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The Poor Academic’s DC-Offset for Reversing Polarity in Electrochemical Cells: Application to Redox Flow Cells

To cite this article: Kiana Amini et al 2022 J. Electrochem. Soc. 169 090527

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We provide a simple and inexpensive manual DC-offset method for extending the accepted voltage range of a battery cycler to negative voltages, without interfering with the actual operation of the electrochemical cell under the test or exceeding the voltage specs of the battery cycler instrument. We describe the working principles of the method and validate the proposed setup by operating short-term and long-term redox flow battery cycling using compositionally symmetric cell, with open-circuit voltage of zero, and full cell configurations. The method can be used to extend the capability of battery cycler instrumentation to operate any electrochemical cell that requires the polarity to be reversed during operation. Applications include cycling of other symmetric cells (e.g., Li-ion cells), implementation of polarity reversal steps for rejuvenation of electroactive species or rebalancing electrochemical cells, and alternating polarity for electrochemical synthesis.

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Supplementary material for this article is available online.
is expensive and, depending on the number of channels, can cost many thousands of dollars. Here, we report a simple and significantly less expensive method for extending the range of the voltage operation on a voltage source. In this method, we manually add a DC-offset to the signal sensed by the instrument. This tricks the system into imposing on the battery the user’s desired voltage, which may be outside of the battery cycler’s voltage range capabilities, while permitting the battery cycler itself to operate within its voltage range. This manual DC-offset can be achieved by a constant voltage source that is incorporated externally from the battery cycler. Any battery chemistry with a relatively flat cell voltage with respect to its state of charge, and a low self-discharge rate, can be used as this constant voltage source. In the present work, we use an inexpensive, commercially available nickel-cadmium (NiCd) battery as a constant voltage source. This battery is chosen because it has a long shelf-life and a cell voltage that barely varies with its state of charge until the majority of its capacity is discharged. As a result, even in the case of self-discharge at open circuit, the OCV of a NiCd battery does not change significantly. We describe the working principles of this system and validate the setup by conducting short-term and long-term operations with redox flow batteries in both full cell and symmetric cell configurations. This manual DC-offset method allows research labs to extend the capability of their battery cycler instrumentation to operate symmetric bench-scale batteries and employ battery protocols that require negative voltage values. While our focus in the present work is on flow batteries, the manual DC-offset method is not restricted to flow cells and can be employed for other cells or protocols requiring negative voltage ranges (e.g., Li-ion symmetric cell operation)

**Experimental**

**Chemicals.**—All solutions were prepared using analytical grade reagents and deionized water. Reagents were used potassium ferrocyanide trihydrate, potassium ferricyanide, potassium hydroxide (all purchased from Sigma Aldrich) and 2,6-DPPEAQ (((9,10-dioxo-9,10-dihydroanthracene-2,6-diyl))bis(oxy))bis(propane-3,1-diyl))bis(phosphonic acid) purchased from TCI Chemicals.

**Flow battery experiments.**—Flow battery experiments were conducted with cell components from Fuel Cell Technologies Inc. (Albuquerque, NM), or in-house cells with PVC end plates. Interdigitated flow fields made up of pyroscos POCO graphite flow plates were used in each half cell of the battery along with 3 layers of carbon paper (SGL 39AA) per side. Long-term ferro-/ferricyanide symmetric cells were used one sheet of woven carbon cloth (AVCarb NCBA 1698) per side. The ferro-/ferricyanide performance in a symmetric cell at pH 14 and its capacity fade due to self-discharge has been extensively studied in a previous work and thus is a well-characterized system for the validation of our setup. The working principle of a battery cycler is described in a simplification of a battery cycler. The setup is capable of maintaining a known potential difference between the working and counter electrodes and records the resulting flow of current. To achieve this, an electronic component called an operational amplifier (op-amp) is employed. An op-amp (Fig. S1a (available online at stacks.iop.org/JES/169/090527/mmmedia)) is a three-terminal electronic component with a DC power supply that is capable of amplifying the voltage difference of the input terminals. The two inlet terminals are connected across an extremely large impedance, so that negligible current can pass between the inlets, and hence the input voltage signal is fed to the amplifier with negligible ohmic drop. The output terminal is connected through a very low impedance and hence current can pass through the output terminal. The output voltage is the result of the amplification of the difference between the two input voltage signals. An op-amp can be designed with a feedback loop, in which the output voltage (Fig. S1b) or a portion of the output voltage (Fig. S1c) is fed back to the inlet terminal. This feedback connection between the output of the op-amp and the input terminal forces the difference between the input voltage terminals to be close to zero, meaning that the output voltage of the op-amp adjusts itself to force the two inlet voltages to be nearly identical.

