MANAGEMENT AND CONTROL OF ALTERNATIVE ENERGY SYSTEMS

FIELD

[0001] Aspects of the present disclosure relate generally to solid oxide fuel cell (SOFC) installations. In particular, one or more aspects of the disclosure relate to apparatuses and methods for operation and use of SOFCs and systems that may comprise SOFCs.

BACKGROUND

[0002] As the world moves away from inefficient energy sources, the need for more efficient, low emission energy sources grows ever more important. Fuel cells are energy conversion devices that offer a low emission solution. Because of their ability to operate using a variety of fuels (e.g., natural gas, biogas, ammonia, and hydrogen) solid oxide fuel cells (SOFCs) may bridge the gap between conventional and alternative technologies and may be integrated into a flexible and efficient energy systems. Moreover, some types of SOFCs (e.g., solid oxide reversible fuel cells) may allow for reversible operation and the reduction of oxidized fuel back to its original state.

[0003] Most solid oxide fuel cells operate at high temperatures (e.g., 600 – 1000 °C). Changes to the flow rate and fuel composition, even in the name of efficiency, may result in reduced fuel cell voltages and/or lead to irreversible fuel cell degradation. Load changes, moreover, may cause rapid temperatures changes in high-temperature fuel cells that may result in harmful thermomechanical or electrochemical stress and cause a significant reduction in performance and/or fuel cell lifetime. One major degradation mechanism in an SOFC is the potential decrease in the amount and/or reactivity of active sites on an electrode (e.g., triple phase boundaries). There are many factors (e.g., electric system effects such as ripple currents) that may contribute to the decrease in the amount and/or reactivity of active sites, and currently, there is no known method to quantitatively measure and monitor these changes operando. Having this capability, however, would be significant as it may allow real-time monitoring of a cell's state while having the ability to control or adjust system operation conditions (e.g., power output). Being able to adjust system operation conditions while monitoring the amount and/or reactivity of active sites may will enable to avoid irreversible materials' degradation and allow any changes to be made in a controlled manner. Additionally, such monitoring abilities could provide other benefits, including tracking the system's overall health status and sending a warning message when a certain threshold has been reached.

BRIEF SUMMARY

[0004] Aspects of the disclosure provide technical solutions that overcome one or more of the technical problems described above and/or other technical challenges. One or more aspects of this disclosure relate to detecting subtle changes in an SOFC's performance during operation, a crucial part of a larger control system to manage the power output and health of an energy system.

[0005] For instance, one or more aspects of the disclosure relate to using Fourier transform alternating current voltammetry (FTacV) alone or FTacV in conjunction with other techniques such as electrochemical impedance spectroscopy (EIS), and/or current-voltage (I-V) measurements to gain a comprehensive and precise understanding of a cells' state and condition during operation. By applying these analytical techniques, active sites in SOFCs may be identified, and changes of the active site followed; this allows degradation mechanisms, that may not normally be easily quantifiable by conventional methods, to be measured and tracked. A method to characterize and monitor the performance of electrode material in an in operando SOFC may serve as an input for feedback and/or control of power modulations.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] Some features of the present disclosure are illustrated by way of example, and not by way of limitation, in the accompanying drawings. In the drawings, like numerals reference like elements and in which:

[0007] FIGS. 1A and 1B show examples of a solid oxide fuel cell (SOFC) in accordance with one or more aspects of the present disclosure as described herein.

[0008] FIG. 1C shows an example arrangement of fuel cells.

[0009] FIG. 2 shows an example of a dual y-axis plot of cell voltage (V) and power density (mW/cm^2) vs current density (mA/cm^2).

[0010] FIGS. 3A – 3C show example diagrams of a region of a SOFC showing triple phase boundaries.

[0011] FIG. 4A shows an example direct current (DC) cyclic potential used in cycle voltammetry (CV).

[0012] FIG. 4B shows an example of a cyclic voltammogram plot used for CV.

[0013] FIGS. 5A through 5C show examples of alternating currents applied to DC voltage curves used for alternating current voltammetry (ACV).

[0014] FIG. 6A shows an example three cell electrochemical sensing device.

[0015] FIG. 6B shows an example perturbation and resulting sensing and signal processing diagram.

[0016] FIG. 7A shows an example plot of time vs power of a non-monitored system experiencing a step-wise modulation.

[0017] FIG. 7B shows an example plot of time vs power of a carefully modulated monitored system.

[0018] FIG. 8 shows an example flow chart for characterizing a fuel cell using different techniques.

[0019] FIGS. 9A through 9D shows examples of AC-voltammograms.

[0020] FIG. 10A shows example accelerated stress test cycles of an SOFC.

[0021] FIG. 10B shows example current density vs time measurements of accelerated stress test cycles of an SOFC.

[0022] FIG. 11A shows an example diagram for phasor determination.

[0023] FIG. 11B shows an example plot of phasor values.

[0024] FIGS. 12A and 12B show example plots of 5th order harmonics using Fourier Transform alternating current voltammetry (FTacV).

[0025] FIG. 13A shows an example plot of a harmonic peak height and oxidized Ni moles from CV vs the number of stress test cycles.

[0026] FIG. 13B shows an example plot of a harmonic peak height and oxidized Ni moles from CV vs the number of stress test cycles.

[0027] FIG. 13C shows an example plot of a harmonic peak height and current density vs the number of stress test cycles.

[0028] FIG. 14 shows an example of electric power distribution system.

DETAILED DESCRIPTION

[0029] In the following description of various illustrative embodiments, reference is made to the accompanying drawings, which form a part hereof, and in which is shown, by way of illustration, various embodiments in which aspects of the disclosure may be practiced. It is to be understood that other embodiments may be utilized, and structural and functional modifications may be made, without departing from the scope of the present disclosure.

[0030] FIGS. 1A and 1B show examples of a fuel cell. Specifically, FIGS. 1A and 1B show examples of a solid oxide fuel cell (SOFC) along with ionic and electronic charge flow in accordance with one or more aspects of the present disclosure as described herein.

[0031] An SOFC is comprised of an anode, a cathode, and an electrolyte. The anode is the electrode of an electrical device through which electrons flow to the cathode through an external circuit. The cathode is the electrode of an electrical device that electrons flow into. The electrolyte is a solid phase ionic conductor. The electrolyte in an SOFC may be a dense oxygen ion-conducting material (e.g., yttria stabilized ZrO_2 (YSZ), doped ceria CeO_2, strontium and/or magnesium-doped lanthanum gallate $La_{1-x}Sr_xGa_{1-y}Mg_yO_3$, etc.).

[0032] In FIGS. 1A and 1B fuel (e.g., methane CH_4) may enter a fuel cell 105 at the anode side. Prior to entering the fuel cell, the fuel may go through a steam-reforming process. Methane may be mixed with hot steam (H_2O), for example, in a steam-reforming process. Chemical reactions caused by a steam-reforming process may cause the formation of hydrogen (H_2), carbon monoxide (CO), and/or carbon dioxide (CO_2), producing a mixture of fuel (e.g., CH_4), H_2, CO, and other gases including CO_2, and H_2O. As the fuel enters the fuel cell 105 at the anode, air or a controlled fluid mixture enters the fuel cell 110 at the cathode side.

[0033] Electrochemical reactions may occur in a fuel cell (e.g., an SOFC). FIG. 1B shows example electrochemical reactions that may occur in an SOFC to generate an electrical current. A dioxygen (O_2) molecule may combine with free electrons 115, at triple phase boundaries (TBP), throughout the volume of the cathode forming two oxide ions (O^{2-}), for example, as the atmosphere diffuses through the cathode. The O^{2-} ions (e.g., negative charge) may pass through the SOFC electrolyte 120. At the anode, an O^{2-} ion may combine with a dihydrogen (H_2) molecule or a carbon monoxide (CO) molecule, for example, forming water (H_2O) or carbon dioxide (CO_2), respectively. In the process of forming water or carbon dioxide at the anode 125, the negative charge is transferred to the anode creating a lower potential and driving the electric current 130.

[0034] Electrochemistry may explain charge (e.g., electron and/or ionic) movement in an oxidation and/or reduction reaction, for example, by using equations based on resistance, capacitance, and/or impedance. FIGS. 1A and 1B also show examples of charge movement. Charge movement may comprise electron transfer (e.g., the transfer of an electron from one atom or molecule to another). Charge movement may comprise, for example, conduction electrons moving in a conduction band (e.g., of an electrode and/or a current carrying wire 130). Charge movement may comprise the transfer of charge at and/or across an interface 115, 120, and/or 125 (e.g., between an electrode and a solution and/or an electrolyte). Charge transfer may involve an oxidation, where electrons are lost 125, and/or a reduction, where electrons are gained 115, reaction as described below:

$$O + ne^- \leftrightarrow R, \tag{1}$$

where n is the number of electrons transferred, and O and R are the oxidized and reduced forms, respectively, of the electroactive material in the system. Charge transfer may also involve ionic charge motion involving vacancy transport and/or interstitial ion transport.

[0035] Methane reactions may occur in an SOFC system (including e.g., a steam-reformation process) and/or an SOFC anode, for example, if methane is used as a fuel. Methane may react, for example, via catalytic thermal reactions and/or electrochemical reactions. Some catalytic thermal reactions (e.g., that may occur during a steam-reforming process) may comprise, for example:

$$CH_4 + H_2O \rightarrow CO + 3H_2; \tag{2}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2; \tag{3}$$

$$CH_4 \rightarrow C + 2H_2; \tag{4}$$

$$C + H_2O \rightarrow CO + H_2; \text{ and} \tag{5}$$

$$2CO \rightarrow CO_2 + C. \tag{6}$$

Some electrochemical oxidation reactions may comprise, for example:

$$CH_4 + O^{2-} \rightarrow CO + 2H_2; \tag{7}$$

$$CO + O^{2-} \rightarrow CO_2; \text{ and} \tag{8}$$

$$H_2 + O^{2-} \rightarrow H_2O. \tag{9}$$

[0036] FIG. 1B shows an example of an SOFC. Specifically, FIG. 1B shows an example of an SOFC along with electrochemical reactions that may drive production of an electrical current. In a cathode (e.g., air electrode) of an SOFC, for example, an electrochemical reaction may involve the capture of electrons by a diatomic oxygen (e.g., O2) molecule. Diatomic oxygen, a gas at standard temperature and pressure (STP) and occurring naturally in air, may capture two electrons in an electrochemical oxygen reduction reaction (ORR), for example:

$$2O_2 + 4e^- \rightarrow O^{2-}. \quad (10)$$

[0037] Oxygen ions formed by ORR at a cathode may be incorporated into the electrolyte, through oxygen vacancies. The ionic oxygen O^{2-} migrates through the electrolyte of an SOFC to the anode (e.g., fuel electrode) of the SOFC. Oxygen-ion conduction may occur through the mechanism of oxygen vacancies or interstitial oxygen ions based on the crystal structure. Charge (e.g., electrons) may migrate through an electrolyte through a process of electron transfer, for example, from oxygen site to oxygen site of the electrolyte from the high electric potential of the cathode toward the low electric potential of the anode.

[0038] In an anode (e.g., fuel electrode) of an SOFC, for example, an electrochemical reaction may involve diatomic hydrogen (e.g., H_2), a hydrocarbon fuel (e.g., methane (CH_4)), and/or carbon monoxide (e.g., CO), for example, chemically combining with ionic oxygen. Potential electrochemical reactions occurring in an anode may comprise one or more of:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-; \quad (11)$$

$$CH_4 + 3O^{2-} \rightarrow CO + 2H_2O + 6e^-; \quad (12)$$

$$CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-; \quad (13)$$

$$C + O^{2-} \rightarrow CO + 2e^-; \quad (14)$$

$$C + 2O^{2-} \rightarrow CO\ 2 + 4e^-. \quad (15)$$

[0039] Exhaust of a fuel cell (e.g., an SOFC) may comprise fuel exhaust 140 and air exhaust 135. The fuel exhaust 140 of an SOFC (e.g., using methane as fuel) may comprise the same constituents of the incoming fuel but with different ratios including higher ratios of water (H_20) and carbon dioxide (CO_2). Like the fuel exhaust 140 of the SOFC, the air exhaust 135 of an SOFC may comprise the same initial constituents but in different ratios including a decrease in the ratio of oxygen (e.g., diatomic oxygen).

[0040] Electrolysis is the process of using electricity to produce hydrogen and oxygen from water. A reversible SOFC operating in electrolysis mode (e.g., a solid oxide electrolyzer (SOE)) may increase the H_2 concentration, while decreasing the H_2O concentration, of the fuel through the process of electrolysis, for example, by using the voltage difference to run the electrochemical reaction in reverse. In this configuration water at the fuel electrode is split into its constituent parts

$$H_2O + 2e^- \rightarrow H_2 + O^{2-}, \tag{16}$$

and at the air electrode, two oxygen ions gain two electrons each and form diatomic oxygen

$$2O^{2-} \rightarrow O_2 + 4e^-. \tag{17}$$

[0041] SOFC systems may provide electricity to a building (e.g., a stadium, a retail center, a commercial building, a house, etc.). Regions with natural gas resources may use an SOFC system to provide electrical power to a larger area (e.g., a community, a city, etc.). Fuel cell devices are electrochemical devices that convert fuel into electrical energy in the form of direct current with a low voltage level. FIG. 1C shows an example arrangement of fuel cells. Specifically, FIG. 1C shows an example an SOFC stack to increase the output voltage with multiple single SOFC cells connected in series. The output voltage level of a system of two or more SOFCs 160a, 160b, 160c may be greater than the voltage level of a single SOFC 150. The voltage level may be increased, for example, by combining multiple two or more fuel cells 150 in a stacked formation in a serial connection. Similarly, output current capacity may be increased by arranging fuel cells in parallel. By providing an appropriate number of SOFC cells an SOFC system may designed to provide consistent, reliable electricity, for example, for a house and/or a large commercial structure. An SOFC cell will have a consistent power output, and by arranging the cells appropriately, different voltage levels, different current levels, and/or different power levels may be obtained. An SOFC may be a part of an electrical system comprising the SOFC, one or more batteries, one or more solar cells, one or more hydropower systems, one or more wind power systems, one or more capacitors, one or more supercapacitors, traditional power delivery methods (e.g., power plant and power lines), etc.

