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(54) Title: CAPACITIVE ENERGY STORAGE CELL, CAPACITIVE ENERGY STORAGE MODULE, AND CAPACITIVE ENERGY STORAGE SYSTEM

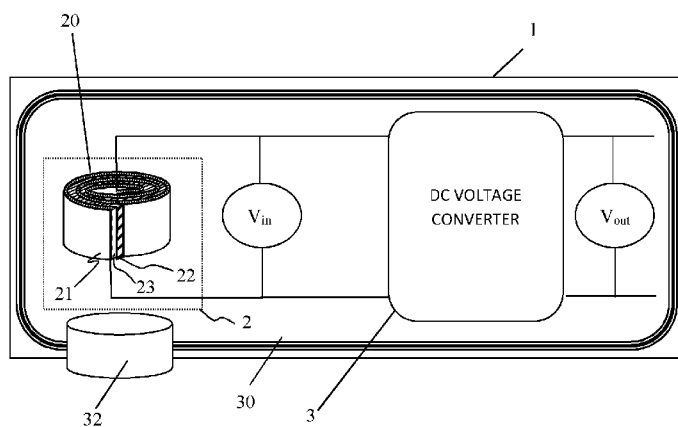


Figure 10

(57) Abstract: The present disclosure provides an energy storage cell comprising at least one capacitive energy storage device and a DC-voltage conversion device. The capacitive energy storage device comprises at least one meta-capacitor. The output voltage of the capacitive energy storage device is the input voltage of the DC-voltage conversion device. The present disclosure also provides a capacitive energy storage module and a capacitive energy storage system.

CAPACITIVE ENERGY STORAGE CELL, CAPACITIVE ENERGY STORAGE MODULE, AND CAPACITIVE ENERGY STORAGE SYSTEM

CLAIM OF PRIORITY

This application claims the priority benefit of U.S. Patent Applications Numbers 15/043,315, 15/043,186, 15/043,209, and 15/043,247, all of which were filed February 12, 2016, the entire contents of all of which are incorporated herein by reference.

FIELD OF THE DISCLOSURE

The present disclosure relates generally to a modular energy storage system to simultaneously enable multiple applications and more particularly to an energy storage cell comprising at least one capacitive energy storage device and a DC-voltage conversion device.

BACKGROUND

Many technical applications can benefit from rechargeable electrical energy storage. Most rechargeable electrical energy storage systems are based on rechargeable batteries. Rechargeable batteries store and release electrical energy through electrochemical reactions. Rechargeable batteries are used for automobile starters, portable consumer devices, light vehicles (such as motorized wheelchairs, golf carts, electric bicycles, and electric forklifts), tools, and uninterruptible power supplies. Emerging applications in hybrid internal combustion-battery and electric vehicles are driving the technology to reduce cost, weight, and size, and increase lifetime. Grid energy storage applications use rechargeable batteries for load-leveling, storing electric energy at times of low demand for use during peak periods, and for renewable energy uses, such as storing power generated from photovoltaic arrays during the day to be used at night. Load-leveling reduces the maximum power which a plant must be able to generate, reducing capital cost and the need for peaking power plants. Small rechargeable batteries are used to power portable electronic devices, power tools, appliances, and so on. Heavy-duty batteries are used to power electric vehicles, ranging from scooters to locomotives and ships. Rechargeable batteries are also used in distributed electricity generation and stand-alone power systems. Such applications often use rechargeable batteries in conjunction with a battery management system (BMS) that monitors battery parameters such as voltage, current, temperature, state of charge, and state of discharge and protects against operating the battery outside its safe operating area. Rechargeable batteries have drawbacks due to relatively large weight per unit energy stored, a tendency to self-discharge, susceptibility to damage if too deeply discharged, susceptibility to catastrophic failure if charged too deeply, limited power availability

per unit weight, limited power availability per unit energy, relatively long charging times, and degradation of storage capacity as the number of charge-discharge cycles increases.

