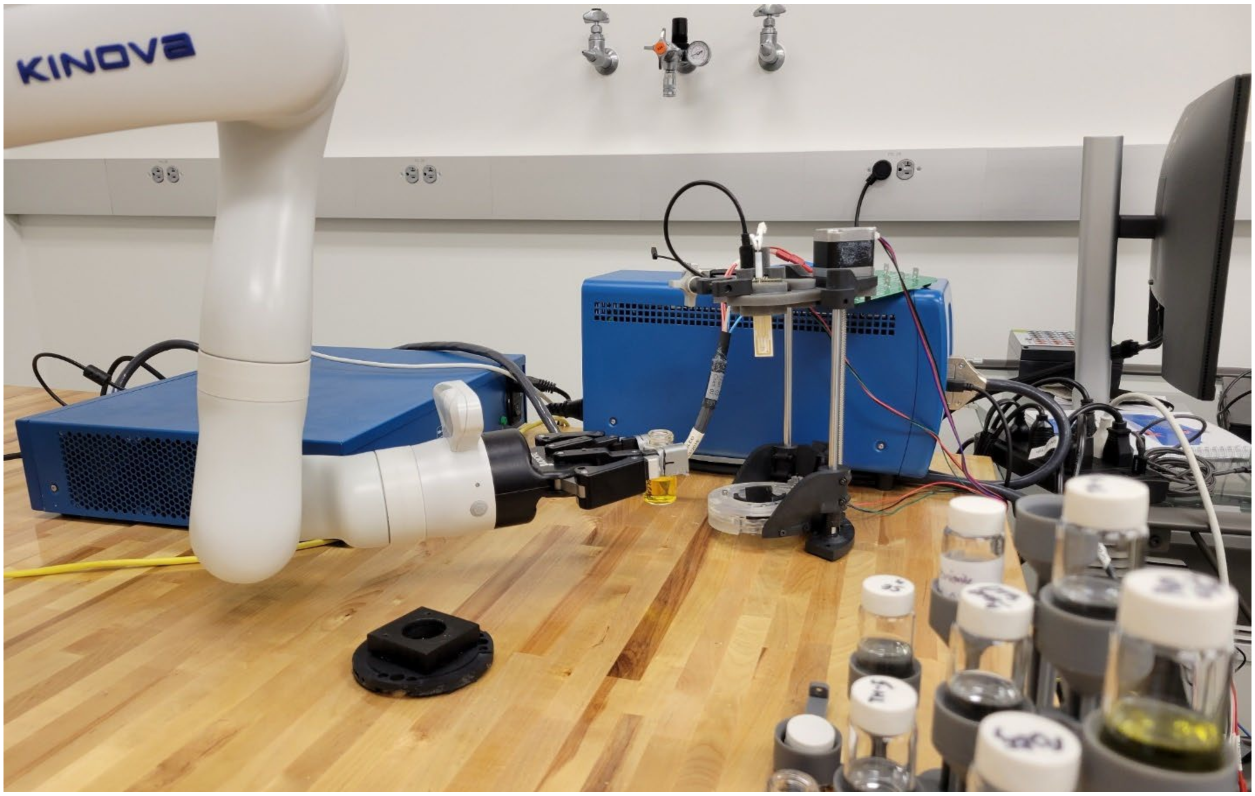
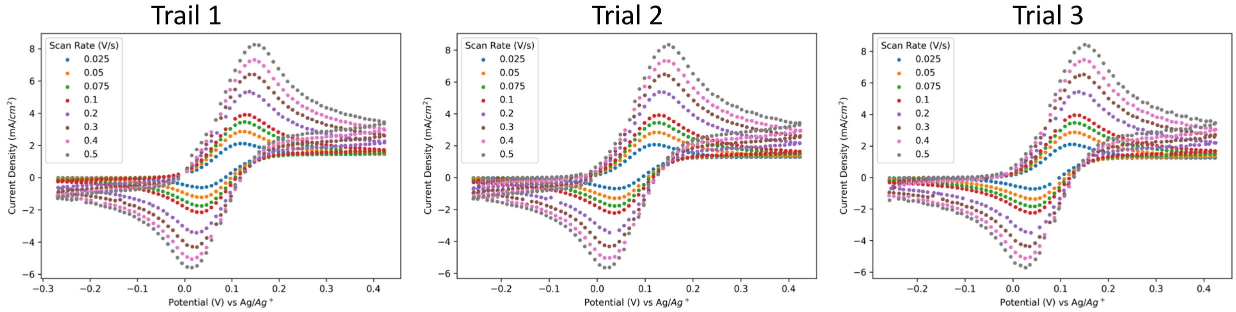


Figure 3. Image of robotic setup.

