

Keysight Technologies

Electrochemistry 3-Electrode Measurement Workflows for Li-ion Cells and Sensors Using the B2900 SMU

Application Note



Summary

The Keysight B2900A Precision Source/Measure Unit (SMU) is used for electrochemical measurements including two widely applied workflows known as cyclic voltammetry (C-V) and chrono-amperometry. Both measurements are based on three-electrode systems including working electrode, reference electrode, and counter electrode. In C-V the potential is scanned and the corresponding current of the electrochemical redox reaction is measured. The voltages and the current of the oxidation and reduction peaks are measured with the values depending on the analyte concentration (Nernst equation) and the kinetic diffusion properties (Fick's law). In chrono-amperometry the current of the redox reaction is measured with respect to time at a given constant potential. Two different electrochemical systems are measured including a Li-ion cell with TiO_2 as the reference electrode and a glucose sensor with a polymer modified electrode. In comparison to the conventional potentiostat-based setup the SMU has very sensitive current and voltage measurement resolution allowing for instance also small electrode systems with low electrochemical currents to be accurately measured. The process control can be done either from the front panel of the SMU or by the PC-based Keysight B2900A Quick I/V Measurement Software. Additionally, Keysight EasyEXPERT group+ Software allows one to control the entire process from measurement setup and execution to analysis and data management. This can be extended also to battery related automated multi-cell electrochemical measurements where the change of many individual parameters (for instance the concentrations of ions in the electrolyte) is studied in a rack of serial half-cells.

Introduction

The field of electrochemistry, essentially the study of the exchange between electrical and chemical energy, is playing an important role in industry and academia as we witness increasing investment in energy-focused research areas such as batteries, capacitors, energy storage devices, photovoltaics, corrosion, hydrogen cells, electrochemical sensors etc. The design of these devices to get optimal performance for real-world applications depends largely on the study of molecular electrochemical processes that underline the macroscopic function. Electrochemical processes utilize redox reactions that consist of individual oxidation and reduction steps. An oxidation involves the loss of one or more electrons from a chemical species while a reduction is the uptake of one or more electrons. When an oxidation and a reduction are paired together in a redox reaction, electrons can flow from the oxidized species to the reduced species. That electron flow can either be spontaneously produced by the reaction and converted into electricity, as in a galvanic cell, or it can be imposed by an outside source to make a non-spontaneous reaction proceed, as in an electrolytic cell. The complete galvanic or electrolytic cell as a whole is a two-terminal system like a standard battery. For typical experiments, instead of the complete cell a half cell is used which offers more flexibility and ease of control. We can picture a complete cell as comprised of two half cells in which a half-cell is one of the two electrodes. For the half cell a reference electrode (RE), a counter electrode (CE), and a working electrode (WE) are required forming a three electrode electrochemical system (please see Figure 1). The voltage applied to the WE is the potential difference between WE and RE. The CE provides a pathway for the current to flow in the electrochemical cell without passing through the RE. For the CE an inert material such as platinum is often used. The RE is usually based on Ag/AgCl which comprises a silver wire that is dipped in molten silver chloride contained in a glass tube with a porous plug. The WE is usually made of a conductive material such as gold or graphite coated with the necessary electrochemically active materials. An appropriate electrolyte (aqueous or molten) containing mobile ions will be selected based on the electrochemical system (please see Figure 2).

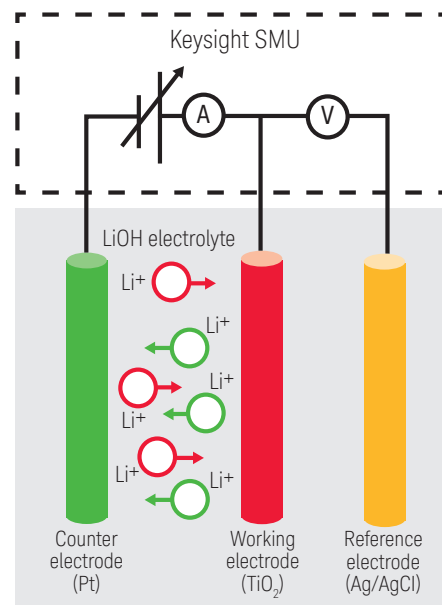


Figure 1. Schematics of Keysight B2900A SMU for three-electrode electrochemistry measurements applied to Li-ion cells with TiO_2 as working electrode.