During battery operation, the user sets the desired potential difference (\(V_{\text{desired}}\)), with reference to the ground. Because \(V_{\text{desired}}\) is connected to the inlet of the op-amp, the voltage drop due to ohmic resistance is extremely negligible and hence the desired voltage is fed to the op-amp with high accuracy. The output current
of the op-amp passes between the counter (CE) and working (WE) electrodes of the battery. The counter sense (CE Sense) and the working sense (WE Sense) of the circuit are connected to an electrometer. Note that an electrometer measures the voltage difference between the input signals without drawing current from the circuit due to the extremely large impedance of the electrometer. Thus, current can pass only between the counter and working electrodes and not the sense electrodes. In Figs. 1a and 1b, the paths where negligible current can pass due to extremely large impedance are shown in green, whereas the path of current with low impedance is shown in orange. The flow of current between the counter and working electrodes results in a potential difference between the two electrodes, which is measured and output by the electrometer. The output voltage of the electrometer is connected to the inlet of the op-amp, creating a feedback loop. The op-amp adjusts Vout until VFeedback is equal to the user’s desired voltage (VDesired). Hence, the desired voltage is accurately applied between the counter and working electrodes, and the resulting current is measured by passing it through a resistor (R) connected to the working electrode.

The voltage set by the user must be within the voltage range of the circuit. In order to set negative voltages outside of the cycler’s voltage range, we simply include one or more NiCd batteries (depending on the amount of offset needed) in the path of the working sense leads. Here, we have shown the circuit for the case where a single NiCd battery is incorporated in the working sense path. Because the NiCd is incorporated into the WE Sense path, no current will pass through the NiCd battery itself and thus it should remain at its OCV. The WE Sense and CE Sense leads measure the difference between counter and working potentials, identical to the case of Fig. 1a. However, the electrometer will measure the voltage between the two sense leads which now includes the OCV of the NiCd battery. Thus, the feedback voltage will have an additional term corresponding to the OCV of the NiCd battery. To ensure that the difference between the inlet potentials entering the operational amplifier is identical to the case of Fig. 1a with no DC-offset, the value of the OCV of the NiCd must be added to our desired set voltage. With this method, we can successfully apply a desired voltage (VDesired) that is outside of the voltage range of the battery cycler, without interfering with the actual operation of the battery being tested or damaging the battery cycler equipment.

In Fig. 1c we show the implementation of the manual DC-offset in practice. On the negative side of the RFB, the CE and CE Sense leads of the battery cycler are connected to the negative terminals of the flow battery, as is standard practice. On the positive side of the RFB, the WE lead of the battery cycler is connected to the positive terminal of the flow battery, similar to the normal operation. However, the WE Sense of the battery cycler is now connected to the positive terminal of a NiCd battery instead of directly connecting to the flow battery. A wire between the negative terminal of the NiCd and positive terminal of the RFB now connects the two batteries in series, as shown in the circuit diagram of Fig. 1b. This configuration allows the user to shift the voltage range of the battery cycler from its standard minimum of 0 V to a new minimum of approximately −1.27 V (negation of the typical OCV for NiCd cells used in this work). Clearly, further negative shifts are possible by using multiple NiCd batteries connected in series.

Half cell electrode potentials in symmetric and full cells with and without manual DC-offset.—For further investigation of the working principles of a manual DC-offset, we monitored the cell voltages as well as positive and negative electrode potentials of an RFB operated with and without a manual DC-offset. This was done for both a flow battery operated in the full cell configuration and the symmetric configuration, as is described below.

First, a full cell flow battery composed of 5 ml of 0.1 M DPPEAQ and 50 ml of 0.1 M ferrocyanide/0.04 M ferricyanide at pH 14 was tested. The battery was first operated normally without any manual DC-offset for a cycle. Battery cycling was done using a CCCV method. A current density of 40 mA cm⁻² was applied.
followed by constant voltages of 1.4 V and 0.6 V until the current dropped to 1 mA cm$^{-2}$. During the operation, the negative (DPPEAQ) and the positive (ferrocyanide/ferricyanide) electrode potentials were also monitored using the in situ reference electrodes described in the experimental section. Although 0.6 V–1.4 V is within the operational range of the voltage source, we added a manual DC-offset with a NiCd battery to understand the effect of the manual DC-offset method within the same device. The OCV of the incorporated NiCd battery was approximately 1.27 V. As described in the previous section, for correct operation, the OCV of the NiCd battery needs to be added to the user’s input voltage values. Hence, the applied voltage cut-off values were changed to 1.87 V and 2.67 V. With no other change, the battery was operated for one cycle. To show the possibility of achieving further voltage shifts, two NiCd batteries connected in series were also incorporated. The two NiCd batteries had OCV values of 1.27 V and 1.30 V, respectively, yielding a total of 2.57 V when connected in series. Hence, the voltage cut-off values were changed to 3.17 V and 3.97 V for the third cycle. The OCV of the NiCd batteries were also monitored during the cycles with DC-offset using a separate potentiostat channel.