Alternatives to batteries for rechargeable energy storage include capacitor-based systems. Capacitors store energy in the form of an electrostatic field between a pair of electrodes separated by a dielectric layer. When a voltage is applied between two electrodes, an electric field is present in the dielectric layer. Unlike batteries, capacitors can be charged relatively quickly, can be deeply discharged without suffering damage, and can undergo a large number of charge discharge cycles without damage. Capacitors are also lower in weight than comparable batteries. Despite improvements in capacitor technology, including the development of ultracapacitors and supercapacitors, rechargeable batteries store more energy per unit volume. One drawback of capacitors compared to batteries is that the terminal voltage drops rapidly during discharge. By contrast, battery systems tend to have a terminal voltage that does not decline rapidly until nearly exhausted. Also, because the energy stored on a capacitor increases with the square of the voltage for linear dielectrics and at a power greater-than or equal to 2 for meta-dielectrics, capacitors for energy storage applications typically operate at much higher voltages than batteries. Furthermore, energy is lost if constant current mode is not used during charge and discharge. These characteristics complicate the design of power electronics for use with meta-capacitors and differentiate the meta-capacitor management system from battery management systems that are presently in use.

It is within this context that aspects of the present disclosure arise.

INTRODUCTION

Aspects of the present disclosure address problems with conventional rechargeable electrical energy storage technology by combining a capacitive energy storage device having one or meta-capacitors with a DC-voltage conversion device having one or more switch mode voltage converters coupled to the terminals of the capacitive energy storage device. Meta-capacitors have greater energy storage capacity than conventional ultracapacitors or supercapacitors. The DC-voltage conversion device regulates the voltage on the capacitive energy storage device during charging and discharging.

A voltage conversion device typically includes a voltage source (an input), one or more active or passively controlled switches, one or more inductive elements (some advanced converters, e.g., charge-pump circuits, do not specifically use inductors per se though there may be parasitic inductance in the circuit board and/or wiring), one or more energy storage elements(e.g., capacitors and/or inductors), some way of sensing output voltage and/or current,

and some way of controlling the switches to create a specific output voltage or current, and terminals to connect this device to external inputs and outputs such as various loads. A standard circuit for producing an output voltage V_{out} that is less than the input voltage V_{in} ($V_{out}/V_{in} < 1$) is called a buck converter, and a standard circuit for producing an output voltage that is greater than the input voltage ($V_{out}/V_{in} > 1$) is called a boost converter. The basic circuit often used to describe buck conversion is a switched LC filter (Figure 1). The load can be thought of as a resistor that will vary its resistance to achieve a set current moving through it. Effectively, this is an LCR low-pass filter, with the capacitor and resistor in parallel. When the switch is closed, the LC network begins to absorb energy, and current begins to flow through the inductor. However, when the switch is opened while current is flowing, the inductor will attempt to maintain the current $i(t)$ and will generate reverse voltage $v(t)$ following equation (1).

$$v(t) = L \frac{di(t)}{dt}, \quad (1)$$

The reverse voltage generated will be extremely high if the incremental change in current di occurs over a sufficiently short increment of time dt , and this may damage or destroy the switching element SW1. Therefore, it is necessary to provide a path to ground so that current can continue to flow. This path can be implemented with a diode that operates as a one-way valve, opening automatically when the inductor tries to pull current out of the switching element SW1 (see Figure 2). This is called a non-synchronous buck converter, because the diode is automatically synchronized with the switching of a power transistor, such as a metal oxide semiconductor field effect transistor (MOSFET). Such a converter does not need to be actively synchronized. A possible issue with this type of circuit is that the turn-on voltage of the diode needs to be reached and be maintained while the switching element SW1 is turned off and the diode is active. This means that there will always be a voltage drop of, e.g., $\sim 0.6V$ across the diode due to current flowing through it, and therefore a power loss. This can be improved by implementing a synchronous converter design, where the diode is replaced with a second switch SW2 (see Figure 3) and the controller actively synchronizes the activity of both switches such that they are never on at the same time.