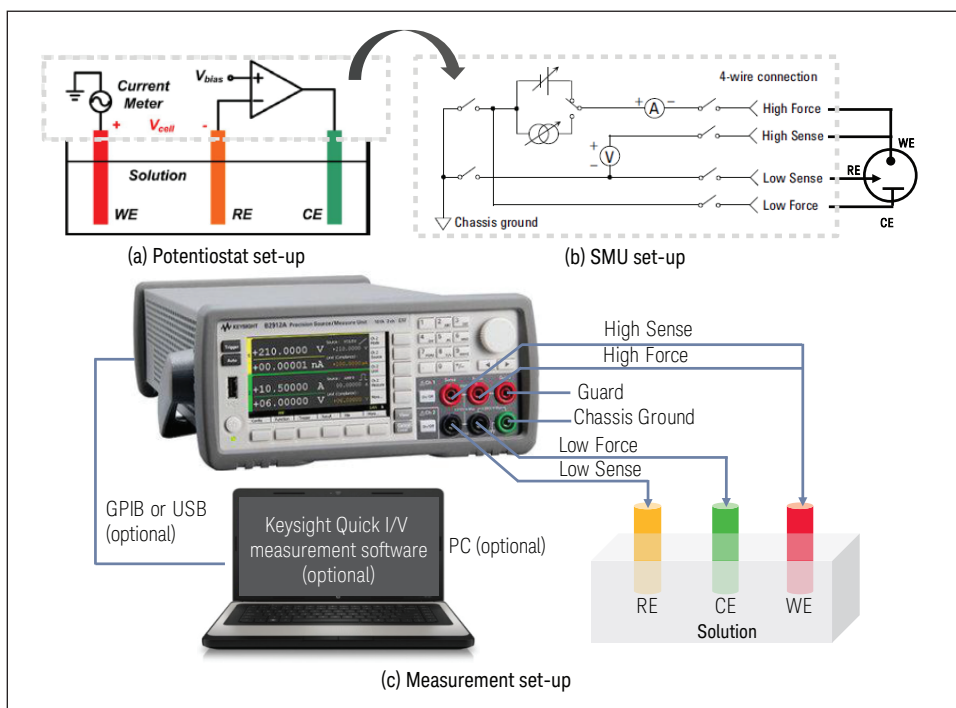


Figure 2. Potentiostat vs SMU setup. (a) The potentiostat gives a constant potential between reference electrode (RE) and working electrode (WE) by adjusting the current through the counter electrode (CE). (b, c) In the SMU, high sense and high force can be combined forming a three terminal connection similar to a potentiostat.

Introduction (continued)

A common measurement technique in electrochemistry is cyclic voltammetry (C-V) which studies the redox and transport properties in an electrolyte solution. When the potential of the WE is more positive than that of a molecular redox couple present in the electrolyte solution, the corresponding species is oxidized (i.e. electrons going from the redox solution to the electrode) and produce an anodic current (please see Figure 3). Similarly, on the return voltage scan, as the WE potential becomes more negative than the reduction potential of the redox couple, reduction occurs (i.e. electrons going from the electrode into the redox solution) causing a cathodic current. The C-V is thus obtained by measuring the current at the WE during the forward and reverse potential scans. Data interpretation of a C-V voltammogram thus depends on four observables, namely, the two peak currents and two peak potentials [1]. By IUPAC convention, anodic currents are positive and cathodic currents negative. In the case of an electrochemistry setup using the potentiostat, the system maintains the potential of the WE at a constant level with respect to the RE by adjusting the current at the CE. The voltage is then scanned in the forward direction i.e. with increasing potential of the WE with respect to the RE until the current peak is surpassed. The reverse scan in the opposite direction is then carried out with decreasing potential of the WE against the RE. The cyclic voltammetry curve is thus generated by plotting the measured current at the WE throughout the complete cycle of potential scan.

In the following material we show that the Keysight B2900A Precision Source/Measure Unit (SMU) is well suited for electrochemical measurements with its capability to source and measure both voltage and current very accurately at 10 fA and 100 nV resolution [2, 3]. No hardware or software changes are required to use the SMU for electrochemical 3-electrode measurements. The SMU offers multiple options for instrument remote control such as the Keysight B2900A Quick I/V Measurement Software which allows users to setup and execute measurements easily on a Windows-based PC. The Quick I/V software has also a user-friendly GUI that can communicate with the B2900A SMU over LAN, USB and GPIB. In addition, the Keysight EasyEXPERT group+ Software supports efficient and repeatable device characterization in the entire process from measurement setup and execution to analysis and data management. The EasyEXPERT group+ makes it easy to perform complex workflows immediately with the ready-to-use measurement and application tests and allows you the option of storing test condition and measurement data automatically after each measurement in a unique built-in database (workspace), ensuring that valuable information is not lost and that measurements can be repeated at a later date.