[0042] The current-voltage (I-V) characteristics of a fuel cell may depend on reactant composition, mass flow, temperature, and/or pressure. Attempting to extract more electrical energy from an SOFC than the input of reactants may allow may lower the fuel cell voltages and may lead to irreversible fuel cell degradation. Additionally, load changes may cause rapid temperature changes in high-temperature fuel cells, resulting in harmful thermomechanical stress, electrochemical stress and/or a significant reduction in fuel cell performance and/or fuel cell lifetime. Therefore, to maintain fuel cell performance and/or fuel cell lifetime, for example, a fuel cell system may be designed to maintain a power load as constant as possible under isothermal conditions and carry out any potential load changes as controllably as possible.

[0043] FIG. 2 shows an example of a cell voltage (V) (left y-axis) and power density (mW/cm^2) (right y-axis) vs current density (j) (mA/cm^2) plot 200. Specifically, FIG. 2 shows an example IV and power curve 200 of a 50 mm SOFC comprised of a NiO-YSZ composite anode, a gadolinium doped ceria (GDC) electrolyte and a lanthanum strontium cobalt oxide (LSC) composite cathode having a 150 ml/min flow of H_2 at the anode, a 500 ml/min flow of air at the cathode, and an operating temperature of 670 °C. The voltage drop across an SOFC may decrease with increasing current, for example, as shown in the cell voltage and power density vs current density plot 200. Although the rate of the voltage drop may decrease with increasing current density, the cell voltage and power density vs current density plot 200 shows that the output power density may increase with the increasing current density. More importantly, while these plots provide details on the output voltage, output power, and/or output power density, they fail to provide details of the underlying electrochemical processes of the fuel cell.

[0044] SOFCs operate at high temperatures (600-1000°C) and as a result are sensitive to temperature changes inside the cell. The main reason for a temperature shift is, by changing the current drawn or the gas flow when trying to change the power output of the cells. The stress on the cells (stacks) as a result of these changes will create cracks and delamination in the SOFC and eventually cause it to fail completely. These are generally referred to as thermal shock.

[0045] FIGS. 3A-3C show example diagrams of a region of a SOFC showing triple phase boundaries. In SOFCs, as shown in FIG. 3A reactions occur at triple phase boundaries (TPB) 305, that are found in the junction between the solid electrolyte, catalyst and reactant. The TPBs 305 must have access to the gas phase (H2 and O2), ionic conducting phase (YSZ, GDC), and electronic conducting phase (Ni, LSCF). If even one of these elements is missing, the location is rendered inactive. Hence, tracking TPBs is one of the most important diagnostic indicators for SOFC health and will either indicate a mass transport issue, conductivity issue, delamination issue or catalyst dissolution or poisoning issues. Currently there are only ex-situ post-mortem techniques for tracking TPBs such as SEM-FIB and tomography which are *expensive* and must be coupled with modeling software (FIGS. 3B and 3C). They cannot predict the systems health in operando. Currently used in-situ electrochemical techniques (e.g., impedance spectroscopy) cannot track

TPBs with high level of certainty due to convolution with other processes impacting the signal at similar frequencies.

[0046] Diagnostics of SOFC systems during their normal operation is a necessity for all industrial and domestic application and many others. These allow the prediction of a failure before it takes place and mitigation of such failures ahead of time, for public and device safety. Unfortunately, fuel cells in general, and Solid-Oxide fuel cells in particular, do not have an elaborate diagnostic technique that will allow the user or even the manufacturer to check the system performance and health and predict failures. One limitation in such devices is that any method used cannot by intrusive and must be of electronic nature of some sort. Herein, FTacV gives a solution for a real-time in-operando diagnosis of SOFCs. It is used for monitoring the triple-phase boundaries (TPB) which cannot be identified discretely as nanoparticles on a support owing to the fact that in SOFCs the active sites are typically boundaries between an electrically conducting phase and an ionically conducting phase (i.e. Ni-YSZ). The degradation analysis vis-a-vis active site tracking is therefore very special for the case of the SOFC.

[0047] An SOFC may have several degradation mechanisms. One major degradation mechanism in an SOFC, for example, may be the potential decrease in the amount and/or the reactivity of active sites on the anode (e.g., triple phase boundaries (TPB)). There are many factors that may contribute to this issue, and currently, there is no known method to quantitatively measure or monitor these change during operation without ambiguity. However, having this capability would be significant as it would allow for real-time monitoring of the cell's state while adjusting system operation conditions. Power output, for example, may be an operating condition that may be changed. Being able to control operating conditions (e.g., power output) may enable changes to be made in a controlled manner, preventing additional degradation to the system components. Additionally, such monitoring abilities could provide other benefits, including tracking the system's overall health status and sending a warning message when a certain threshold has been reached.

[0048] Degradation in SOFCs primarily comes from three categories of sources: (a) increased electronic or ionic resistance in a pathway leading to an active site which itself is still "connected" (i.e. the locale is still considered a TPB, but access to this site is met with increased resistance); (b) the complete disconnection of an active site from the cell due to either an insurmountable barrier for gas, ions, or electrons to reach the site. Note that lack of only one of these will render the site completely inactive; and (c) active sites which are poisoned (e.g. H_2S) but still connected to the cell. Techniques such as electrochemical impedance spectroscopy (EIS) and current-voltage (I-V) measurements cannot unambiguously differentiate between degradation in categories (a), (b), and (c)

[0049] Charge transfer across an electrodes comprises Faradaic and non-Faradaic processes. Faradaic processes involve the transfer of electrons to an electroactive specie on the electrodes. Reduction or oxidation of the metals on the electrodes are examples of a Faradaic reaction. Moving an ion from an electrolyte phase to an electrode (e.g., as is done in metal plating), or dissolving an atom, from the electrode, as an ion, into the electrolyte, are examples of non-Faradaic processes. Faradaic processes of an electrode may characterized to some extent using an IV plot (e.g., as described herein in FIG. 2). In Faradaic processes a charge transfer process may be established.

[0050] In non-Faradaic processes some ions and/or other electrochemical species that enter the electrode may not be able to leave. These additional electrochemical species may involve atoms that are part of the electrode itself or a. In essence, the chain of reactions is stopped, as is the transfer of charge (e.g., ions and/or electrons) across the electrode. This charge capture in non-Faradaic processes can be analyzed to determine a capacity or capacitance (C) which is the reason non-Faradaic processes are called capacitive processes. Non-Faradaic processes may be probed by perturbing an electrochemical species in steady-state with an alternating signal and observing the system response.

[0051] Cyclic voltammetry (CV) is a technique to measure electrochemical characteristics of a material. A linearly varying DC voltage in time may be induced across electrodes and the resulting current measured. FIG. 4A shows an example direct current (DC) cyclic potential. Specifically, FIG. 4A shows an example DC cyclic potential varied linearly in time from a starting voltage to a midpoint voltage then returning from the midpoint voltage to the starting voltage. The DC cyclic potential shown in FIG. 4A may be varying at a rate of 1 mV/s.

[0052] FIG. 4B shows an example measured current (I) response. Specifically, FIG. 4B shows an example measured current (I) in response to the example DC cyclic potential (e.g., as shown herein in FIG. 4A) varying at a rate of 1 mV/s. Moreover, the electrochemical device measured in is an SOFC comprised of a NiO-YSZ composite anode, a gadolinium doped ceria (GDC) electrolyte and a lanthanum strontium cobalt oxide (LSC) composite cathode operating at 650 °C in 1% H_2 +

99% N_2 fuel with a total flow rate of 100 ml/min on the anode and 200 ml/min of air on the cathode. CV curves may be used to analyze the Faradaic processes by identifying Faradaic waves.

[0053] Alternating current voltammetry (ACV) is an electrochemical analysis technique that may use a large amplitude alternating (e.g., sinusoidal) voltage superimposed on a direct current (DC) voltage signal (e.g., as described herein in FIG. 4A) to generate an alternating current in an electrochemical device. FIGS. 5A through 5C show examples of alternating voltages superimposed on a DC voltage signal. The DC voltage signal may be constant (e.g., the dashed line in FIG. 5A). The DC voltage signal may be sawtooth (e.g., the dashed line in FIG. 5B and as described herein in FIG. 4A). The DC voltage signal may be a slowly alternating signal (e.g., the dashed line in FIG. 5C). The underlying DC voltage may take on various changes in amplitude (e.g., a square wave, a sawtooth, a constant, etc.) provided the voltage does not change polarity. The alternating voltages (e.g., sinusoidal) may be driven by an alternating current (AC) signal generator. The AC signal may be sinusoidal.

[0054] One or more cells of a fuel cell system may be used as test cells. These test cells experience the same external parameters (e.g., fuel and air flow, temperature, gas pressure, etc.) as the remaining cells of the fuel cell system. FIG. 6A shows an example three electrode electrochemical sensing device. Specifically, FIG. 6A shows an example of a three-electrode method that may be used for analyzing electrochemical reactions. The three electrodes comprise a working electrode, a counter electrode, and a reference electrode. Operational amplifiers and/or high impedance bridge ensure current does not pass between the working and reference electrodes. The cell (working electrode) potential is monitored by the reference electrode and the current is measured through the counter electrode. Current passes from/to the counter electrode to the working electrode bypassing the reference electrode, so that it does not cause a drift in the measure potential.

[0055] FIG. 6B shows an example perturbation and resulting sensing and signal processing diagram. An AC driven perturbation voltage $V_P(t)$ 605 may be added to the DC input voltage V_o 610 to create a total time dependent voltage $V(t) = V_o + V_P(t)$. The total time dependent voltage $V(t)$ may be applied, for example, to the counter electrode described herein in FIG. 6A. The response (e.g., from the working electrode described herein in FIG. 6A) may be measured and processed 620.

[0056] An AC current may be applied to electroactive species, for example, to deconvolute between linear processes such as capacitance and resistance to non-linear processes (non-Faradaic processes) such as redox activity (Faradaic processes). The Faradaic processes generates harmonic frequencies at integer multiples of the fundamental harmonic, and these harmonic frequencies may be observed as signals in the power spectrum. The lower harmonics may be more affected by linear processes (e.g., capacitive charging and discharging and system resistance) while the higher harmonics (e.g., generally, above the fourth) may be mainly sensitive to the reaction kinetics on the electrode and may represent Faradaic processes. These Faradaic responses may be related, for example, to the active sites that are electrochemically accessible. At low frequencies (e.g., where the kinetics of the redox transition is practically reversible), the peak current of the harmonics may be directly proportional to the surface concentration of the electroactive species and may be used to extract the electrochemical accessible site density. The use of advanced simulations may facilitate data analysis and may enable the extraction of valuable insights regarding the system probed.

[0057] A Faradaic process may involve electric current generated by a reduction or oxidation of a chemical at an electrode (e.g., a cathode and/or anode). Faradaic processes are non-linear and can be discriminated form linear process such as capacitance and resistance using FTacV which generates harmonic components at f, 2f, 3f, …, nf, (n+1)f, etc.. Harmonic components may be used to study charge transfer processes that may not be related to other electrochemical processes. Harmonics generated may be resolved using Fourier transforms (FT) or fast Fourier transforms (FFT). FFT may be used to convert a time domain response into a frequency domain. A frequency harmonic of an input signal may be extracted, for example, by band selecting. Once the frequency harmonics are determined, the signal may be converted back to the time domain.

[0058] A method to monitor the performance and health of an SOFC while the SOFC is operating (e.g., an in operando method) may serve as a feedback and control for power modulations. Methods to characterize a fuel cell (e.g., an SOFC) may comprise applying an AC voltage to a fuel cell and measuring the current response according to FIG. 6B. Baseline for modulation rate can be built under lab conditions, and FTacV can be used as a sensing method to monitor the system's health, mainly the electrochemically active site density (EASD), which indicates the loss of active sites as function of system degradation. Hence, the FTacV output will be used as a sensing feedback to the system modulation process and will alert any deviation in the system health which will require a change or stop of the modulation. FIG. 7A shows an example plot of a non-monitored system experiencing a step-wise modulation, while FIG. 7B shows an example plot of a carefully modulated monitored system. Specifically, FIG. 7A shows a non-monitored system experiencing a step-wise modulation and the possible overshoots which can be produced using current methods (following the expected power output) in comparison to FIG. 7B which shows a design of a careful modulation and the sensitive feedback from the FTacV which allows very small overshoots from the planned program.