To test and validate our system, we perform CV experiments for eight well-known electro-active systems[44-51] (**Figure S8**): Ferrocene (Fc), *N*-[2-(2-methoxyethoxy)ethyl]-phenothiazine (MEEPT), dimethylphenazine (DMPZ), 4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy (4-MeOTEMPO), 1,4-di-tert-butyl-2,5-dimethoxybenzene (DBB), 1,4-di-tert-butyl-2,5-bis (2-methoxyethoxy)benzene (DBBB), thianthrene (TH) and N-ethylcarbazole (ECZ). First, we constructed an ExpFlow *Template* for the following process: Run one CV scan on a supporting electrolyte solution to confirm electrode cleanliness, select a redox-active solution, perform one benchmark CV scan at 100 mV/s and determine the optimum voltage range, collect eight cyclic voltammograms (each at a different scan rate with the optimum voltage range), and process all data. From this *Template*, we generated a *Robotic Workflow* for performing this experiment on the eight distinct solutions (**Figures S6-7**). (See Methods section for more information on solution preparation and experiment procedure.) Robotic experiments were then performed from this workflow, and the workflow was completed three times (trials) with new solutions and electrodes each trial, so the experiment was run in triplicate for each electro-active system. Starting with pre-mixed solutions, one trial of CV experiments and data processing for all eight systems took approximately 90 minutes.

The scan-rate dependent voltammograms for all eight systems are provided in **Figures 5** and **S9**. All the compounds except ECZ exhibited reversible first oxidation in 0.25 M $TEABF_4$/ACN electrolyte and the peak potentials are invariant with the scan rate. DMPZ showed reversible first and second oxidation. Notably, the data processors correctly flagged ECZ, which has a known irreversible first oxidation,[49, 52] as irreversible (**Figure S9**) and identified both the first and second oxidations for DMPZ. The average peak to peak separation for reversible oxidations at different scan rates is 0.104 V, which is wider than the ideal peak separation for a reversible process. A major factor contributing to wider peak is the current lack of iR compensation in our experiments.

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



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

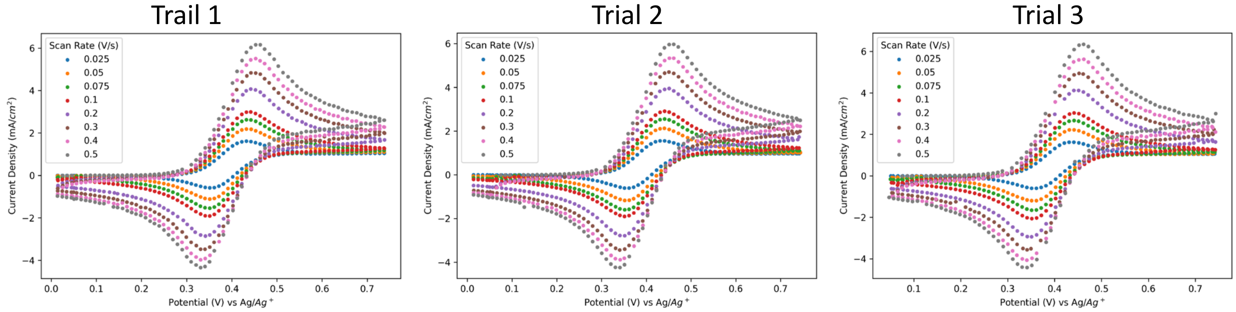


Figure 4. CV plots produced by the embedded data processors for all trials of Fc (top) and MEEPT (bottom) at 0.01 M in 0.25 M $TEABF_4$/acetonitrile electrolyte at room temperature and are reported using IUPAC convention. More information about experimental conditions and all other CVs (**Figure S12**) are located in methods and SI Section 3.

