

Article



Design of an Extended Experiment with Electrical Double Layer Capacitors: Electrochemical Energy Storage Devices in Green Chemistry

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Abstract: An extended undergraduate experiment involving electrochemical energy storage devices and green energy is described herein. This experiment allows for curriculum design of specific training modules in the field of green chemistry. Through the study of electrical double layer capacitors, students learned to assemble an electrical double layer capacitor and perform electrochemical measurements (cyclic voltammetry and galvanostatic charge-discharge) to evaluate the effect of various electrolytes. In addition, students powered a diode with the electrical double layer capacitors. We use the laboratory module to successfully connect electrochemistry with green chemistry through the study of a real-world application. In addition, a green chemistry case study was introduced to the laboratory curriculum. During the experiment, students acquired fundamental experience in electrochemistry and gained analysis skills, critical thinking, and scientific literacy. The results of this work can be used as a case study on green chemical education that considers the students' awareness of renewable and clean energy fields.

Keywords: curriculum; undergraduate research; laboratory equipment/apparatus; green chemistry; electrochemistry

1. Introduction

The development of environmentally benign, sustainable, and renewable energy sources, as well as new technologies for energy conversion and storage, is economically and ecologically critical. The depletion of fossil fuels and increasing environmental pollution necessitate advances in the fields of green chemistry and renewable energy [1,2]. Up to now, sustainable and renewable energy sources, including solar power, ocean waves, and wind, have been widely utilized in the world. Electrochemical energy storage devices (e.g., supercapacitors, secondary batteries, etc.) are well positioned to store regional and seasonal energy [3,4]. For training future scientists to create these tools, Shihezi University has developed green energy (green chemistry) courses for undergraduate students. These courses respond to the increasing energy needs of modern society and emerging ecological concerns.

Green chemistry is an essential part of modern chemical education [5,6] and is critical for future innovation and industrial applications to meet society's growing demand for sustainable products and processes. Chemical educators should continue to refine laboratory curricula to reflect these principles. Increasing evidence suggests that laboratory courses improve students' knowledge of scientific methods, and engagement with chemistry [7,8]. These courses enhance the ability to think scientifically and critically, as well as to communicate effectively. The green energy curriculum established at our institution involves both the theory and practice of green chemistry. It gives students

the tools to design and manufacture next-generation chemicals and products without harming human health or the natural environment [9,10].

The basis of the lecture component of these green chemistry courses is instruction in alternative energy sources (i.e., wave, tide, and solar). Students are also exposed to green energy storage devices; this article focuses on electrical double layer capacitors (EDLCs). EDLCs are novel energy storage components between batteries and electrostatic capacitors [11,12]. As the first reversible energy storage devices, EDLCs have attracted significant attention due to their high power density, long lifecycle, and ability to bridge the energy gap between traditional dielectric capacitors and batteries. A typical EDLC consists of two electrodes, a separator, and an electrolyte that can be classified into two types: aqueous and organic. However, purely classroom-based instruction in electrochemistry has significant limitations. Therefore, we describe herein a laboratory protocol that is suitable for students, and teaches the essential details about EDLCs. This laboratory component will help to create a new generation of green-minded researchers.

2. Methods

Students were involved in this experiment as a three-stage project in a first-semester undergraduate electrochemistry laboratory. The first stage (pre-class) included discussions of the principles of green chemistry, how the EDLC worked and was assembled, and how to generate cyclic voltammetry and galvanostatic charge-discharge curves with the electrochemical workstation. The second stage (in-class) allowed students to assemble an EDLC and practically test the product. The third stage (after-class) involved analyzing the test results and finishing lab reports. The process of "teaching" and "learning" in the three-stages was designed to involve experimentation, implementation, and reflection, as shown in the Supplementary Materials. Figures 1 and 2 express the teaching idea, purpose, and the time arrangements of the experimental curriculum.



Figure 1. Experimental design and concept of green chemistry.



Figure 2. The time arrangements of the experimental curriculum.