[0059] Fourier transform alternating current voltammetry (FTacV) and electrochemical impedance spectroscopy (EIS) may be useful in determining complex electrochemical reactions and/or mechanisms of electron and/or ionic transfer that drive electrocatalytic reactions. FTacV and EIS are electrochemical analysis techniques that impose an alternating current (e.g., a sine wave with a frequency, *f*,) on a DC signal (e.g., a DC scanned potential ramp as described in FIG. 3A). FTacV and EIS differ, however, in that FTacV uses a large amplitude perturbation whereas EIS uses a low amplitude perturbation.

[0060] FTacV and EIS, for example, may use a generated potential comprising a sine wave potential having a frequency, f, added to a linearly scanned potential ramp (see e.g., FIG. 3A as described herein). The generated potential is applied to an electrochemical device (e.g., an SOFC) to characterize the electrochemical mechanisms. Two cases may exist, for example, in the electrochemical device: the first, the non-Faradaic case, if there are no electroactive species present in the cell, or alternatively, the second, the Faradaic case, if there are electroactive species present in the cell. An AC current may originate from capacitance charge and/or discharge of the cell (e.g., non-Faradaic), for example, if there are no electroactive species in the cell. Alternatively, the AC current may involve a combination of both faradaic and non-faradaic contributions, for example, if an electroactive species exists in the cell.

[0061] FIG. 8 shows an example flow chart for characterizing a fuel cell using different techniques. Specifically, FIG. 8 shows an example flow chart for characterizing a fuel cell using a current vs applied voltage technique, with the option of further characterization using AC techniques including FTacV (e.g., FTacV or FTacV and EIS). FIG. 8 only shows an example and is not meant to limit characterization.

[0062] In step 805 a device may apply a total potential (e.g., as described herein in FIGS. 5A – 5C) to a fuel cell. The device may use techniques as described herein in FIGS. 6A and 6B. In step 810 the device may measure the current response of the fuel cell to determine an I-V curve.

[0063] In step 812, the device may determine if additional analysis methods are to be used. Analysis may end 835, for example, if no further analysis is needed. Alternatively, the device may determine, for example, if an alternating voltage was applied and if FTacV is to be performed. If it was determined in step 812 that an FTacV technique is to be performed, the power spectrum may be determined, for example, in step 815.

[0064] For FTacV, the current may be measured versus the potential (e.g., as shown herein in FIGS. 9A through 9D), the data filtered, and single harmonics extracted. To extract the harmonics, in step 815 the total current (e.g., in the time domain) may be converted to the frequency domain by using a Fourier transform (FT) or fast Fourier Transform (FFT) algorithm. FT and FFT differ in that the former is for transforming a continuous input while the latter is for transforming a discrete input, as such FT may be used in place of FFT in the analysis described herein.

[0065] In step 820, the harmonics may be determined from the power spectrum (e.g., via band selecting). An inverse Fourier transform (IFT) may be performed, in step 825, around the determined harmonics. FIGS. 12A and 12B show examples of IFTs around the 5th harmonic from FTacV. The peaks may apply to oxidation and/or reduction sites. The harmonic peaks may be measured over time to determine changes in the oxidation and/or reduction site reactivity and/or density.

[0066] Additional techniques may be performed on the SOFC. In step 827, for example, it may be determined that EIS may be performed in conjunction with FTacV. If it is determined in step 827 that additional techniques are not to be performed, the characterization may end at step 835. Alternatively, if it is determined that EIS is to be characterized, together with FTacV, in step 827, for example, phasors of the current (e.g., as described herein in FIGS. 11A and 11B) may be determined in step 830 in conjunction with the FTacV analysis performed in steps 815 through 825.

[0067] Although FTacV may have been used in fuel cells before (e.g., on proton exchange membrane fuel cells (PEMFC)), FTacV has not been executed on SOFCs. The challenge lies in identifying potential active sites (e.g., triple-phase boundaries), which may not be easily distinguished as discrete nanoparticles or atoms on a support, as in PEMFCs. In SOFCs, active sites exist as boundaries between electrically conducting phases (typically Ni),ionically conducting phases (typically YSZ), and pores, making degradation analysis and active site tracking unique and challenging. This is because complementary materials analysis techniques cannot quantitatively track the degradation of active sites in SOFCs. FTacV measures the current of a reversible redox reaction taking place in the fuel cell. FTacV, when applied to SOFCs may enhance the data collected by current "state-of-the-art" techniques, such as EIS or differential resistance.

[0068] EIS, also known as alternating current impedance spectroscopy, provides another tool to explore kinetic and mechanistic data of various electrochemical systems. EIS, like FTacV, relies on applying an AC voltage or AC current to an electrochemical system, and measuring the output response (e.g., the output voltage and/or current). EIS may model the behavior of an electrochemical system based on circuit consisting of a resistor and a capacitor. The time constant, τ, of a process, where:

$$\tau = RC,$$

where R is the resistance of a resistor in ohms and C is the capacitance of a capacitor in farad.

[0069] A response of an electrochemical system may include charging or discharging of the electric double layer at the electrode or electrolyte interface, kinetic faradaic reactions, and diffusion of a redox species from a bulk solution to an electrode surface. Different responses may have different time constants and behaviors over time.

[0070] FIGS. 9A through 9D shows examples of AC cyclic voltammograms. Specifically, FIGS. 9A through 9D shows examples of a cyclic voltammogram for sine waves having varied applied frequencies but a common 150 mV amplitude. The applied frequencies of the cyclic voltammograms of FIGS. 9A through 9D are, starting in the upper right and proceeding clockwise, 1.8331 Hz, 2.442 Hz, 4.883 Hz, and 3.662 Hz respectively.

[0071] FIG. 10A shows example accelerated stress test cycles of an SOFC. Specifically, FIG. 10A shows accelerated stress test cycles of a 50 mm SOFC cell comprised of a NiO-YSZ composite anode, a gadolinium doped ceria (GDC) electrolyte and a lanthanum strontium cobalt oxide (LSC) composite cathode . The stress test consisted inducing sharp load changes of the SOFC from a 52% load to a 91% load as described herein in FIG. 2.

[0072] FIG. 10B shows example current density vs time measurements of accelerated stress test cycles of an SOFC. Specifically, FIG. 10B shows an example current density of the accelerated test cycle described herein in FIG. 10B. The current density is shown to change from a current density near 151 mA/cm2 (e.g., as shown herein in FIG. 2) at 52% load to a current density near 318 mA/cm2 (e.g., as shown herein in FIG. 2) at 91% load. As shown the current density over time shows power output, but conveys no details on the underlying electrochemical active sites.

[0073] In an electrochemical reaction, the resulting current consists of two parts:

[0074] FIG. 11A shows an example diagram of phasor determination. Phasors show the relationship of two or more sinusoidal waves having the same frequency, but offset by a phase angle φ. Phasors may be used to graphically represent the magnitude and phase of sinusoidal waves in an AC circuit.

[0075] FIG. 11B shows an example plot of phasor values of a fuel cell (e.g., an SOFC). Specifically, FIG. 11B shows an example plot of phasor values of a 50 mm SOFC cell comprised of a NiO-YSZ composite anode, a gadolinium doped ceria (GDC) electrolyte and a lanthanum strontium cobalt oxide (LSC) composite cathode . A phasor plot comprises the imaginary and real parts of the phasor plotted on the complex plane. The length of the vector represents the magnitude and the angle represents the phase difference between the components. The phasor plot allows the SOFC to be analyzed and described using characteristics and terms associated with circuit behavior.

[0076] FIGS. 12A and 12B show example plots of 5th order harmonics using FTacV. Specifically, FIGS. 12A and 12B show example plots of the 5th order harmonics using FTacV after multiple cycles of AST, done with low fuel utilization, showing an evolution of an oxidation and/or reduction process. In FIGS. 12A and 12B the 5th order harmonic peaks at 0.7 V and 0.8 V may be associated, for example, with Ni oxidation to NiO and with NiO reduction to Ni.

[0077] A reversible redox reaction on an operating cell may need to be identified for FTacV to work. In the platinum group metal (PGM)-free example of FTacV as applied to PEMFCs the active metal site was iron. An iron active metal site may take on multiple oxidation states in a reasonable potential range without disturbing the surrounding catalyst structure. In SOFCs, a first challenge is to identify a redox reaction that may occur at the same location as the catalytic reaction of the working cell where the active sites are interfacial, as opposed to the active sites of PEMFCs. In a H_2 concentration of 5%, the oxygen partial pressure may be high enough to cause Ni oxidation to NiO at around 0.7 V, but the oxygen partial pressure may not be high enough to damage the cell (e.g., an SOFC in “standby mode” may be held in a 5% H_2 atmosphere to protect the anode). Under such conditions, Ni is oxidized to NiO, but importantly, since the oxidation is electrochemically driven and not thermochemically driven, the oxidation only occurs at the Ni-YSZ interfaces. This phenomenon is in contrast to the thermochemically-driven bulk oxidation of Ni to NiO under oxidizing atmospheres which is well-known to rapidly damage the cell owing to cell-expansion and related strains.

[0078] The electrochemically-driven interfacial Ni oxidation to NiO in NiO-YSZ composite anodes of an SOFC operating at 650°C has been shown to be feasible (e.g., Fig. 4B, Fig 9A-D). The process of performing an FTacV may not cause harm to the cell, for example, appropriate FTacV parameters, including gas composition, frequency, amplitude, sweep rate, sweep range, and bypass filter settings. Both the NiO and cell performance may be tracked, for example, by the 5th FTacV harmonic. The utilization of the fuel cell may be kept lower and the cell may be found to be much more durable and able to withstand numerous cycles, for example, based on tracking of the NiO and cell performance. Real-time diagnosis of a system's health, adjustment of power output in a controlled manner, and improved predictive maintenance capabilities may be performed, by combining the in operando method to determine the performance and health of the SOFC with Fonto Power's algorithms and modifications to the SOFC system. Rather than damaging a fuel cell with daily interruptions to perform FTacV, fuel cell performance and lifetime are improved.

[0079] In addition to showing the nature of the Ni to NiO oxidation and the NiO to Ni reduction, the evolution of the peaks with stress cycles of the fuel cell described in FIGS. 10A and 10B, FIGS. 12A and 12B show how the peak positions and heights change with increasing stress cycles.

[0080] FIG. 13A shows an example plot of a harmonic peak height and oxidized Ni moles from CV. Specifically, FIG. 13A shows an example plot showing the correlation of the number of oxidized Ni mols (e.g., indicating the number of active sites) to 5th order harmonic (e.g., 0.7 V peak) CV peak areas vs. the number of low utilization AST cycles.

[0081] FIG. 13B shows an example plot of a harmonic peak height and current density vs the number of stress test cycles. Specifically, FIG. 13B shows an example plot showing the correlation the number of oxidized Ni mols (e.g., indicating the number of active sites) to 5th order harmonic (e.g., 0.7 V peak) CV peak areas (vs. the number of high utilization AST cycles.

[0082] FIG. 13C shows an example plot of a harmonic peak height and oxidized Ni moles from CV. Specifically, FIG. 13C shows an example plot showing the correlation of the trend of the current density (e.g., from an IV curve as described herein in FIG. 2) to 5th order harmonic peak heights (e.g., 0.7 V peak) vs the number of high utilization AST cycles.

[0083] FIG 14 shows an example of electric power distribution system. Specifically, FIG. 14 shows an example electric power distribution system comprising an SOFC and one or more other electric power supply (e.g., an electrical power distribution line), electric power generation devices (e.g., one or more solar cells, one or more wind generators, etc.), and/or electric power storage devices (e.g., a battery).

[0084] An electrical power distribution system 1400 may comprise an electrical subsystem inductively coupled (e.g., transformers) to high power electrical power distribution lines. The electrical power distribution system 1400 may comprise multiphase distribution (e.g., 3 phase electrical power), but for ease of discussion only a single phase will be discussed herein. The AC bus that may be inductively coupled to an electrical power distribution line.

[0085] An AC bus may have a specified voltage level, a specified current level, and/or a specified frequency depending on regulations, safety concerns, and/or load requirements. An electrical power distribution system 1400 may comprise one or more AC buses, for example, wherein each bus may have different voltage, current, and/or frequency specifications.

[0086] A DC bus may have a specified voltage level and/or a specified current level depending on regulations, safety concerns, and/or load requirements. An electrical power distribution system 1400 may comprise one or more DC buses, for example, wherein each bus may have different voltage, current, and/or frequency specifications.

[0087] An SOFC may comprise one or more cells (e.g., as described herein in FIG. 1C) arranged to provide one or more DC bus voltages at one or more peak current values. Other DC power sources may comprise one or more batteries, one or more solar power systems or devices, one or more wind power systems or devices, one or more hydropower systems or device, one or more thermal power systems or devices, etc. The one or more batteries may be charged by one or more of the other DC power sources.

[0088] Sensors and controls (e.g., S/C) may comprise, for example, one or more of flow, temperature, gas composition, relative humidity, voltage, current and/or power sensors and/or control switches, regulators, and/or shunts. Sensors and/or controls may be configured to operate for different AC and/or DC buses. One or more sensors may be configured, for example, for AC and/or DC voltages of one or more of one or more AC and/or DC buses. One or more sensors may be configured, for example, for AC frequencies of one or more of one or more AC buses. One or more sensors, for example, for AC and/or DC currents of one of more of one or more of one or more AC and/or DC buses. Although not shown, a system may have series of additional buses that allow DC devices to charge the battery and/or provide variable DC power to other DC and/or AC devices.