The B2900A SMU can be used not only for 3-electrode electrochemical C-V measurements but also the acquisition of charge-discharge cycles of battery cells is possible using 4-electrode Kelvin connections. The enhanced range of 3 A continuous current and 10.5 A pulsed current allows to perform these measurements under widely used and realistic conditions without the need of a booster amplifier. Additionally, the B2900A series includes also one and two channel models that can be easily cascaded and controlled remotely by the Keysight BenchVue software which allows running customized measurement scripts for automated large scale measurements. Finally, for very challenging electrochemical measurements including nanoscopic electrodes with high resistances and low currents (sub-fA) the B2980 series of battery operated Femto/Picoammeters and Electrometers can be used. They provide voltage measurement input resistances of more than 200 Tera-Ohm and current measurements down to 0.01 fA with significant accuracy. An integrated voltage source up to 1000 V allows thereby resistance measurements of up to 10 Peta-Ohm.

Materials and methods

SMU connections and settings: The four terminals of the SMU are modified to provide a three-terminal connection for a half cell electrochemical system as shown in Figure 2. High force and high sense are combined and connected to the working electrode (WE). Low sense is connected to the reference electrode (RE) which is a Ag/AgCl electrode, while the low force is connected to a platinum electrode as the counter electrode (CE). As shown in Figure 3, when the instrument is programmed to source voltage, internal sensing provides a feedback voltage that is measured and compared to the programmed voltage level. If the feedback voltage is less than the programmed voltage level, then the voltage source is increased until the feedback voltage equals the programmed voltage level. Remote sensing compensates for the voltage drop in the WE and the compensating unit ensures that the programmed voltage level is delivered to the WE. The Keysight B2912A SMU was used as shown in Figure 4 together with a liquid cell with three electrodes half-submerged in the solution, and a laptop which has the Quick I/V software installed.

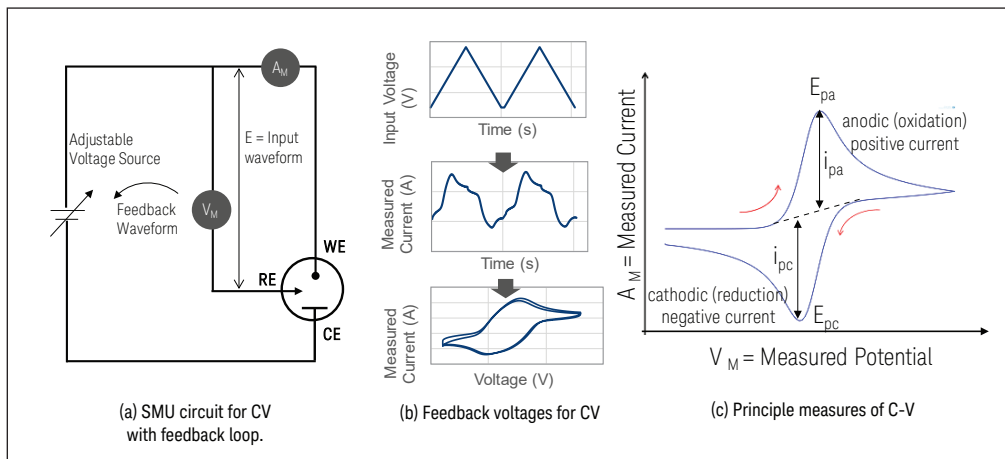


Figure 3. Principles of Cyclic Voltammetry. (a) SMU circuit for C-V measurement with feedback loop, (b) Input waveform feedback voltages for C-V measurement, (c) Principle measures of C-V including cathodic reduction and anodic oxidation.