2.1. Preparatory Phase: Obtaining Knowledge and Forming Green Practice Groups

This phase contained three main parts: laboratory assistant preparation, students obtaining knowledge, and forming green practice groups. The latter two sections were based on a network education platform.

The laboratory assistant prepared the materials and apparatus ahead of time. The materials included activated carbon, CR2032 coin cell case, spacer disk, wave washer, Celgard separator, tweezer, pipette, electric wire, clip connector, light emitting diode, 6.0 mol/L KOH (50 mL), 1.0 mol/L Li₂SO₄ (50 mL), and 1.0 mol/L LiPF₆ (50 mL). The apparatus included punching machine, sealing machine, glove box, and electrochemical workstation.

The teacher assigned tasks on a network education platform. Thereafter, the students were divided into self-selected groups of three students each to evaluate the voltage window of three electrolytes (KOH, Li₂SO₄, and LiPF₆) and study the effects of these electrolytes on the chemical performance of the EDLC.

2.2. Operation: Training Practical Green Chemistry Ability and Fostering the Spirit of Cooperation

This module took approximately 4 h, during which students completed EDLC assembly, performed testing, and powered the diode. Figure 3 shows the EDLC assembly sequence. The students first added the electrolyte to the gap between the separator and gasket. The edge of the spacer was prone to roll up when it contacted the electrolyte, so tweezers were required to smooth the separator. The battery center of the two electrodes was then closed with tweezers and carefully controlled to prevent the separator from breaking during this process. The samples underwent tableting with a tablet machine after assembly, and the capacitor should be placed in the center of the carrier tablet.



Figure 3. (a) EDLC operation schematic and (b) EDLC installation sequence.

Equation (1) [15,16]:

The electrochemical performance of the EDLC was determined by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests performed using a CHI600A electrochemical workstation. Cyclic voltammetry can rapidly provide a diverse range of data, including the reversibility and mechanism of electrode reactions and adsorption of the electrochemical material. Galvanostatic charge-discharge is another method used to study electrode materials via characterization of specific capacitance and cycle performance [13,14]. The students studied the change in potential as a function of time at a constant current. They then analyzed the capacitance via GCD curves and calculated the specific capacitance of the electrode material based on the continuous current discharge curve and

$$C_{m} = \frac{4It}{m \cdot \Delta \overline{V}}$$
(1)

where m is the weight of the electrode material in the electrode layer (g), I is the constant current value (A), t is the discharge time (s), and is the average voltage drop of the discharge curve (V).

Students used different electrolytes in the EDLC and observed the diode brightness as a function of time as the EDLC was charged and discharged.

2.3. Feedback and Summary: Calculation and Analysis of the Specific Capacitance Data and Finished Lab Reports

In this stage, the students learned how to measure and draw CV and GCD curves using Origin software. They observed the voltage window from CV curves of the three electrolytes and calculated and analyzed the specific capacitance of the EDLC from the corresponding GCD curves. Finally, the students completed their lab reports and shared the results with each other.

3. Hazards

Potassium hydroxide (KOH) is a strong base which is caustic. It is essential to wear gloves during the assembly of the EDLC to avoid damaging skin and clothing. If there are any spills, the area should be rinsed with ample amounts of water. The organic electrolyte should be used in the glove box.

4. Results and Discussion

4.1. Independent Study

Students reached conclusions through reviewing literature information, finding that the capacitance of the electrode was a function of the potential-dependent accumulation of electrostatic charge at the interface. During charging, electrons accumulated on the supercapacitor electrodes and traveled from the negative to the positive electrode, as shown in Figure 4. Within the electrolyte, cations moved towards the negative electrode, while the anions moved to the positive electrode. This process formed the electric double layer at the solid-liquid interface. The reverse processes occurred during discharge and decreasing electrical potential between the two plate electrodes was observed. In this type of EDLC, no charge transfers across the wire or electrolyte interface occurred, and no net ion exchange between the electrode and electrolyte were observed. This indicates that the electrolyte concentration remained constant during charging and discharging. The energy was stored in the double-layer interface using this method.