The flow cell voltage, negative and positive electrode potentials, and the OCV of the NiCd batteries during operation with the above-described conditions are shown in Fig. 2. As can be seen, the overall cell voltage of the battery is shifted up by ~1.27 V and ~2.57 V when one and two NiCd batteries are incorporated in the battery setup, respectively. Nevertheless, the addition of these NiCd batteries has induced virtually no voltage shift in the negative and positive electrode potentials (Figs. 2c and 2d). As discussed previously in relation to Fig. 1b, the addition of a NiCd battery (or multiple NiCd batteries) should not affect the actual potential changes in the positive and negative electrodes. The function of the NiCd batteries is to merely add a constant voltage value to the sensed voltage difference to trick the cycler into accepting the applied/measured voltage. Additionally, because the NiCd batteries are incorporated in the path of the WESense lead, no current is passing through them and therefore they always remain at their open circuit voltage.

Figure 2b shows the monitored OCV of a single NiCd battery using a separate potentiostat channel. As can be seen, there were no changes in their voltage during the CCCV operation of the battery. Next, a flow battery in the symmetric configuration was constructed. It was composed of 0.1 M ferro-/0.1 M ferricyanide in 1 M KOH, with a 4 ml CLS and a 50 ml NCLS. The battery was operated using a potentiostat capable of applying negative voltage
values (±15 V) to be able to directly investigate the effect of the manual DC-offset in one device. The symmetric cell was first cycled with constant charging and discharging voltages of ±0.2 V until the current drops to 1 mA cm\(^{-2}\) (constant voltage method). Next, a single NiCd battery with an OCV of ∼1.27 V was incorporated in the battery setup. Hence, the operational condition in the second cycle was changed to +1.07 V and +1.47 V. Similar to the full cell configuration, the addition of the manual DC-offset affected only the overall measured cell voltage of the symmetric battery (Fig. 3a), with no changes induced in the negative and positive electrode potentials (Figs. 3c and 3d). Additionally, the NiCd battery always remains at its OCV during the operation as shown in Fig. 3b. As can be seen, to run a symmetric cell, we need a voltage source that is capable of applying both negative and positive voltages (±0.2 V), however with this simple manual DC-offset, we are able to run the symmetric cell using a voltage source (such as a battery cycler) that is capable of applying only positive voltage values (+1.07 V and +1.47 V) without any interference to the flow battery operation.

**Long-term operation of redox flow batteries with manual DC-Offset.**—To investigate the possibility of employing the manual DC-offset method during prolonged operation of redox flow batteries, long-term cycling of a flow battery in full cell configuration and symmetric cell configuration, with and without manual DC-offset, was conducted. First, a full cell composed of 5 ml 0.1 M DPPEAQ in the negolyte and 50 ml 0.1 M ferro-/0.04 M ferricyanide at pH 14 was constructed. The battery was operated for more than 4 d using the CCCV method. At each cycle a constant current of 40 mA cm\(^{-2}\) and voltage cut-off values of 0.6 V and 1.4 V, in the absence of a manual DC-offset, were applied until the current density dropped to 1 mA cm\(^{-2}\). After 4.5 d, the battery was stopped and a single NiCd battery (OCV ∼1.27 V) was incorporated in the setup in the manner described previously. The cut-off values were changed to 1.87 V and 2.67 V (Fig. S2), and the battery was operated for another ∼4.5 d. As shown in Fig. 4, the incorporation of the manual DC-offset has had no effect on the measured coulombic efficiency (∼100% in both cases) or the capacity fade rate of the battery (∼0.06%/day in both cases) over several days of operation, demonstrating that the incorporated NiCd has not affected the operation of the flow battery. We tentatively attribute the jump in discharge capacity upon adding the DC offset to the moving of the cell and reservoirs, which might have shaken loose a droplet of electrolyte clinging to the reservoir wall in the head space. When users do not have access to a cycler capable of applying negative voltages, a full cell battery, such as the one put together in the

![Figure 3](image-url)
present work, can be used for validation of their setup before using the setup for symmetric cell cycling or for an operation that requires application of negative voltages.