The delay between turn-off and turn-on of the MOSFETs in a synchronous design needs to ensure that a shoot-through event does not occur. Although two separate pulses can be set up with a delay, a better solution would only need a single PWM channel set up and automatically derive the second signal. With a little bit of thought, this can be achieved using digital buffers (or inverters) to introduce a time delay into the switching signals applied to the switches SW1 and SW2 shown in Figure 3. Typical gates have 2-10ns propagation delay, but programmable logic

devices such as a complex programmable logic device (CPLD) or field programmable gate array (FPGA) can be programmed with variable propagation delay. Figure 4 demonstrates the signal treatment required to generate a pair of signals, S' and $!S \& \& !S''$ correspondingly to switches SW1, SW2 with the required time delay spacing, with the only inputs being a pulse-width modulated signal, S , and a time delay, t_{delay} . $S'(t) = S(t+t_{\text{delay}})$ and $S''(t) = S(t+2*t_{\text{delay}})$. In Figure 4, it is assumed that a switch is “closed”, i.e., conducting, when the switching signal is high and “open”, i.e., non-conducting when the switching signal is low. In Figure 4, S is an input PWM input signal. S' is the input signal S delayed by t_{delay} . S'' is S' delayed by $2*t_{\text{delay}}$, $!S$ is the inverse of the input signal S , $!S''$ is the inverse of signal S'' , and $!S \& \& !S''$ is the logical AND of $!S$ with $!S''$.

When deciding between synchronous or non-synchronous it is important to consider the efficiency losses due to switching (e.g., energy needed to move charge on and off the gate of a MOSFET) and those due to conduction through the diode. Synchronous converters tend to have an advantage in high-ratio conversion. They are also a fundamental building block of the split-pi-bidirectional converter because the extra switches are needed to provide dual-purpose buck or boost.

In the off-state, the boost converter delivers the supply voltage directly to the load through the second switch element SW2 in Figure 5. The process of increasing the voltage to the load is started by opening the switching element SW2 and closing the switching element SW1 (Figure 6). Due to the additional voltage drop on inductor $L1$, current flowing through inductor $L1$ will increase over time (see, equation (2)).

$$i(t) - i(t_0) = \frac{1}{L1} \int_{t_0}^t v(t) dt, \quad (2)$$

When the circuit is returned to the “OFF” state, the inductor will attempt to maintain the same current that it had before by increasing its voltage drop proportional to the change in current (see, equation (3)).

$$v(t) = L1 \frac{di(t)}{dt}, \quad 3)$$

In the “off state” the switching element SW2 is closed so that this increased voltage gets translated to the output capacitor. The output capacitor provides filtering; averaging between V_{in} and the inductor’s voltage spikes.

N-channel MOSFET (NMOS), P-channel MOSFET (PMOS), and push-pull complementary metal oxide semiconductor (CMOS) topologies of a stacked MOSFET for fully integrated implementations in Honeywell's 150nm SOI Radiation Hardened process described in following paper (Jennifer E et al., "High-Voltage Switching Circuit for Nanometer Scale CMOS Technologies" Manuscript received April 30, 2007), which is incorporated herein by reference. The stacked MOSFET is a high-voltage switching circuit. A low-voltage input signal turns on the first MOSFET in a stack of MOSFET devices, and the entire stack of devices is turned on by charge injection through parasitic and inserted capacitances. Voltage division provides both static and dynamic voltage balancing, preventing any device in the circuit from exceeding its nominal operating voltage. The design equations for these topologies are presented. Simulations for a five device stack implemented in Honeywell's 150 nm process verify the static and dynamic voltage balancing of the output signal. The simulated stack is shown to handle five times the nominal operating voltage.