[0089] The system may sense different DC power production levels and change which DC device(s) power a DC bus and at what ratio each DC device contributes. The system may, for example, ramp down an SOFC as DC power produced by a solar power cell increases. Similarly, the system may, for example, ramp down the SOFC as DC power produced from wind and/or hydropower sources increases. The system may base the ramp up speed both on the change in power currently being monitored as well as use machine learning to use past power changes to further anticipate a future change in power needs.

[0090] The system may be arranged so that the SOFC runs in a reversible mode to regenerate fuel during off times. The SOFC may be regenerated, for example, during the day when solar power provides enough DC power. Similarly, the SOFC may be regenerated, for example, while wind and/or solar power are providing DC power.

CLAIMS

1. A method, comprising:

applying a voltage signal to perform a direct current (DC) sweep associated with a fuel cell;

superimposing an alternating current (AC) voltage signal over the voltage signal;

measuring a current response, to the applied voltage signal and superimposed AC voltage, associated with reactive sites of the fuel cell; and

using a controller to control output power of the fuel cell based on the current response.

2. The method of claim 1, wherein controlling output power of the fuel cell comprises at least partially controlling a load or controlling a rate of change of power output.

3. The method of claim 1, wherein measuring the current response comprises:

performing Fourier transform alternating current voltammetry (FTacV) using the current response, wherein the FTacV comprises:

converting the current response from a time domain to a frequency domain using one of a Fourier transform (FT) or a fast Fourier transform (FFT);

determining one or more frequency harmonics, in the frequency domain, associated with the applied voltage signal;

performing an inverse Fourier transform (IFT) around one or more of the one or more determined frequency harmonics;

characterizing the fuel cell performance by monitoring the triple phase boundaries (TPB) in operando based on the IFTs; and

wherein based on the current response is at least partially based on the characterizing the fuel cell.

4. The method of claim 1, wherein applying the voltage signal comprises applying a voltage signal with an alternating current voltage signal, and measuring the current response comprises:

performing electrochemical impedance spectroscopy (EIS) using the current response, wherein EIS comprises converting the current response into phasors comprising an imaginary component of the current response and a real component of the current response;

characterizing the fuel cell performance based on the phasors; and

wherein based on the current response is at least partially based on the characterizing the fuel cell.

5. The method of claim 1, wherein measuring the current response associated with reactive sites comprises:

determining reactive sites;

collecting data associated with the reactive sites, wherein the data comprises at least one of a current-voltage (I-V) curve, Fourier transform alternating current voltammetry (FTacV), and electrochemical impedance spectroscopy (EIS); and

analyzing the data associated with the reactive sites, wherein the analyzing the data comprises one or more of analyzing the data at the time of data collection and analyzing the change in data over time.

6. The method of claim 1, wherein a reactive site is associated with a Faradaic process.

7. An apparatus, comprising:

a fuel cell (FC);

a sensing cell physically associated with the fuel cell, and at least partially sharing fuel or exhaust gas flow, and outputting a signal responsive to a measurement of the sensing cell; and

a controller, coupled to the sensing cell, to control output power of the fuel cell based on the signal from the sensing cell.

8. The apparatus of claim 7, wherein the sensing cell comprises:

two electrodes, an anode and a cathode, separated by a solid electrolyte;

a fuel flow, wherein the fuel flow passes by/against the anode;

an air/oxygen flow, wherein the air flow passes by/against the cathode;
a voltage generator, wherein the voltage generator generates a variable voltage; and
one or more of a voltage sensing device and a current sensing device.

9. The apparatus of claim 7, wherein the fuel cell comprises:
two electrodes, a fuel electrode and an air electrode, separated by an electrolyte;
a fuel flow, wherein the fuel flow passes by/against the anode; and
an air flow, wherein the air/oxygen flow passes by/against the cathode.

10. The apparatus of claim 7, wherein the fuel cell is a solid oxide fuel cell (SOFC).

11. The apparatus of claim 7, wherein the sensing cell is a FC configured with at least one input voltage test point and one or more of a output voltage test point and a output current test point.

12. The apparatus of claim 7, wherein the sensing cells comprise one or more cells of one or more fuel cells.

13. The apparatus of claim 7, wherein the sensing cell shares, with the FC, one or more of:
fuel flow;
air flow;
anode gas inlet composition;
anode gas outlet composition;
relative humidity;
load;
operating pressure; and
operating temperature.

14. A system, comprising:
a local electrical power distribution system;

one or more fuel cells electrically connected to the local electrical power distribution system, the one or more fuel cells comprising one or more sensing cells, each of the one or more sensing cells configured for outputting a first signal responsive to a measurement of the respective one or more sensing cells;

one or more sensors coupled to the local electrical power distribution system that output a second signal responsive to a measurement of the electrical power distribution system; and

one or more controllers to monitor and control output power of the local electrical power distribution system responsive to the one or more first signals and the one or more second signals.

15. The system of claim 14, further comprising one or more electrical power generation or storage systems electrically connected to the local electrical power distribution system, wherein the electrical power or storage systems comprise batteries, hydropower systems, wind systems, and solar cells.

16. The system of claim 14, wherein the one or more sensors comprise one or more of current measurement devices, voltage measurement devices, and power measurement devices.

17. The system of claim 14, wherein the fuel cells are solid oxide fuel cells (SOFC).

18. The system of claim 14, further comprising one or more of:

an upstream power conductor, electrically connected to a direct current (DC) high voltage bus of the local electrical power distribution system;

a downstream power conductor, electrically connected to a DC low voltage bus;

power conductors comprising power circuit nodes, wherein the power conductors electrically connect the upstream power conductor to the DC high voltage bus, high voltage sides of the power circuit nodes, and high voltage sides of one or more of the one or more fuel cells, and electrically connect the downstream power conductor to the DC low voltage, low voltage sides of the power circuit nodes, and low voltage sides of one or more of the one or more fuel cells bus, and components of the system that generate or use electrical power; and communication conductors electrically connecting communication components of the system, the one or more sensors, and the one or more controllers.

19. The system of claim 14, wherein modulating the output power between 0-100 % and anything in between comprises:

controlling the rate at which the solid oxide fuel cell (SOFC) provide power to the power load system;

modulating the SOFC that provide power to the electrical system; and

modulating power to power sources.

20. The system of claim 14, further comprising communication lines between the controller and the one or more fuel cells.

ABSTRACT

Methods, systems, and apparatuses are described for solid oxide fuel cells (SOFC) to detect changes in the SOFC's performance during steady state and non-steady state operation, allowing careful power modulation using techniques involving applying an alternating current (AC) to a fuel cell and monitoring the response. Using an AC signal Faradaic responses of electrochemically active sites in the fuel cell may be discriminated form other process, and allow sensitive and accurate monitoring of the system's health, by analyzing to determining changes in active site characteristics or density. The application of this electrochemical sensing technique will allow careful modulation of SOFC power and avoid system degradation and failure.

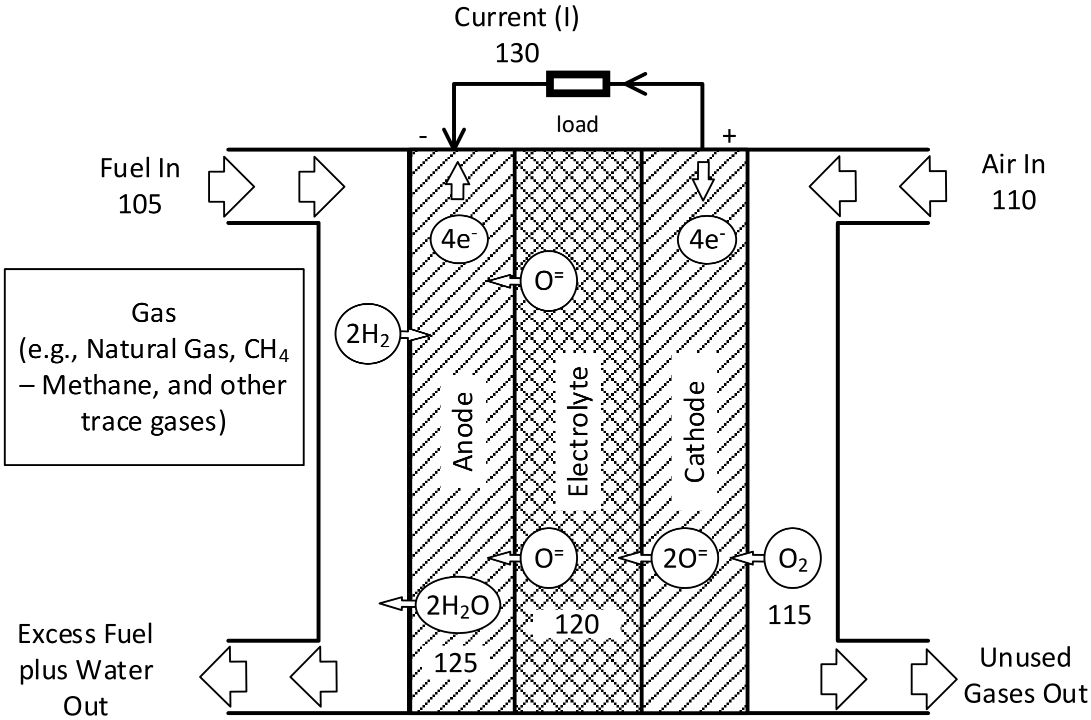

Current (I)
130
load
-
+
Fuel In
105
Air In
110
4e-
4e-
O=
Gas
(e.g., Natural Gas, CH4 – Methane, and other trace gases)
2H2
Anode
Electrolyte
Cathode
O=
2O=
O2
2H2O
120
115
125
Excess Fuel plus Water Out
Unused Gases Out

FIG. 1A

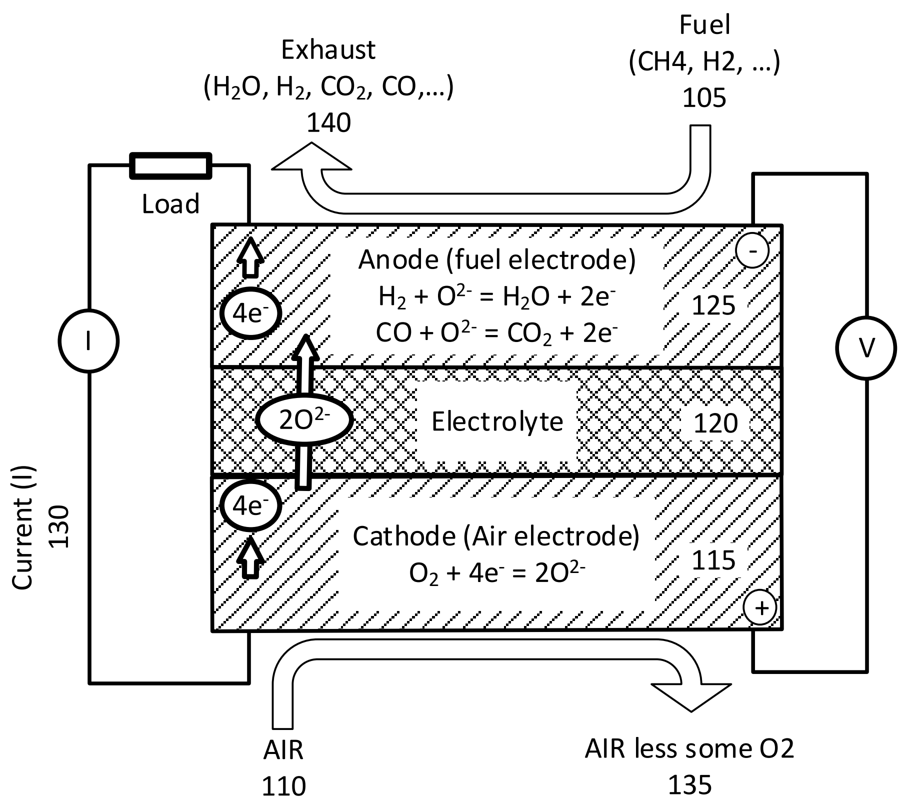
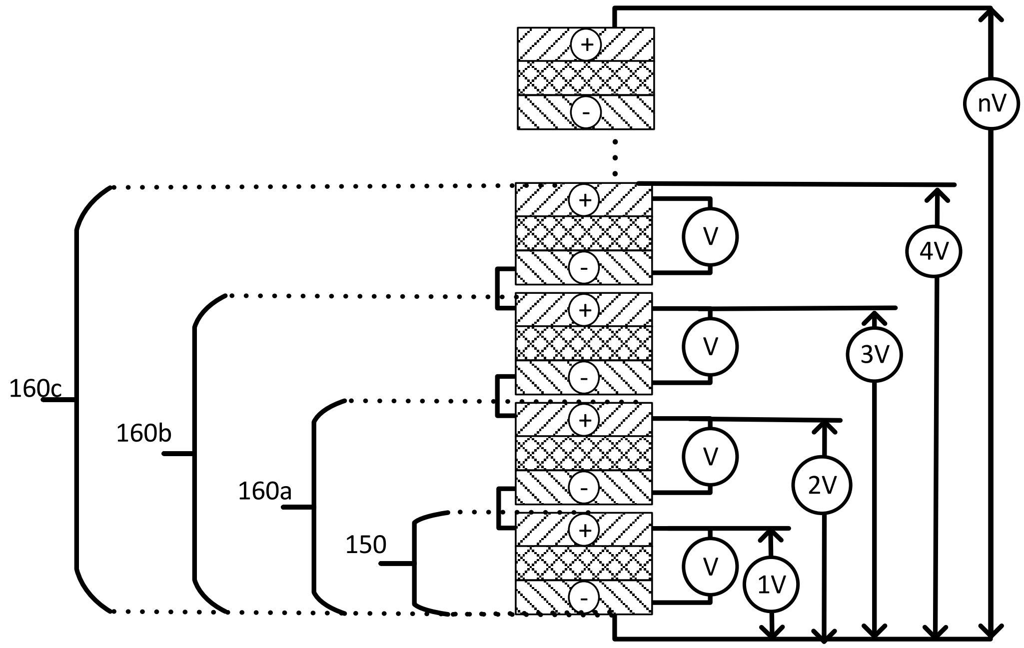
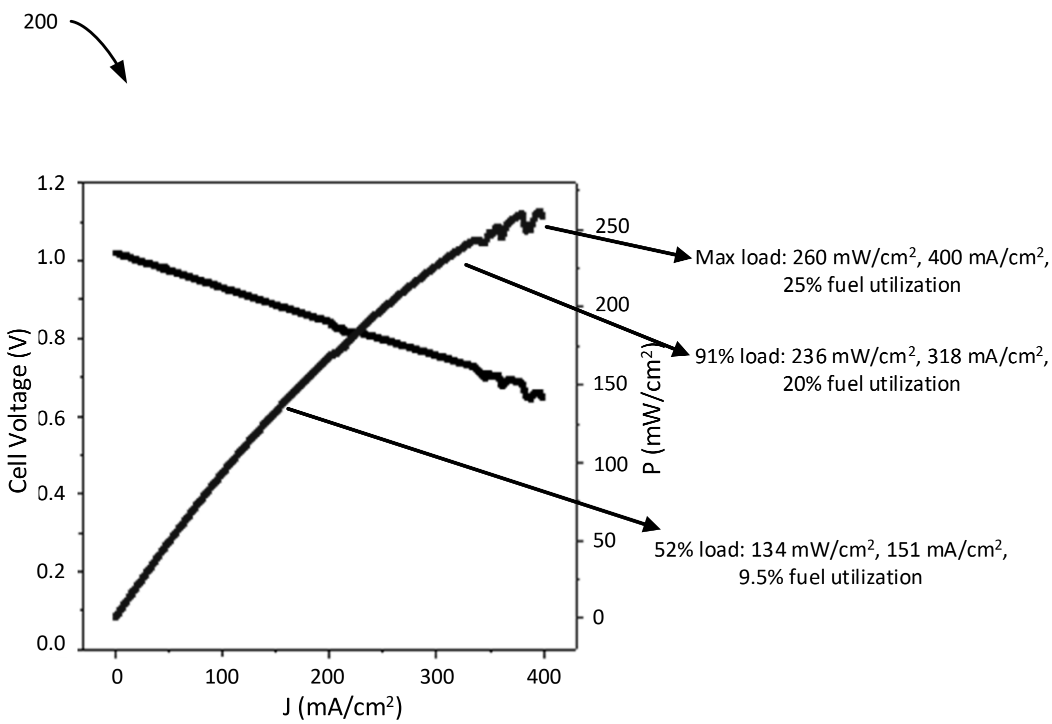