The students were self-divided into groups of three people. The students obtained information regarding the three electrolytes from reading the literature, as this was a critical component of the EDLC. The electrolyte provided ionic conductivity and facilitated charge compensation for each electrode in the cell. The electrolyte played a fundamental role in the EDLC and determined EDLC performance. This laboratory procedure evaluated both aqueous and organic electrolytes. With the aqueous electrolytes, including alkaline (KOH) and neutral (Li_2SO_4), the potential window was approximately 1.0–1.6 V. These electrolytes are inexpensive and can easily be handled in the laboratory without special conditions, greatly simplifying the fabrication processes. Organic electrolytes (such as $LiPF_6$) currently dominate the commercial market due to their extensive operation potential window

(approximately 2.5–4.5 V), and the CV experiment evaluated the cycling performance of the EDLC and determined its voltage.



Figure 4. Schematic illustration of charge/discharge process in EDLC. (**a**) The charging process, (**b**) EDLC after charging, and (**c**) the discharging process.

4.2. Experimental Illustration of Green Energy

The experiment was performed a total of 11 times. The CV and GCD curves shown in the following parts are representative results obtained by the students.

The CV results were used to evaluate the cycling performance of the EDLC and determine its voltage range. Figure 5 shows representative CV curves for the KOH, Li_2SO_4 , and $LiPF_6$ electrolytes. KOH and Li_2SO_4 exhibited an excellent current response, and their CV curves were rectangular. This approached an ideal EDLC curve that was perfectly square, whereas the CV curves for $LiPF_6$ deviate from this trend. The results indicated that KOH and the Li_2SO_4 exhibited better electrochemical performance with the active carbon electrode than that of $LiPF_6$.



Figure 5. Representative CV curves of (a) KOH, (b) Li_2SO_4 , and (c) $LiPF_6$ electrolytes at different scan rates using a two-electrode testing setup. (d) CV curves of the three samples at a sweep rate of 5 mV s⁻¹.

As the scanning speed increased, the CV curves flattened (Figure 5a–c). Some students thought it was because ions could not easily access the electrode for charging and discharging at a high scan rate. However, the charge stored on the electrode did not increase at a steady rate. This decreased the active material on the electrode and tilted the CV curve. Figure 5d shows that the voltage windows were 0–1, 0-1.4, and 0-3.0 V for the KOH, Li₂SO₄, and LiPF₆ electrolytes, respectively.

Figure 6 shows the GCD curves of the KOH, Li_2SO_4 , and $LiPF_6$ electrolytes when measured at different current densities using a two-electrode testing system. The KOH and Li_2SO_4 samples exhibited symmetrical shapes and a relatively small internal resistance (IR) drop. The slight curvature in the GCD curves corresponded to the redox reaction of the active species in the sheet. In addition, the GCD curves in the $LiPF_6$ specimen remained constant at different current densities and showed no visible IR drops.



Figure 6. GCD curves of (**a**) KOH, (**b**) Li_2SO_4 , and (**c**) $LiPF_6$ electrolytes at different current densities determined using a two-electrode testing setup. (**d**) GCD curves of the three samples at a current density of 5 A g⁻¹.

Figure 7a exhibits the specific capacitance with the KOH electrolyte was 231.4 F g⁻¹ at 0.5 A g⁻¹ based on Equation (1). This value was twice as much as that of the Li₂SO₄ electrolyte (115.4 F g⁻¹) and four-fold greater than the LiPF₆ electrolyte (55 F g⁻¹), as shown in Figure 7b,c. At a current density of 1 A g⁻¹, the specific capacitance of the KOH electrolyte remained as high as 205.3 F g⁻¹ with a capacitance retention rate of 88.8%. The Li₂SO₄ electrolyte reduced the performance by 25.4% or 86 F g⁻¹. The LiPF₆ electrolyte exhibited a specific capacitance of 16.8 F g⁻¹, a reduction of 69.4% under constant parameters. These data showed that the specific capacitance of the EDLC gradually decreased as the current density gradually increased, and the KOH formed an excellent electrical double layer, showing good electrode conductivity.