As a final demonstration of the DC-offset method, we employed the technique in the long-term operation of a symmetric cell RFB, in which negative voltages are required for cell cycling. A 0.1 M ferro-/0.1 M ferricyanide symmetric cell at pH 14 (5 ml CLS vs 10 ml NCLS) was cycled potentiostatically at ±0.2 V on a Novonix channel equipped with a DC-offset, as seen in Fig. 6. After approximately four days, cycling was paused, the Novonix DC-offset was replaced by a NiCd DC-offset (as described in previous sections) and cycling was continued. The OCV of the NiCd on its own was first measured to be ∼1.27 V, thus when connected in series with the symmetric RFB, charge/discharge cycling was performed at 1.07 V/1.47 V to mimic the desired ±0.2 V cycling protocol typically employed. We observed no change in the capacity fade trend upon switching to our manual NiCd DC-offset (Fig. 5a), demonstrating that the incorporated NiCd offset has not affected the operation of the flow battery.

As explained previously, the NiCd battery remains at its open-circuit potential at all times during the experiment. The stability of the OCV of the NiCd battery during the course of the experiment is essential for achieving an accurate offset. Hence, we monitored the change in the OCV of a NiCd battery over the course of two months by storing a NiCd battery in a glovebox and measuring its OCV periodically, as seen in Fig. 6a. During that time, the NiCd demonstrated an overall self-discharge rate of roughly 12 μV per day over the span of two months. However, OCV measurements at approximately day 21 and 42 show a significant departure from the self-discharge trend. As seen in Fig. 6b, the temperature within the glovebox typically oscillated between 20 and 22 °C, due to diurnal temperature swings within the lab. However, temperature spikes coinciding with the OCV measurement outliers were observed, due to elevated temperature cycling of RFBs being conducted in a separate
experiment within the same glovebox. The separate experiments provided unintended data regarding the effect of temperature on the NiCd OCV, which decreased by approximately 2 mV for a 4 °C increase in glovebox temperature. Therefore, it is clearly demonstrated that, if temperature excursions are minimized, NiCd batteries can be used as DC-offsets for multiple weeks before any adjustment of the applied voltage for cycling needs be made, if required to counteract the OCV change. Alternatively, for experiments expanded over many months, the NiCd battery could be replaced or Li-ion batteries with significantly lower self-discharge rates could be employed. No matter the chosen battery chemistry for use as DC-offset, the outlined method provides an extremely cost-effective alternative to cycler manufacturer protocols that require negative voltage values. The method is not restricted to flow batteries with and without the proposed manual voltage offset and by monitoring half cell potentials using in situ reference electrodes. The method is further validated by conducting long-term symmetric and full cell cycling experiments. The proposed manual DC-offset method is an inexpensive technique for extending the capability of the battery cycler instrumentation to operate symmetric flow batteries and employ battery protocols that require negative voltage values. The method is not restricted to flow cells and can be employed for extending the voltage range of a cycler for operation of other electrochemical cells.

Conclusions

In the present work, we introduced a simple and inexpensive method to manually extend the voltage range of a battery cycler. In this method, a nickel-cadmium battery is incorporated in the path of the battery cycler’s voltage sense, tricking the instrument into accepting the user’s desired applied voltage, while permitting the battery cycler itself to operate within its voltage range. The working principles of this proposed manual DC-offset are described and validated by operation of flow batteries with and without the proposed manual voltage offset and by monitoring half cell potentials using in situ reference electrodes. The method is further validated by conducting long-term symmetric and full cell cycling experiments. The proposed manual DC-offset method is an inexpensive technique for extending the capability of the battery cycler instrumentation to operate symmetric flow batteries and employ battery protocols that require negative voltage values. The method is not restricted to flow cells and can be employed for extending the voltage range of a cycler for operation of other electrochemical cells.

Acknowledgments

K.A. was supported in part by U.S. DOE award DE-AC05–76RL01830 through PNNL subcontract 535264 and in part through the Natural Sciences and Engineering Research Council of Canada (NSERC) Postdoctoral Fellowship (PDF) program [application number PDF – 557232–2021]. EMF was supported by the National Science Foundation through grant CBET-1914543.

References