An example of a reliable circuit configuration for stacking power metal-oxide semiconductor field effect transistors (MOSFETs) is described, e.g., in R. J. Baker and B. P. Johnson, "Stacking Power MOSFETs for Use in High Speed Instrumentation", Rev. Sci. Instrum., Vol. 63, No. 12, December 1992, pp. 799 – 801, which is incorporated herein by reference. The resulting circuit has a hold off voltage N times larger than a single power MOSFET, where N is the number of power MOSFETs used. The capability to switch higher voltages and thus greater amounts of power, into a 50 ohm load, in approximately the same time as a single device is realized. Design considerations are presented for selecting a power MOSFET. Using the design method presented, a 1.4 kV pulse generator, into SO 50 ohm, with a 2 ns rise time and negligible jitter is designed.

Another voltage switching circuit configuration is based on an Integrated Gate-Commutated Thyristor (IGCT). The integration of a 10-kV-IGCT and a fast diode in one press pack is an attractive solution for Medium Voltage Converters in a voltage range of 6 kV – 7.2 kV if the converter power rating does not exceed about 5 – 6MVA. (see, Sven Tschirley et al., "Design and Characteristics of Reverse Conducting 10-kV-IGCTs", Proceedings of the 39th annual Power Electronics Specialist Conference, pages 92-98, 2008, which is incorporated herein by reference). Tschirley et al describe the design and characterization of the world's first reverse conducting 68mm 10-kV-IGCTs. On-state-, blocking and switching behavior of different IGCT and diode samples are investigated experimentally. The experimental results clearly show, that 10-kV-RC-IGCTs are an attractive power semiconductor for 6 – 7.2 kV Medium Voltage Converters.

Capacitors with high volumetric energy density, high operating temperature, low equivalent series resistance (ESR), and long lifetime are critical components for pulse-power, automotive, and industrial electronics. The physical characteristics of the dielectric material in the capacitor are the primary determining factors for the performance of a capacitor. Accordingly, improvements in one or more of the physical properties of the dielectric material in a capacitor can result in corresponding performance improvements in the capacitor component, usually resulting in performance and lifetime enhancements of the electronics system or product in which it is embedded. Since improvements in capacitor dielectric can directly influence product size, product reliability, and product efficiency, there is a high value associated with such improvements.

Compared to batteries, capacitors are able to store energy with very high power density, i.e. charge/recharge rates, have long shelf life with little degradation, and can be charged and discharged (cycled) hundreds of thousands or millions of times. However, capacitors often do not store energy in small volume or weight as in case of a battery, or at low energy storage cost, which makes capacitors impractical for some applications, for example electric vehicles. Accordingly, it may be an advance in energy storage technology to provide capacitors of higher volumetric and mass energy storage density and lower cost.

SUMMARY

Aspects of the present disclosure address problems with conventional rechargeable electrical energy storage technology by combining a capacitive energy storage device having one or more meta-capacitors (further described below) with a DC-voltage conversion device having one or more switch mode voltage converters coupled to the terminals of the capacitive energy storage device. Meta-capacitors have greater energy storage capacity than conventional ultracapacitors or supercapacitors. The DC-voltage conversion device regulates the voltage on the capacitive energy storage device during charging and discharging.

As used herein, a meta-capacitor is a dielectric film capacitor whose dielectric film is a meta-dielectric material, which is disposed between a first electrode and second electrode. In one embodiment, said electrodes are flat and planar and positioned parallel to each other. In another embodiment, the meta-capacitor comprises two rolled metal electrodes positioned parallel to each other. Additionally, a meta-dielectric material comprises of Sharp polymers and/or Furuta polymers.

The present disclosure provides an energy storage cell comprising a capacitive energy storage device having one or more meta-capacitors and a DC-voltage conversion device having

one or more switch mode voltage converters. The power port (consisting of a positive terminal and a negative terminal, or anode and cathode) on the capacitive energy storage device is connected to the capacitor-side power port on the DC-voltage conversion device. The DC-voltage conversion device has one or more other power ports, which may interface to external circuitry. The power ports are intended to convey power with associated current and voltage commiserate to the specification for the cell. Each terminal in the port is a conductive interface. Each cell may include means to monitor and/or control parameters such as voltage, current, temperature, and other important aspects of the DC-voltage conversion device.