Figure 7. The specific capacitance of active carbon materials calculated by GCD curves using various electrolyte: (**a**) KOH, (**b**) Li₂SO₄, and (**c**) LiPF₆.

It can be seen that, the specific capacitance of active carbon was affected by various factors, especially for electrolytes. Generally, the capacitance of activated carbons is higher in aqueous electrolytes (ranging from 100 F g⁻¹ to 300 F g⁻¹) than that in inorganic electrolytes (less than 150 F g⁻¹). In this manuscript, the student's experimental data (55–231 F g⁻¹) is similar to the results summarized in Ref. [3].

The students connected a diode to the EDLC after charging it on the electrochemical workstation. The intensity of the diode is shown in Figure 8. The diode was rated at 5 V, and its brightness increased with applied voltage when the voltage was less than 5 V. The diode powered by an EDLC with LiPF₆ electrolyte was the brightest followed the diode powered by the Li_2SO_4 and KOH EDLCs. These results were consistent with the CV and GCD data.



Figure 8. Diode brightness using (a) KOH, (b) Li₂SO₄, and (c) LiPF₆ electrolytes in EDLC.

4.3. Green Chemistry Application and Connecting Ideas

Feedback from students suggested that the developed method delivers on the desired learning outcomes. This was concluded through three major aspects. First, this approach stimulated students' interest in a topic typically seen as abstract, as EDLCs are rarely featured in undergraduate lab experiments. It allowed the students to observe how electrolyte selection affected EDLC performance and enabled them to gain a better understanding of electrochemistry, increase familiarity with energy store device technology, and provided valuable hands-on experience with electric charges and circuits.

Second, these chemistry topics provided exciting opportunities, created green chemistry laboratory activities, and encouraged discussion among the students. We endeavored to improve the students' analytical ability, critical-thinking skills, and understanding of energy science. All of these goals were achieved, as evidenced by a post-course questionnaire. For instance, the students began to think about which electrolyte would be suitable for petroleum coke electrode material in EDLCs after experimental data analysis, which electrode material was best for EDLCs, how to improve the voltage window, how to reduce hazardous waste, among other suggestions. Novel ideas were inspired, discoveries were made, and memories created by these electrochemical experiments and are worth implementing in the laboratory course component.

Third, this experiment shaped the student-centered teaching and study-based learning modules, which did not rely on implanting knowledge and skills to students, but inspired students to think and focus on participatory learning. For example, the students passionately participated in the online platform and chose electrolytes of their own volition, which highlights the success of the experiment. Furthermore, this experiment orients education towards system-based thinking, including the use of interdisciplinary, experiential, and inquiry-based methods.

In general, green chemistry curricula will play a central role in establishing a course on sustainability. This experiment could attract students into science and allow them to think about the proper relationship between natural and artificial environments using an integrated view of social, political, ecological, economic, and possibly cultural dimensions. In addition, the students will gain valuable experience to pursue careers in green chemistry.

5. Conclusions

To improve teaching and research, an experiment testing electrochemical performance was designed and integrated into the green chemistry curriculum. This 4 h module (EDLC) significantly progressed student understanding of electrochemistry and energy storage equipment. It also sustained and enhanced their intellectual enthusiasm and passion for both education and research. This laboratory module will unleash the potential of students and cultivate their responsibilities and obligations toward green chemistry via consultation of the scientific literature and participation in the experiment. Overall, the primary objective of this curriculum is to increase student knowledge of electrochemistry. However, they also develop important skills related to green chemistry, such as problem-solving, analytical skills, critical reasoning, and creative thinking. Therefore, more such experiments involving green chemistry should be integrated into the undergraduate chemistry curriculum.

Supplementary Materials: Teaching plan and learning plan are available online at http://www.mdpi.com/2071-1050/10/10/3630/s1.

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