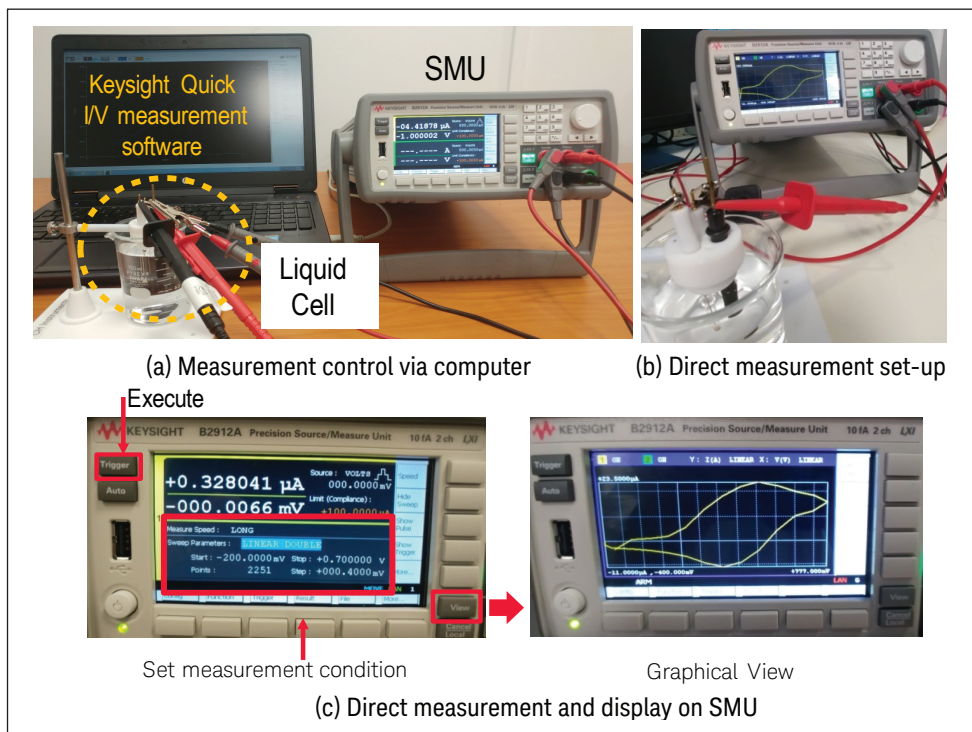


Figure 4. SMU connection and setup. Electrochemical measurement can be carried out in two modes. (a) Control using Keysight B2900A Quick I/V Measurement Software installed on the computer, or (b, c) Direct control and measurement on the SMU front panel could be carried out by pressing the "Trigger" button to execute the measurement. Results could be displayed on the SMU panel as single or graphical view by toggling the "view" button. Measurement data can be exported as raw data or graphical jpeg files using USB drives.

Materials and methods (continued)

Quick I/V software: Measurement is set-up and triggered via the Quick I/V software or by direct control and display on the SMU panel. As shown in Figure 5, the software allows the setting of the measurement function as either the “source & sampling” or “sweep” mode. For C-V the “sweep” mode is used in which the starting and ending potentials are entered. The sweeping profile is selected and the measurement delay and speed entered. The number of cycles of the C-V measurement are specified, followed by the scan rate, number of repeated cycles, measurement delay and step size.

Electrochemical system:

1. Li-ion: We have studied the C-V measurement of the Lithium intercalation in TiO_2 using a working electrode formed of 100 nm thick TiO_2 on a gold backing on glass, a Pt wire as counter electrode, and a Ag/AgCl reference electrode. The electrolyte is Lithium Hydroxide Monohydrate $\text{LiOH}\cdot\text{H}_2\text{O}$ at a concentration of 1mol/L.
2. Glucose sensor: The WE is gold coated with an osmium-complex redox mediated polymer [4, 5] containing the redox enzyme glucose oxidase (GOx). The fabrication and exact composition of the redox mediated polymer could be found in References. 4 and 5. Upon contact with the WE, glucose undergoes a catalyzed chemical reaction in the presence of this enzyme and electrons are donated in sequence from glucose molecules to the WE and measured by the SMU as current. The current is proportional to the concentration of glucose in the solution.