Exhaust
(H2O, H2, CO2, CO,...)
140
Fuel
(CH4, H2, ...)
105
Load
Anode (fuel electrode)
H2 + O2- = H2O + 2e-
CO + O2- = CO2 + 2e-
125
4e-
I
V
2O2-
Electrolyte
120
4e-
Current (I)
130
Cathode (Air electrode)
O2 + 4e- = 2O2-
115
-
+
AIR
110
AIR less some O2
135

FIG. 1B



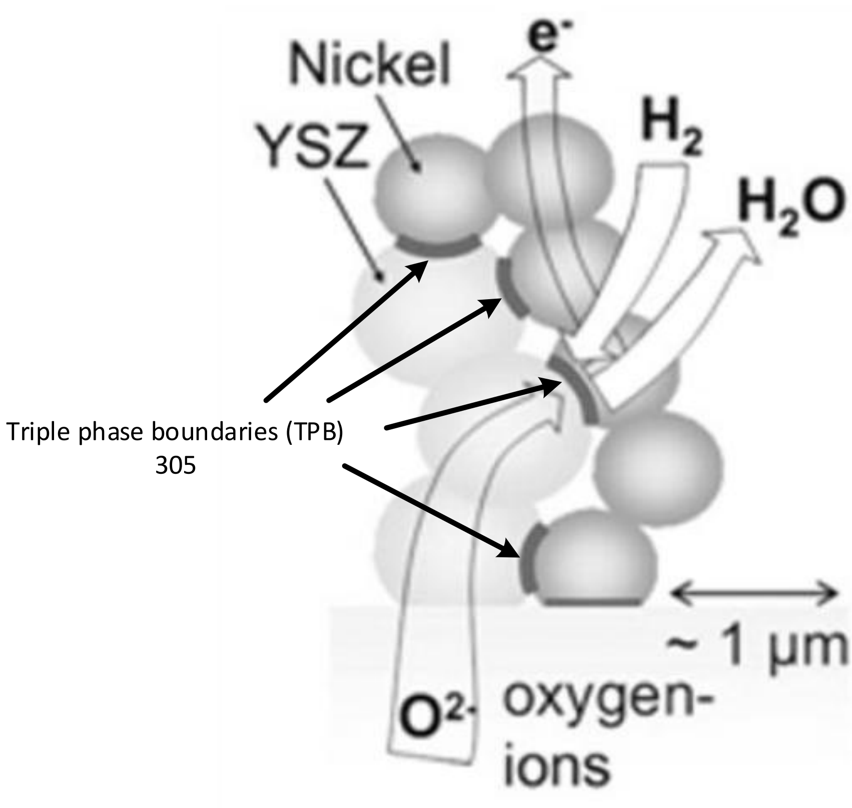
+
-
nV
V
4V
3V
2V
1V
160c
160b
160a
150

FIG. 1C



200
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Cell Voltage (V)
0
100
200
300
400
J (mA/cm2)
250
200
150
100
50
0
P (mW/cm2)
Max load: 260 mW/cm2, 400 mA/cm2, 25% fuel utilization
91% load: 236 mW/cm2, 318 mA/cm2, 20% fuel utilization
52% load: 134 mW/cm2, 151 mA/cm2, 9.5% fuel utilization

FIG. 2


Nickel
YSZ
e-
H2
H2O
Triple phase boundaries (TPB)
305
~ 1 µm
O2-
oxygen-
ions

z

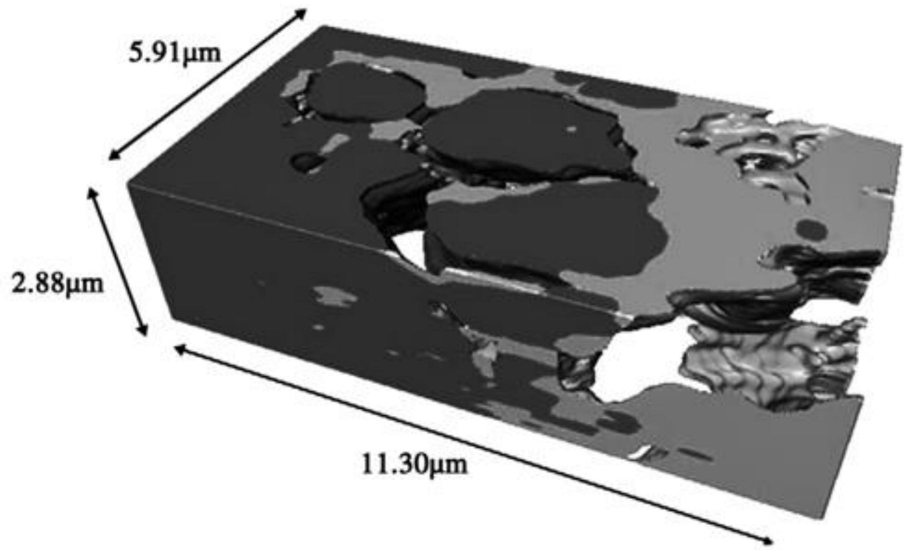


FIG. 3B

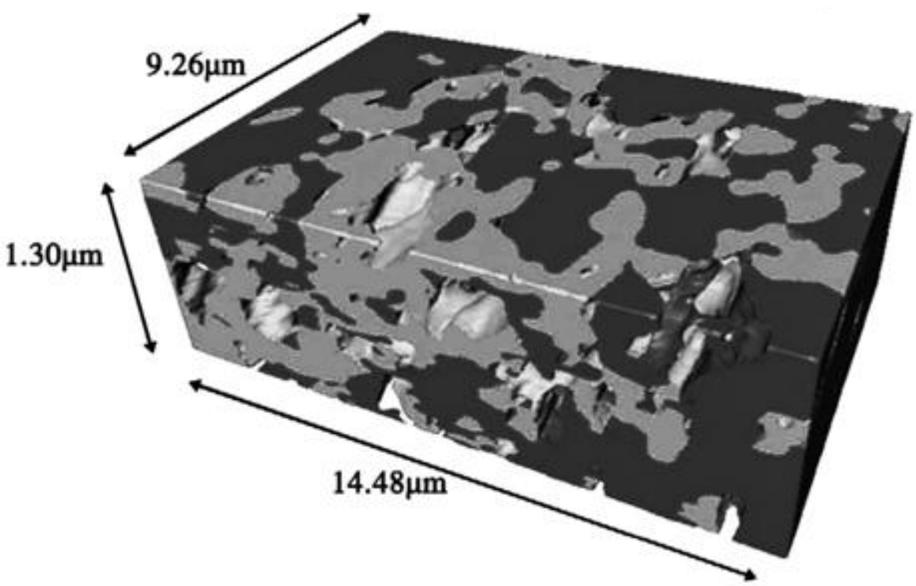


FIG. 3C

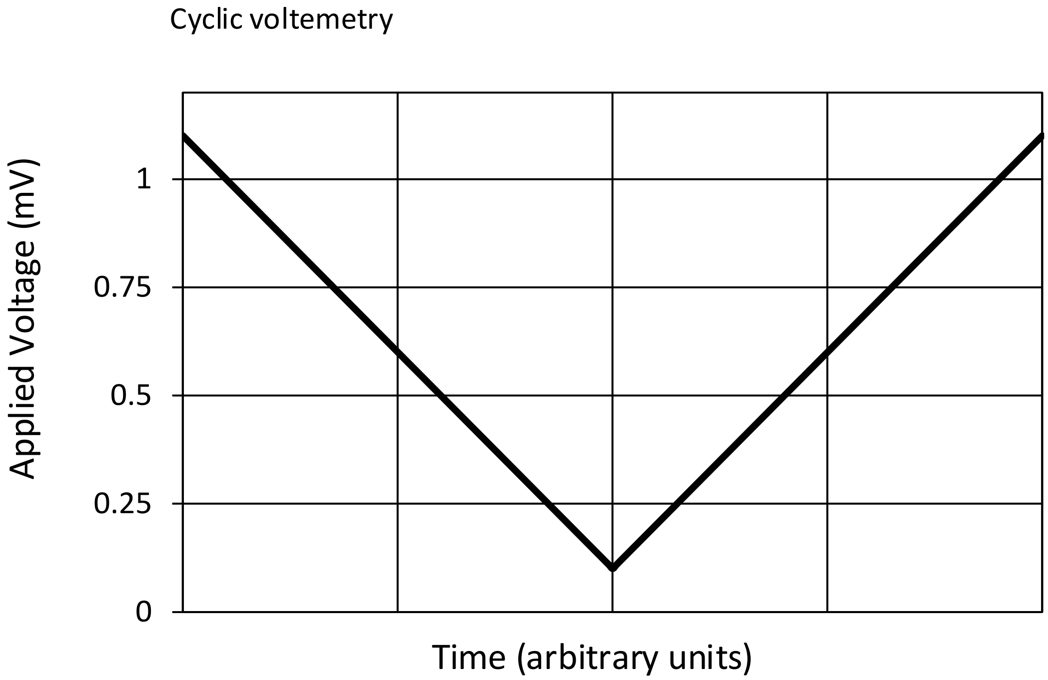

Cyclic voltemetry
Applied Voltage (mV)
1
0.75
0.5
0.25
0
Time (arbitrary units)