For each system, the embedded data processing determined (among other properties) the oxidation potential(s) and cathodic diffusion coefficient, and these were compared with literature-reported values. For example, the measured half-wave redox potential (at 100 mV/s) for Fc of 0.082 ± 0.001 V vs. Ag/Ag^+ aligns well with the literature-reported[53] potential of 0.086 V vs. Ag/Ag^+. Additionally, the measured diffusion coefficient of $1.73 \pm 0.06 \times 10^{-5}$ cm^2/s is consistent with the literature-reported[54] coefficient of 2.10×10^{-5} cm^2/s. Similar results were observed for MEEPT, another well studied redox-active system known for its high stability and solubility.[55-57] The measured half-wave redox potential for MEEPT is 0.396 V vs. Ag/Ag^+, which is comparable with the potential (0.41 V vs. Ag/Ag^+)[58] reported for *N*-methylphenothiazine. Since there are no literature-reported oxidation potentials for MEEPT vs. Ag/Ag^+, the potential is estimated relative to Fc/Fc^+ using the potential gathered for Fc in the robotic experiments as the standard. The measured oxidation potential of 0.314 V vs. Fc/Fc^+ aligns very well with the literature-reported[56] potential of 0.310 V vs. Fc/Fc^+. The measured diffusion coefficient of 0.93 ± 0.06 × 10^{-5} cm^2/s is also close to the literature-reported[56] coefficient of 1.15 × 10^{-5} cm^2/s.

The collected electrochemical data for all eight systems, compares well with literature-reported results (**Figure 6**, see **Tables S2** and **S3** for raw data).[46, 53, 54, 56, 58-64] The robotic experiment oxidation values have an almost perfect one-to-one correlation with literature-reported values. While the robotic experiment diffusion coefficients correlate well with the literature-reported values, the values do trend lower than the literature reports. That these results are consistent with the literature not only validate our robotic setup and data processing, but also demonstrate the potential for machine-readable procedures and automation to enable reproducibility experiments.