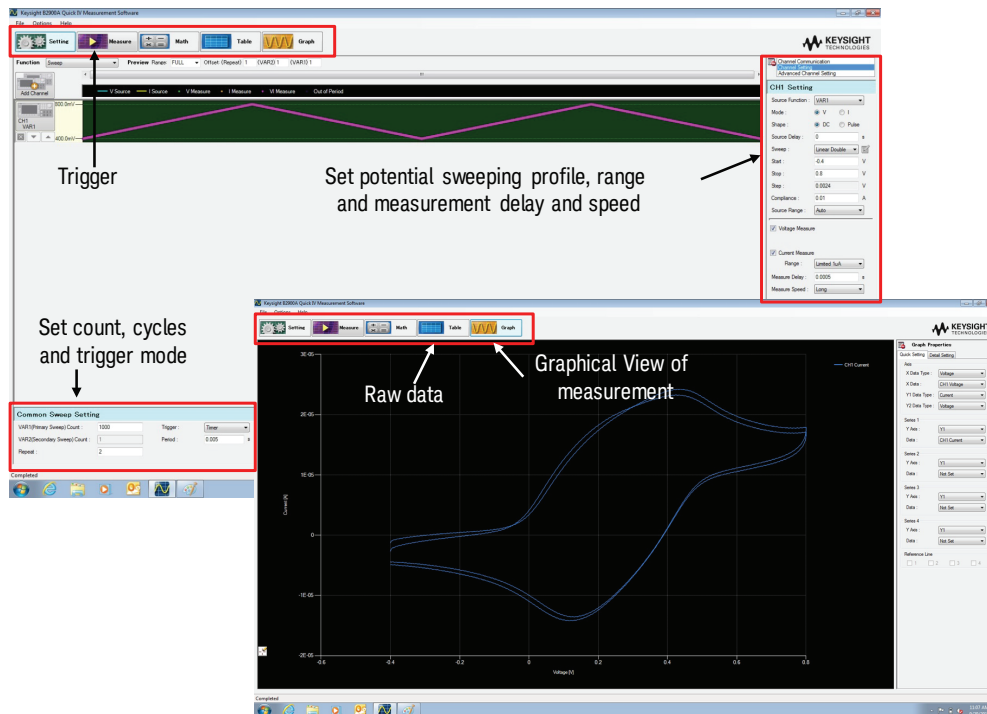


Figure 5. Quick I/V software for C-V curves. Easy and quick measurement on PC using Keysight B2900A Quick I/V Measurement Software. Software interface is user friendly in setting the measurement parameters and results could be displayed either as raw tabulated data or as graphical plots.

Results and discussion

To use the B2900A SMU for electrochemical measurements the four quadrant source and measurement capabilities of the SMU need to be properly connected to the three terminal connections of the electrochemical half-cell (please see Figure 2). The high sense and high force are connected to the WE, while the CE is connected to low force and the RE to the low sense. In such configuration, the SMU applies a voltage source for the potential scan between the WE and CE. The potential between the RE and WE is measured while the overall applied voltage by the SMU is adjusted to maintain the desired potential at the WE with respect to the RE. During this process, any resulting current flowing to or from the WE is being measured with the SMU resulting in the cyclic voltammogram (C-V) curve (please see Figure 3). Figure 6b shows a C-V curve of the redox metal-polymer mediator in glucose buffer solution measured with the B2912A. The potential was swept from -0.4 V to 0.8 V with a step size of 2.4 mV corresponding to 500 points. The sweep time was set to 2.5 seconds which corresponds to 5 milliseconds per point. In order to allow the set potential to stabilize before the measurement of the current the parameter “Measure Delay” was set to 500 microseconds. The parameter “Measure Speed”, which affects the integration time and therefore the noise level of each measurement, was set to “LONG”. The step size was adjusted by setting the number of counts to 500 over the potential range. The potential was first scanned starting from -0.4 V to 0.8 V and in the reverse direction from 0.8 V to -0.4 V. The voltammogram was measured over two complete cycles.

In this specific electrochemical glucose system, GOx enzymes immobilized on the surface of the electrode catalyzed both surface-limited oxidation and reduction of the multi-valent osmium metal ion complex (please see Figure 6c). When the enzyme-immobilized electrode was immersed in the glucose (ie. the analyte) solution, glucose molecules donated electrons to GOx to convert GOx to the reduced form. The reduced form of the GOx subsequently passed the electrons to the osmium complex as the mediator to convert it from Os^{3+} to Os^{2+} . During the forward scan (positive-going potential), the peak at ~ 0.4 V corresponds to the oxidation reaction of Os^{2+} to Os^{3+} in which the peak current, termed as the anodic current, was picked up by the SMU when the lost electron was passed to the electrode. In the reverse scan, an