FIG. 4A

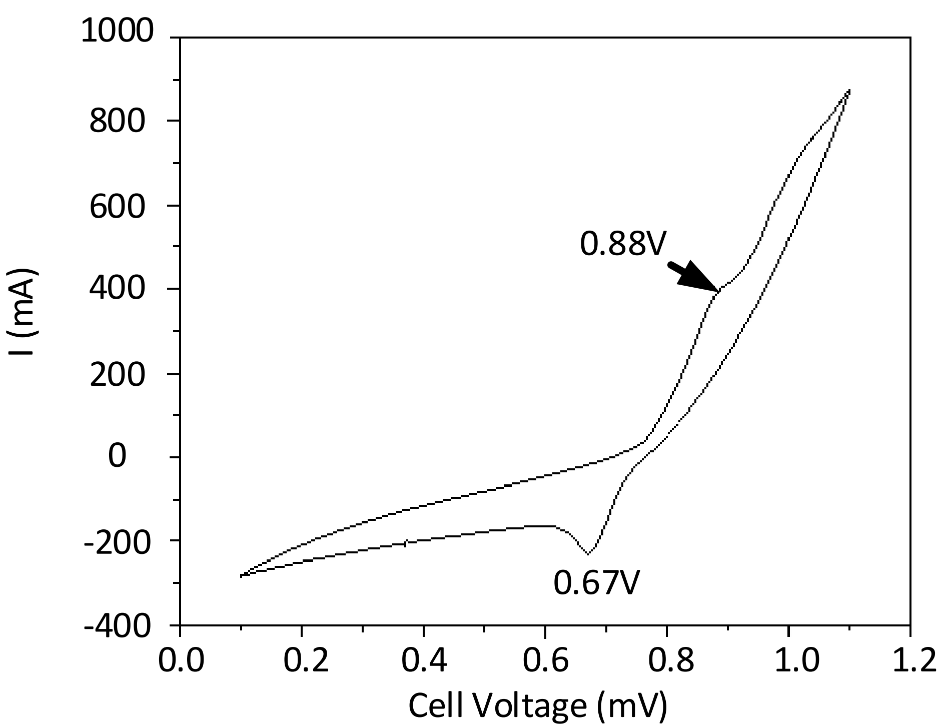

1000
800
600
400
200
0
-200
-400
I (mA)
0.88V
0.67V
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Cell Voltage (mV)

FIG. 4B

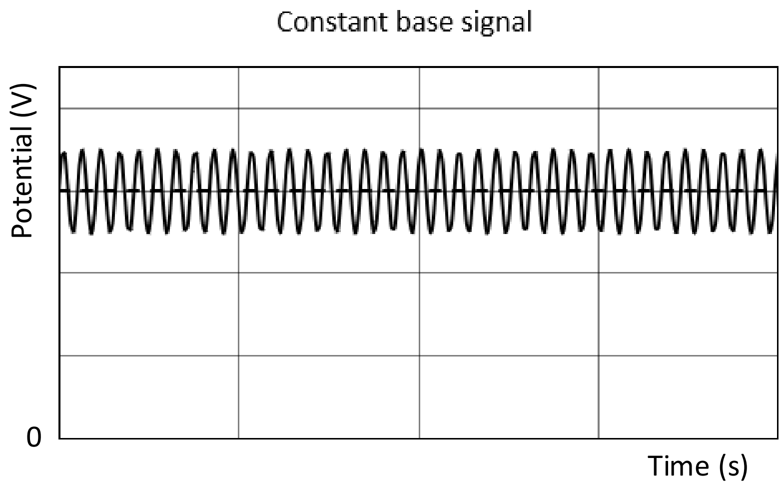


FIG. 5A

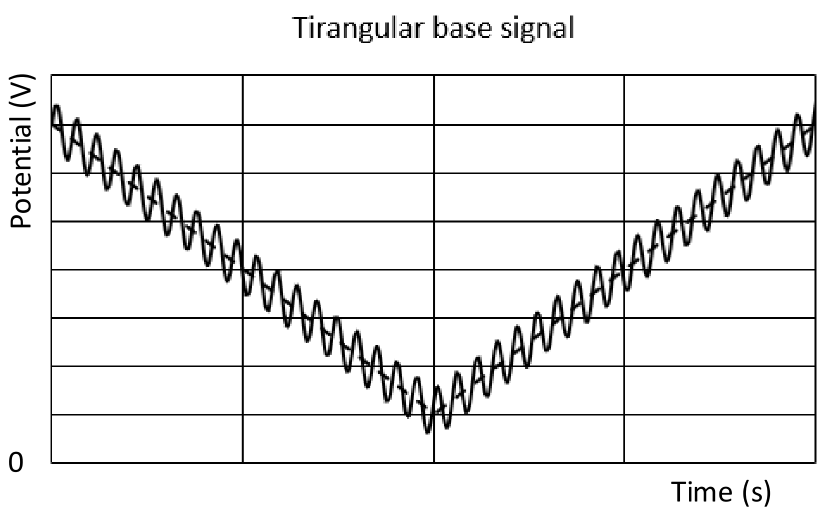


FIG. 5B

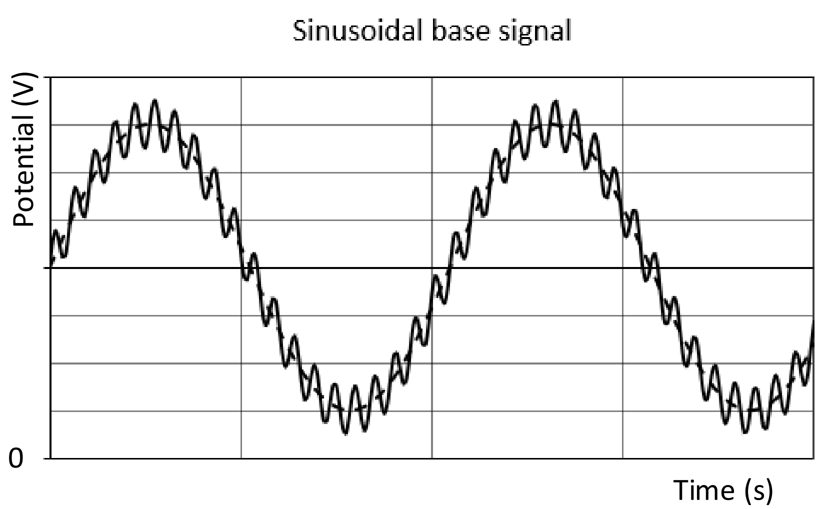
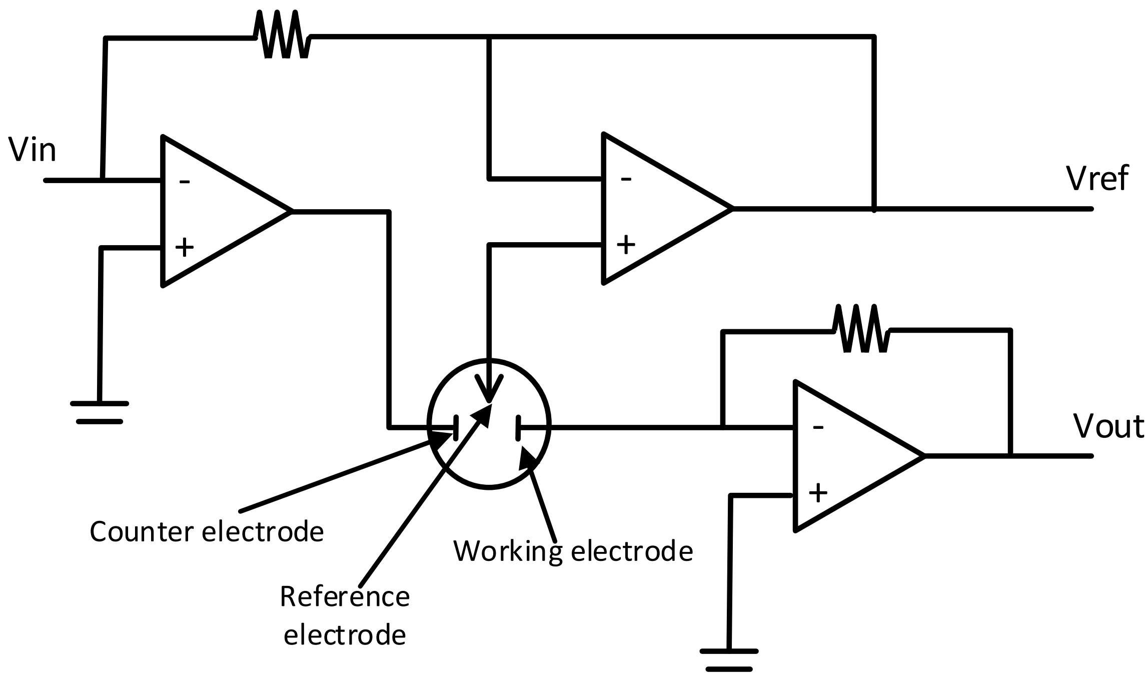
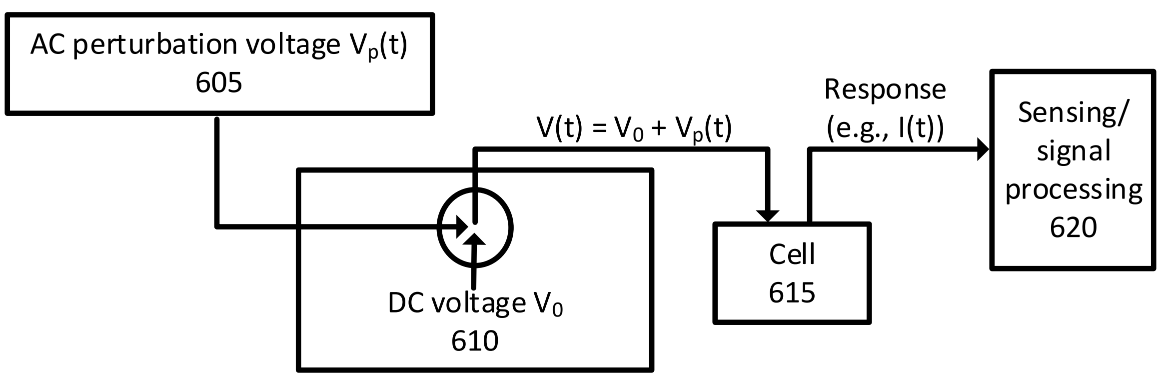


FIG. 5C



Vin
-
+
-
+
Vref
-
+
Vout
Counter electrode
Reference electrode
Working electrode

FIG. 6A



AC perturbation voltage $V_p(t)$ 605
$V(t) = V_0 + V_p(t)$
Response (e.g., I(t))
Sensing/ signal processing 620
Cell 615
DC voltage V_0 610