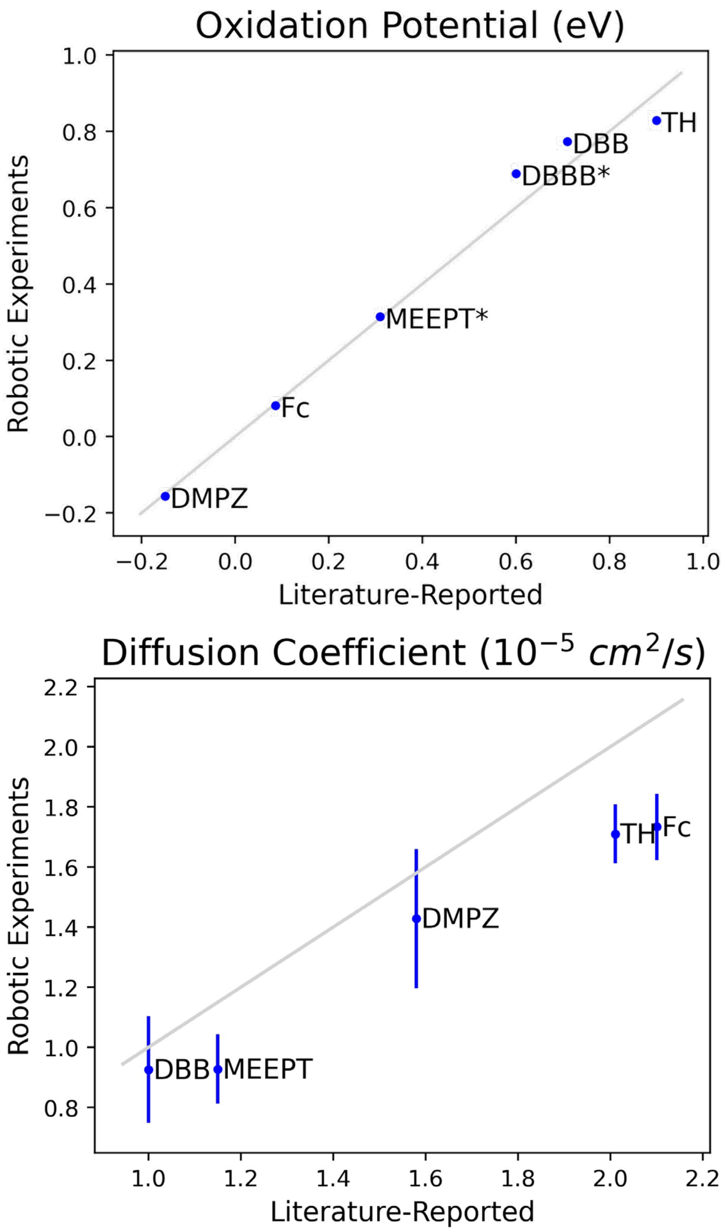


Figure 5. Comparison of values produced during robotic experimentation and literature-reported values for oxidation potential (top) and diffusion coefficient (bottom). Robotic experimental values are reported as the average value across the three trials where the error bars are twice the standard deviation. The gray line represents an ideal one-to-one correlation between the robotic and literature-reported values. All robotic potentials are measured vs. Ag/Ag^+. For all raw data, see **Tables S2** and **S3**. For comparison, literature-reported oxidation potentials are reported referenced to Ag/Ag^+, except for MEEPT and DBBB (as denoted by the *); the oxidation potentials for MEEPT and DBBB are estimated relative to Fc/Fc^+ using the potential measured for Fc in the robotic experiments as the standard.

Conclusions

Here we present ExpFlow, a software that allows researchers to systematically encode their laboratory workflow through an intuitive graphical interface. These encoded workflows standardize experimental practices to capture all experiment metadata and increase reproducibility. Currently, ExpFlow supports data parsing for CV experiments. Machine-readable ExpFlow procedures also facilitate the translation of human-developed laboratory procedures to robotic experimentation, as we demonstrate for robotic electrochemistry experiments. We used an ExpFlow *Template* and a robotic hardware and software setup to perform automated electrochemistry experiments in triplicate for eight well-known electroactive systems. The resulting oxidation potentials and diffusion coefficients are consistent with literature-reported values, validating our setup and demonstrating the utility of robotic experimentation in promoting reproducibility.

While this proof-of-concept robotics phase demonstrates the software and basic hardware needed for translating human-conceived electrochemistry experiments to robotic actions, there is still room for improvement. Future additions may include liquid dispensing and solution mixing as well as additional characterization metrics such as viscosity, solubility, spectroscopy etc. We also plan to fine-tune the potentiostat data collection methods to ensure that the robotic experiments produce high quality data on par with current literature standards.[29, 65] Ultimately, the advances demonstrated here will facilitate reproducibility, automated labs, and eventually autonomous design of experiments[66] for electrochemistry.

Data Availability

ExpFlow is available for researchers at https://d3tales.as.uky.edu/expflow.

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Acknowledgements

This work was generously supported by the National Science Foundation (NSF) under Cooperative Agreement Number 2019574. We thank Dr. Andrew Horvath for testing ExpFlow and providing a researcher's prospective on the software design, and we thank Dr. Judy Jenkins for her expert advice regarding the robotic electrochemistry setup. Finally, we wholeheartedly thank the entire D3TaLES (https://d3tales.as.uky.edu/) team for their insights into the development of this workshop.

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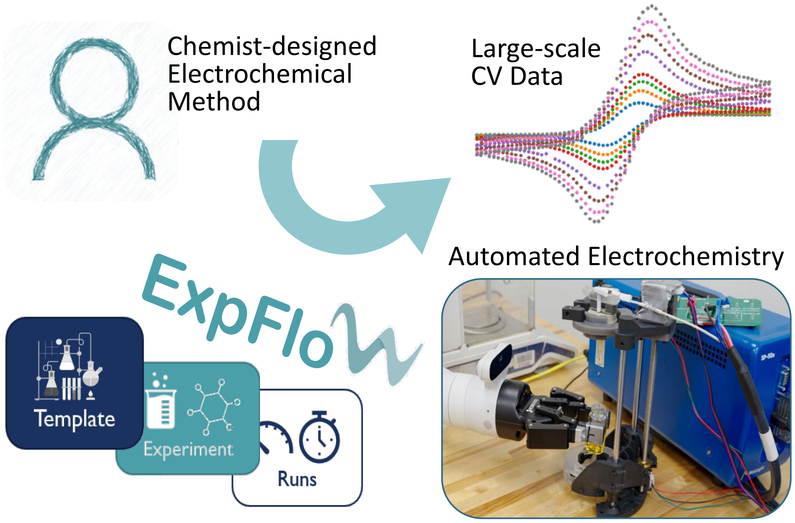
Chemist-designed
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