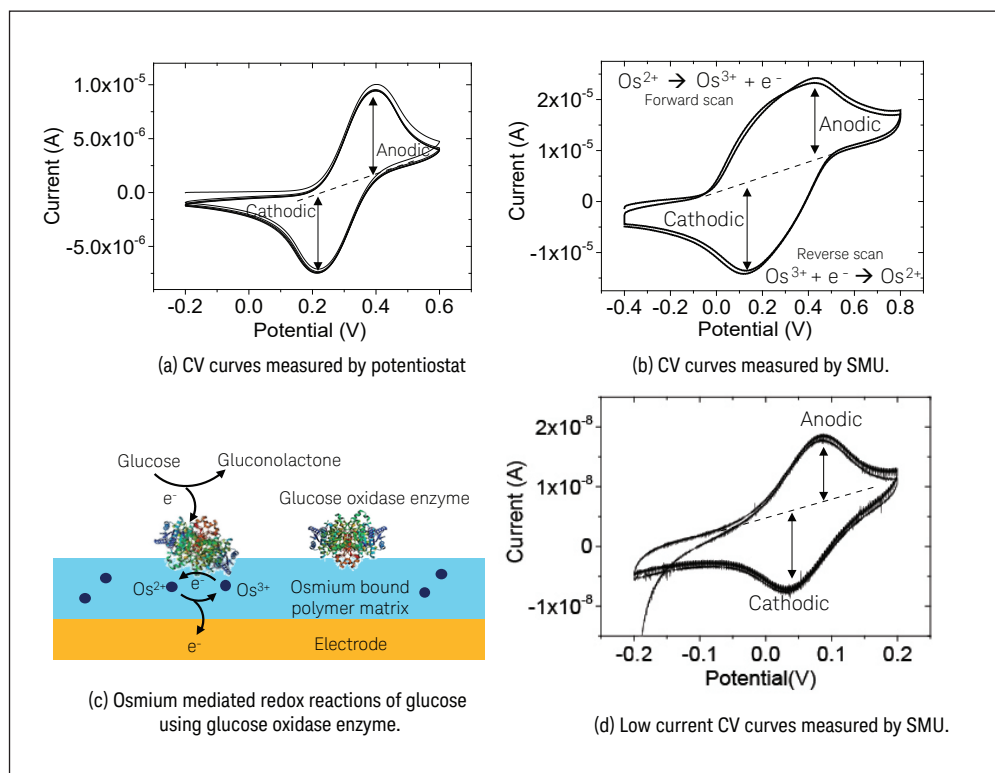


Figure 6. C-V results for specific glucose-redox reaction. Keysight SMU has been used to measure C-V curves of a redox polymer mediated glucose solution using glucose oxidase (GOx) enzyme. (a) C-V curves measured by potentiostat (CHI instruments), (b) C-V curves measured by SMU of electrode with higher surface area hence higher current, (c) Schematics of Osmium-mediated enzymatic glucose-redox reaction. (d) Low current C-V curves measured with another electrode of lower surface area hence lower current.

Results and discussion (continued)

opposite peak at ~ 0.2 V corresponds to the reduction of Os^{3+} to Os^{2+} of which the peak current is termed as the cathodic current. In the ideal case of a surface-limited redox reaction, these two peaks should occur at the same potential but in opposite sides of the current, as also observed in this work. The slight shift of the potential of the two current peaks is observed in many practical situations due to non-ideal conditions such as capacitive current and limited time-constant of the redox reaction. From the C-V curve typically the concentration of the analyte and the kinetics of the redox reaction can be observed [5]. The reduction and oxidation peaks won't occur until the potential is sufficiently large to reduce and oxidize the analyte, respectively. The corresponding potentials are depending on the concentrations based on the Nernst equation. The currents depend on the kinetic rate at which the analyte can diffuse to the surface of the electrode according to Fick's law.

Another common measurement in electrochemistry is chrono-amperometry where the electrolytic current is measured at the WE with respect to time while keeping the potential fixed at the WE (please see Figure 7). While in C-V information is received on the specific type of electro-chemical reaction and corresponding potentials and currents, chrono-amperometry results in quantitative electrochemical process kinetic data. Hence chrono-amperometry is usually carried out as a complementary measurement to C-V. Figure 7 shows the chrono-amperometry measurement of current over time generated by the glucose redox mediator reactions at a fixed potential of 0.5 V, compared between potentiostat-based (please see Figure 7c) and SMU-based (please see Figure 7d) electrochemical measurement. The current of the redox reaction drops substantially within the first few seconds in which the current is based on a large non-faradaic component due to charging of the double-layer capacitance at the electrode surface. The non-faradaic current decays exponentially with time constant RC, where R is an uncompensated resistance and C is the double layer capacitance [4].