FIG. 6B

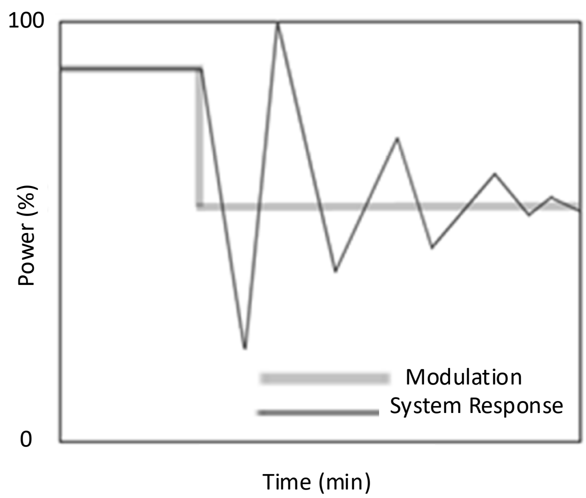

100
0
Power (%)
Time (min)
Modulation
System Response

FIG. 7A

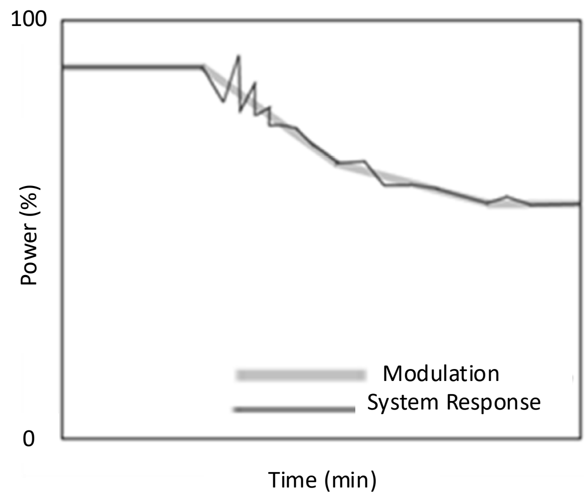

100
0
Power (%)
Time (min)
Modulation
System Response

FIG. 7B

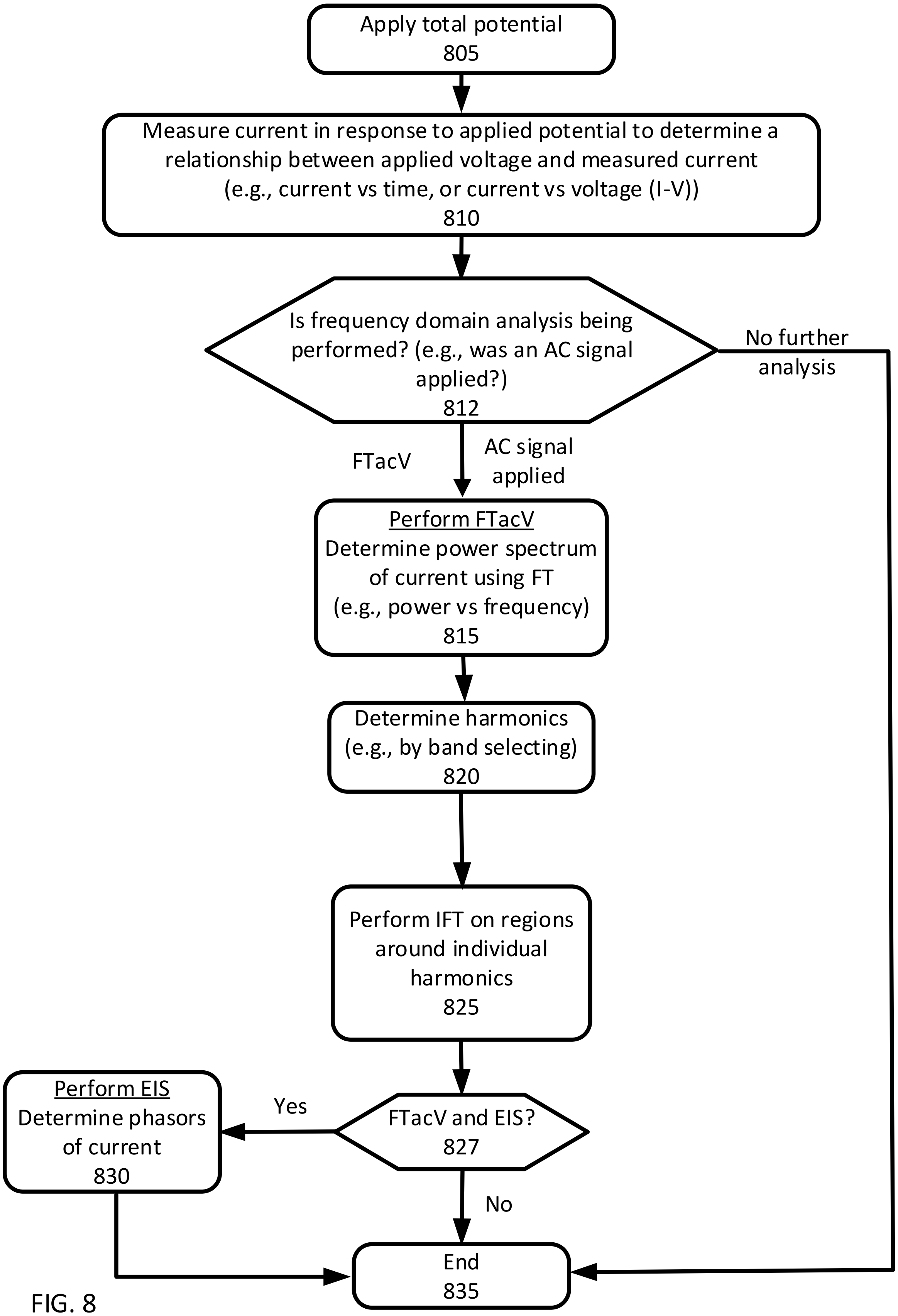

Apply total potential
805
Measure current in response to applied potential to determine a relationship between applied voltage and measured current (e.g., current vs time, or current vs voltage (I-V))
810
Is frequency domain analysis being performed? (e.g., was an AC signal applied?)
812
No further analysis
FTacV
AC signal applied
Perform FTacV
Determine power spectrum of current using FT (e.g., power vs frequency)
815
Determine harmonics (e.g., by band selecting)
820
Perform IFT on regions around individual harmonics
825
FTacV and EIS?
827
Yes
Perform EIS
Determine phasors of current
830
No
End
835

FIG. 8

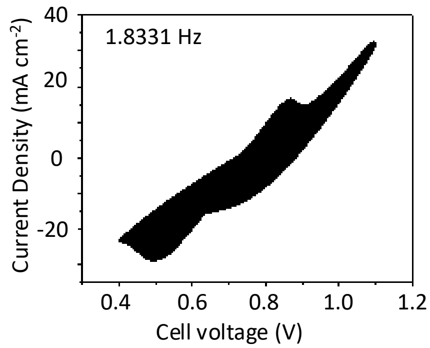


FIG. 9A

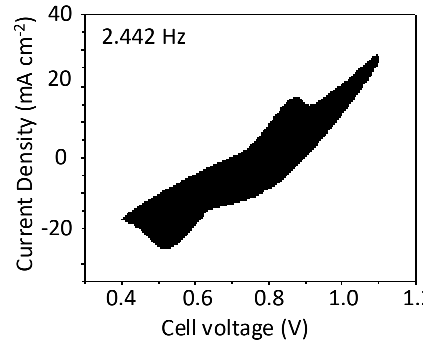


FIG. 9B

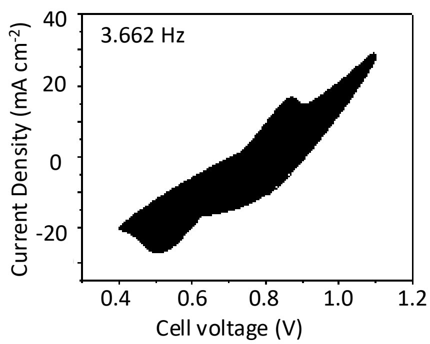


FIG. 9C

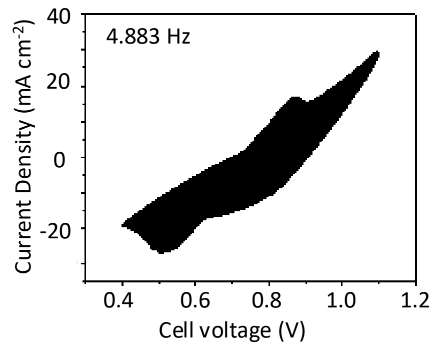


FIG. 9D

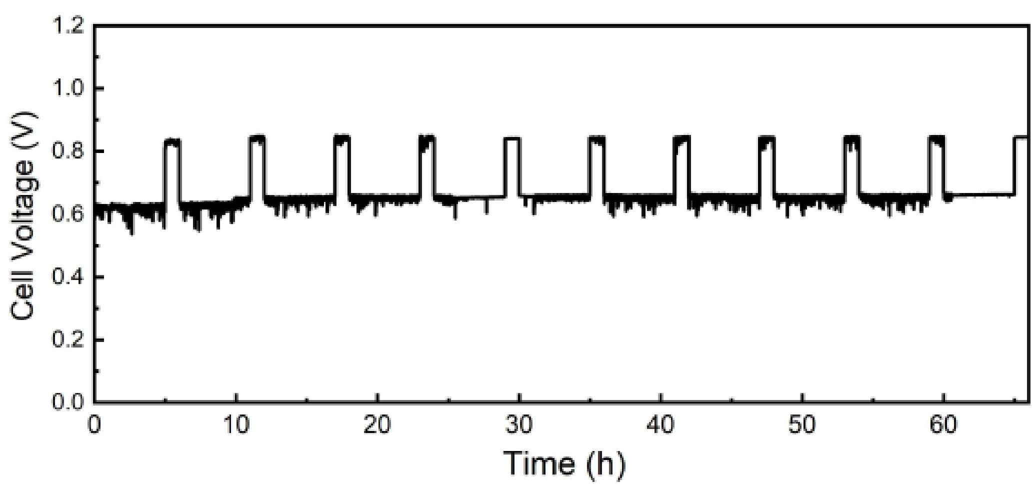
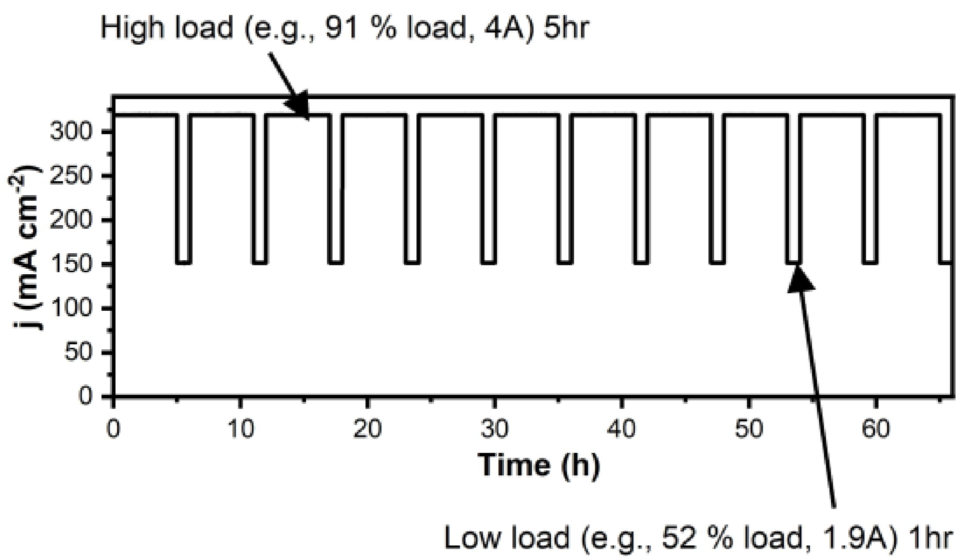


FIG. 10A



High load (e.g., 91 % load, 4A) 5hr
j (mA cm-2)
300
250
200
150
100
50
0
0
10
20
30
40
50
60
Time (h)
Low load (e.g., 52 % load, 1.9A) 1hr

FIG. 10B

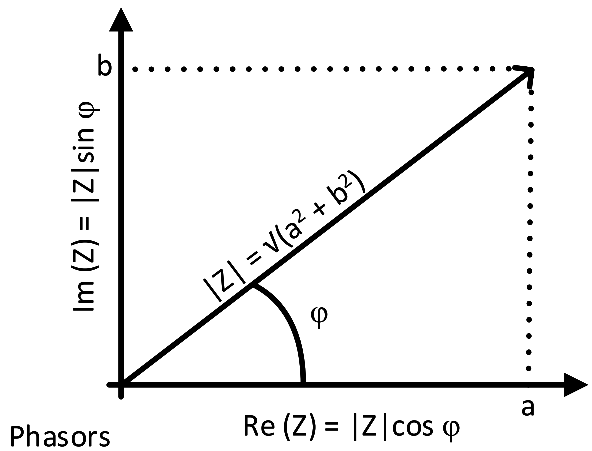


FIG. 11A

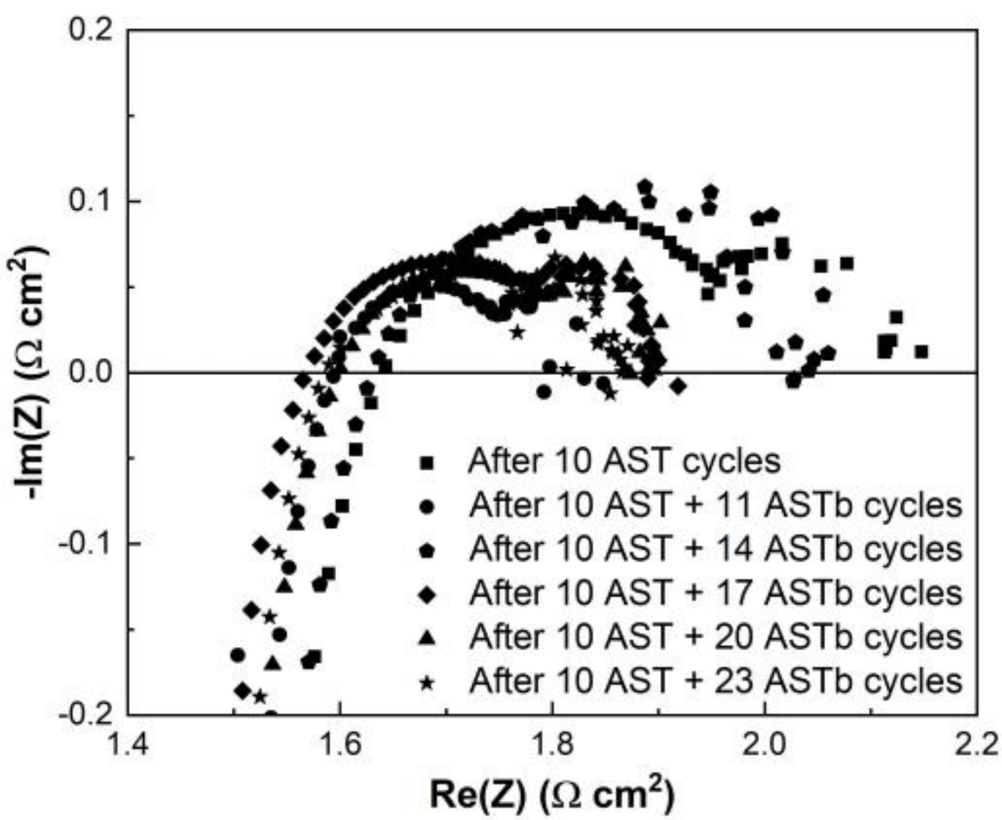


FIG. 11B

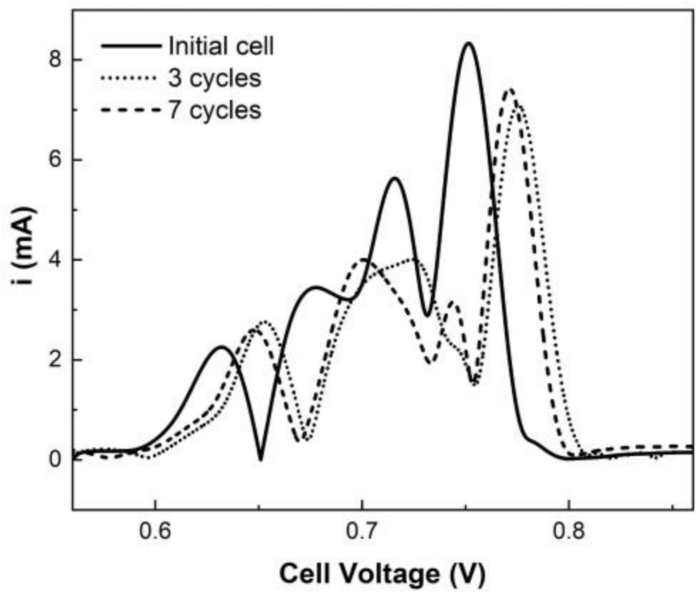

Initial cell
3 cycles
7 cycles
8
6
4
2
0
i (mA)
0.6
0.7
0.8
Cell Voltage (V)

FIG. 12A

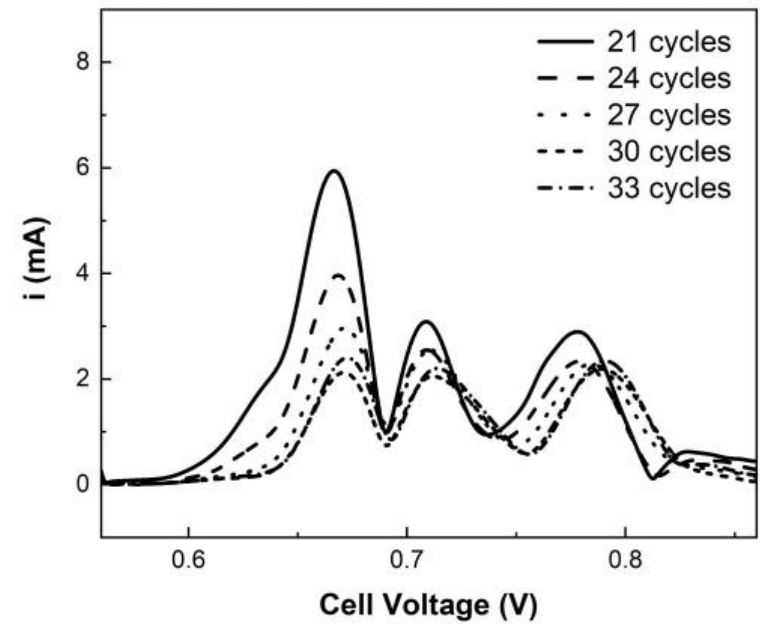


FIG. 12B

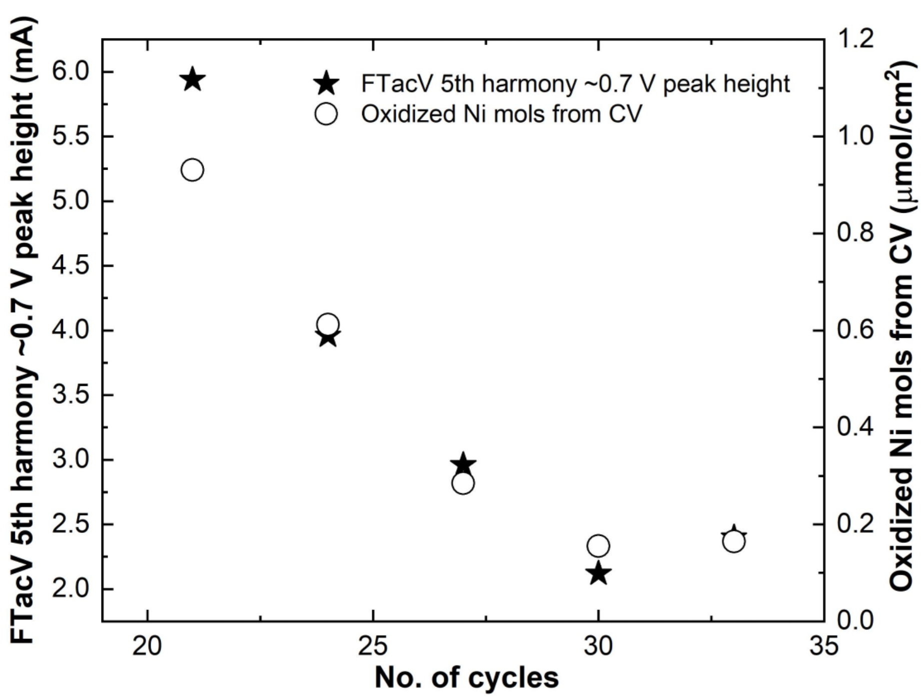


FIG. 13A

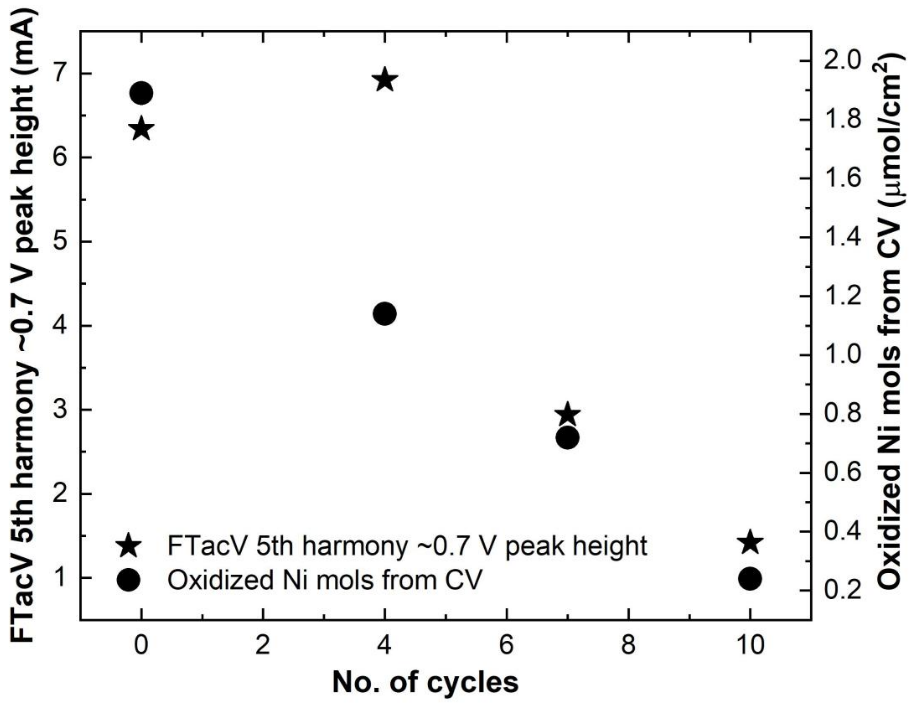

FTacV 5th harmony ~0.7 V peak height (mA)
Oxidized Ni mols from CV (μmol/cm²)
No. of cycles
FTacV 5th harmony ~0.7 V peak height
Oxidized Ni mols from CV
0
2
4
6
8
10
1
2
3
4
5
6
7
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

FIG. 13B

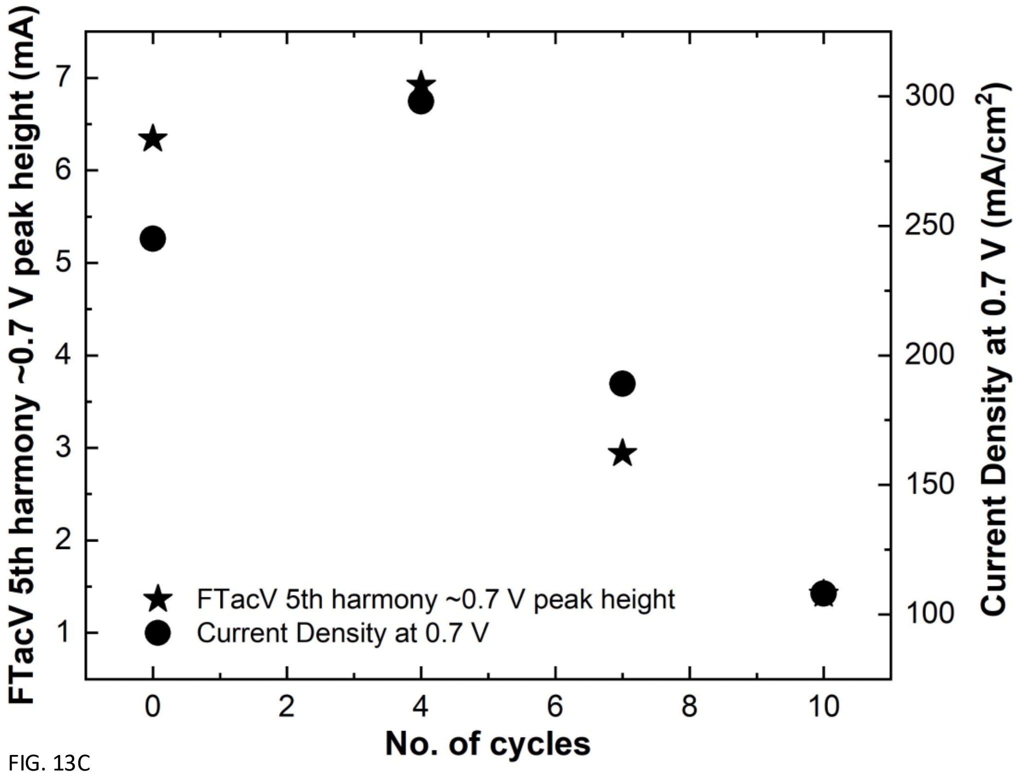

FTacV 5th harmony ~0.7 V peak height (mA)
Current Density at 0.7 V (mA/cm2)
No. of cycles
FTacV 5th harmony ~0.7 V peak height
Current Density at 0.7 V
0
2
4
6
8
10
1
2
3
4
5
6
7
100
150
200
250
300

FIG. 13C

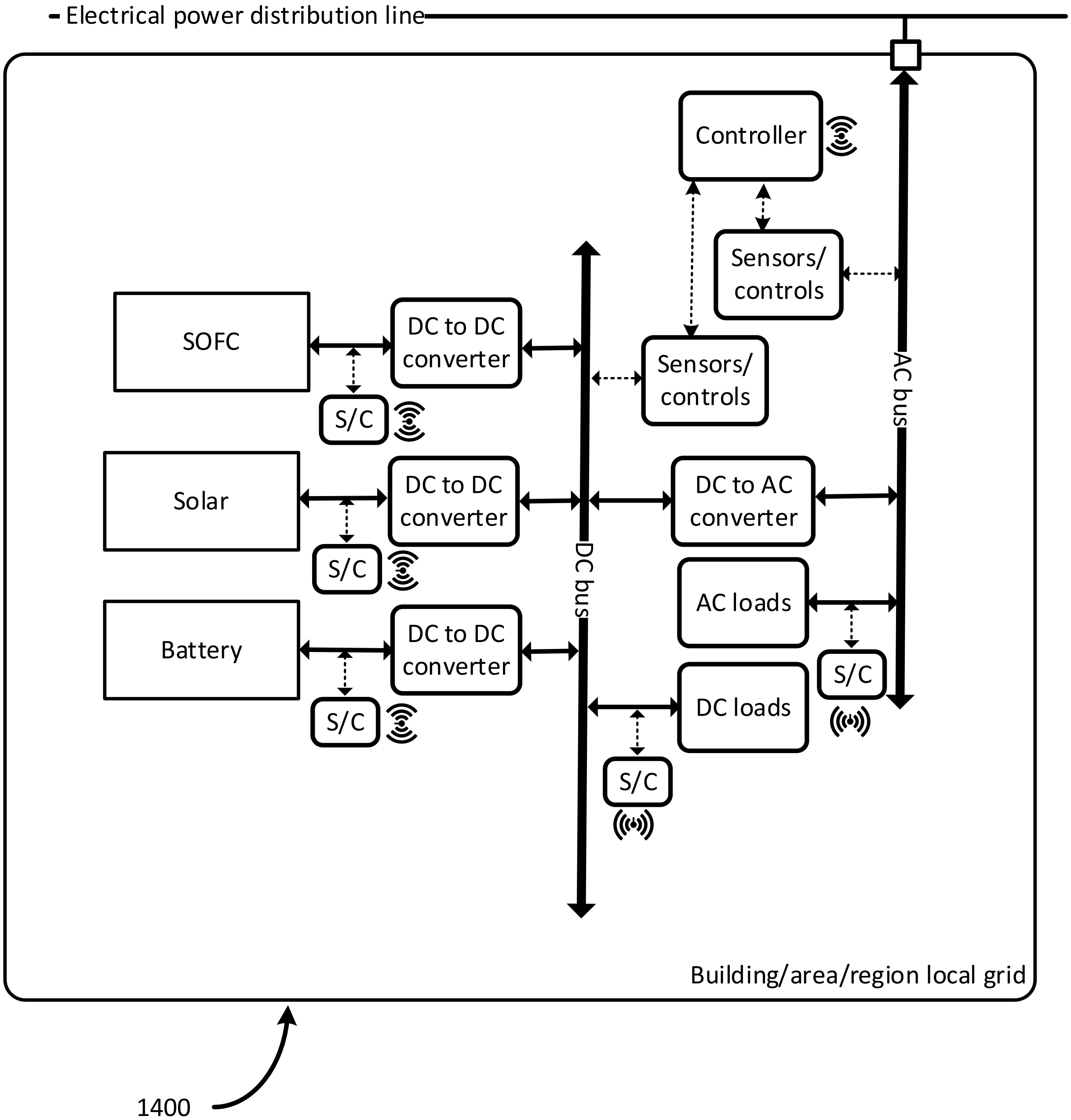

Electrical power distribution line
Controller
Sensors/
controls
SOFC
DC to DC
converter
Sensors/
controls
AC bus
S/C
Solar
DC to DC
converter
DC to AC
converter
S/C
DC bus
AC loads
Battery
DC to DC
converter
S/C
S/C
DC loads
S/C
Building/area/region local grid
1400

FIG. 14