Finally, we show the application of the SMU to study the Li-ion intercalation in TiO_2 electrode in aqueous solution (please see Figure 8). TiO_2 has an open crystal structure and the Ti^{4+} ions have a variable electronic structure. As a result, TiO_2 can accept electrons from different ions and provide empty sites for intercalation such as Li^+ , H^+ , and Na^+ .

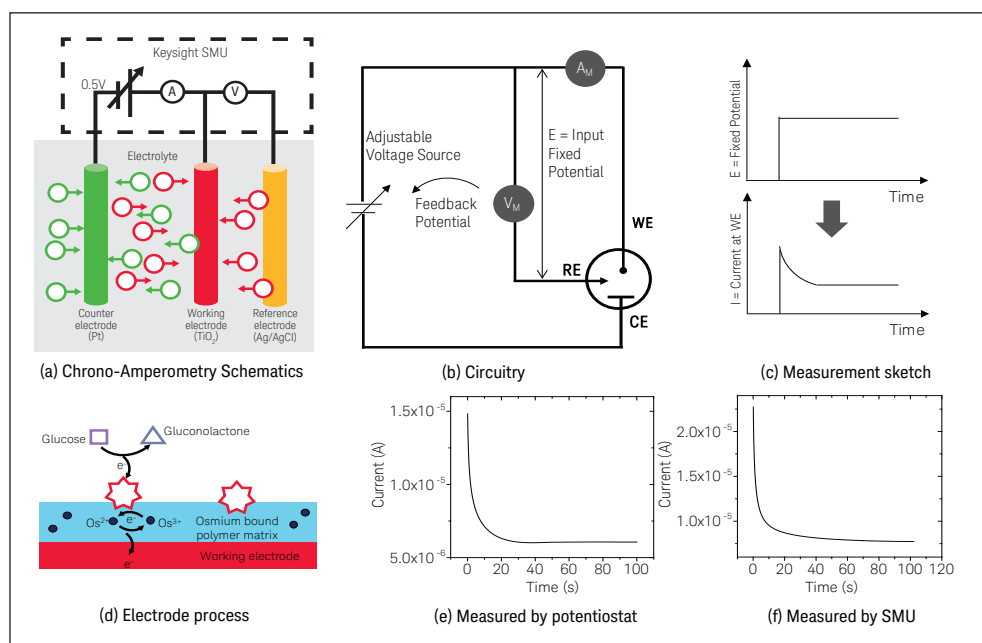
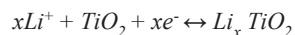


Figure 7. Chrono-amperometry (current vs time). (a) Current-time set-up schematics and (b) circuit measurement (c) set at a fixed potential of 0.5V. (d) The measurement was carried out on a modified working electrode with polymer mediated glucose solution using glucose oxidase (GOx) enzyme. (e) Current-time measurements by using (c) potentiostat (CHI instruments) and (d) Keysight SMU.

Results and discussion (continued)

To maintain charge neutrality, electrons will accompany cations such as Li^+ -ions into the TiO_2 lattice (please see sketch in Figure 1). Lithium intercalation into and de-intercalation from TiO_2 can be expressed as the following ionic reaction while the reversibility of this reaction is related to its cycling performance:



where x is the coefficient for Lithium intercalation. The value of x is related to the morphology, microstructure, and surface defects of the TiO_2 material. During the Lithium intercalation process, the TiO_2 is transformed from cubic to orthogonal Li_xTiO_2 . We have studied the C-V curves of the Lithium intercalation in TiO_2 with the SMU using a 3 electrode system with TiO_2 the working electrode (Figure 8a; please see Materials & Methods for more details). As shown in the C-V curve in Figure 8b, there is a redox couple during scan comprising of a cathodic peak with negative current at about -0.02 V in the reduction process and an anodic peak with positive current at 0.38 V in the oxidation process. The peaks can be attributed to the reversible insertion at the cathodic peak (intercalation; Li^+ ions are reduced and inserted into the TiO_2) and de-insertion at the anodic peak (de-intercalation; metallic Li from the TiO_2 is oxidized to Li^+ and moves into the electrolyte). The peak current is typically a function of the scan rate (i.e. how fast the voltage is swept) and depends on a surface charging mechanism [6].

The case study here presents a unique combination of Lithium titanium oxide (LiTiO_2) electrode materials combined with an aqueous LiOH electrolyte in contrast to conventional organic and polymer-based electrodes. We have chosen LiTiO_2 since TiO_2 -based materials have been one of the most widely studied battery materials due to its non-toxicity and high chemical stability. It has also been earlier demonstrated that lithium intercalation can be electrochemically induced to occur reversibly on TiO_2 using a simple aqueous lithium alkali solution. The use of an aqueous electrolyte in contrast to organic and polymer electrolytes used in conventional lithium batteries has its unique advantages. Aqueous electrolytes could enable the batteries to be applied at a higher cycling rate with lower electrolyte resistance since they have higher conductivity as compared to their organic and polymer counterparts. With the lower electrolyte impedance of the aqueous electrolyte, the lithium batteries could have higher discharge rates and lower voltage drops. Such battery materials of high power and high capacity will have potential applications for electric vehicles and grid storage [6].

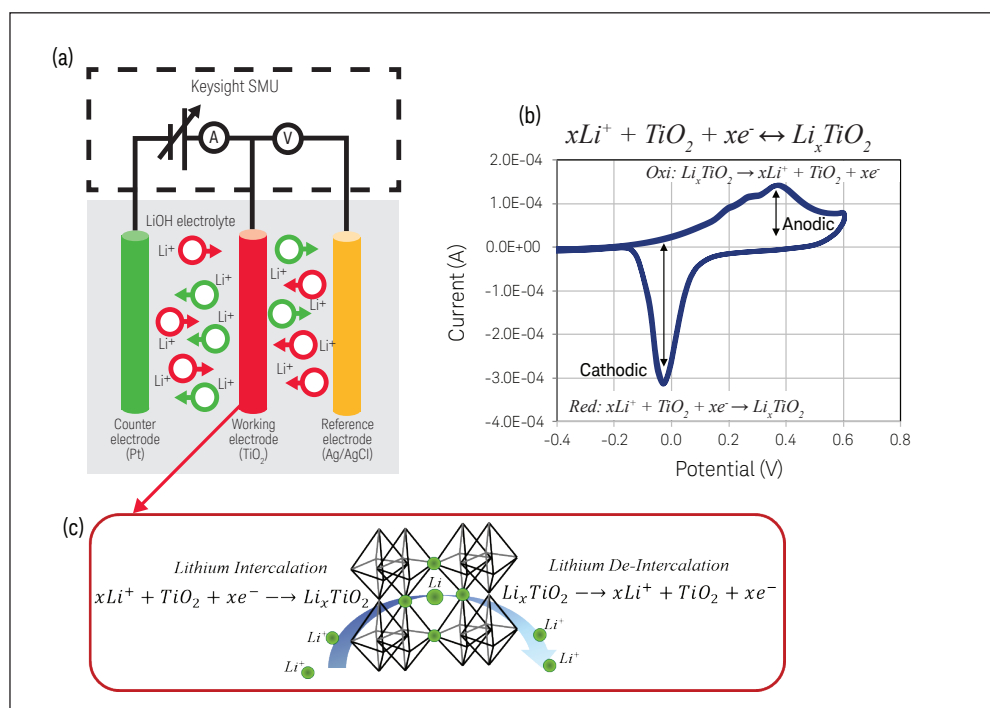


Figure 8. Li-ion intercalation in TiO_2 electrode. (a) Schematic of the 3-electrodes and LiOH electrolyte used for the experiments. (b) C-V measurements showing the oxidation and reduction peak of the Li-ion cell. (c) Sketch showing the intercalation and de-intercalation of Li in TiO_2

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The B2900 family contains products that perform both precision sourcing and precision measurement.

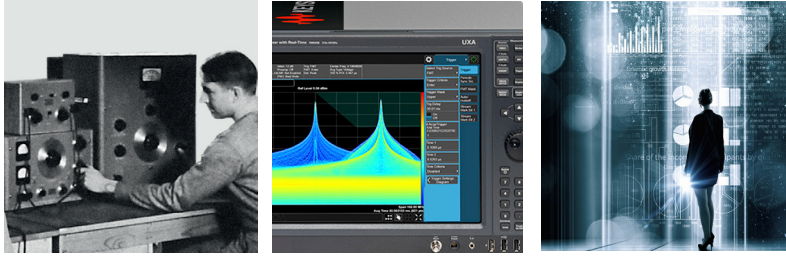
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