In one aspect, a capacitive energy storage module may include one or more individual capacitive energy storage cells and one or more power buses consisting of an interconnection system, wherein a power bus connects the power ports of the individual energy storage cells, in parallel or series, to create common module power ports consisting of common anode(s) and common cathode(s) of the capacitive energy storage module. The module may have additional sensors to monitor temperature, module power, voltage and current of the interconnection system, and may include a communication bus and/or communication bus protocol translator to convey these sensor values as well as the values from the individual cells.

In another aspect, a capacitive energy storage system may include one or more of the aforementioned capacitive energy storage modules, an interconnection system and a system control computer that monitors, processes, and controls all the values on the aforementioned communication bus.

Additional aspects and advantages of the present disclosure will become readily apparent to those skilled in this art from the following detailed description, wherein only illustrative embodiments of the present disclosure are shown and described. As will be realized, the present disclosure is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, all without departing from the disclosure. Accordingly, the drawings and description are to be regarded as illustrative in nature, and not as restrictive.

INCORPORATION BY REFERENCE

All publications, patents, and patent applications mentioned in this specification are herein incorporated by reference to the same extent as if each individual publication, patent, or patent application was specifically and individually indicated to be incorporated by reference.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 schematically shows the buck conversion device based on the switched LC filter.

Figure 2 schematically shows the non-synchronous buck conversion device.

Figure 3 schematically shows the synchronous buck conversion device.

Figure 4 demonstrates the signal treatment required to generate a pair of signals with the required time delay spacing.

Figure 5 schematically shows a boost converter in an “on state”.

Figure 6 schematically shows a boost converter in an “off state”.

Figure 7A shows a capacitive energy storage device containing a single capacitive element connected to a two terminal port.

Figure 7B shows an alternative configuration of a capacitive energy storage device containing multiple elements connected to a two terminal port.

Figure 7C shows an alternative configuration of a capacitive energy storage device containing multiple elements connected to a two terminal port.

Figure 7D shows an alternative configuration of a capacitive energy storage device containing multiple elements connected to a two terminal port.

Figure 8A schematically shows a switch-mode voltage converter implementing a standard boost circuit.

Figure 8B schematically shows a switch-mode voltage converter implementing a standard buck circuit.

Figure 8C schematically shows a switch-mode voltage converter implementing a standard inverting buck/boost circuit.

Figure 8D schematically shows a switch-mode voltage converter implementing a standard non-inverting and bi-directional buck/boost circuit.

Figure 9A schematically shows a DC-voltage conversion device having two power ports and separate one or more boost and one or more buck converters for charging a meta-capacitor and separate one or more boost and one or more buck converters for discharging the meta-capacitor.

Figure 9B schematically shows an alternative DC-voltage conversion device having two power ports and a one or more buck converters for charging a meta-capacitor and one or more buck boost converter for the discharging the meta-capacitor.

Figure 9C schematically shows another alternative DC-voltage conversion device having two power ports and one or more boost converters for the charge and one or more buck converters for discharging a meta-capacitor.

Figure 9D schematically shows another alternative DC-voltage conversion device having two power ports and one or more buck/boost converters for charging a meta-capacitor and one or more buck/boost converters for discharging the meta-capacitor.

Figure 9E schematically shows yet another DC-voltage conversion device having two power ports and one or more bidirectional boost/buck converters for the charging and discharging a meta-capacitor.

Figure 9F schematically shows still another DC-voltage conversion device having three power ports and separate one or more boost and one or more buck converters for charging a meta-capacitor and separate one or more boost and one or more buck converters for discharging the meta-capacitor.

Figure 9G schematically shows another DC-voltage conversion device having three power ports and a one or more buck converters for charging a meta-capacitor and one or more buck boost converter for discharging the meta-capacitor.

Figure 9H schematically shows another DC-voltage conversion device having three power ports and one or more buck/boost converters for charging a meta-capacitor and one or more buck/boost converters for discharging a meta-capacitor.

Figure 9I schematically shows yet another DC-voltage conversion device having three power ports and one or more bidirectional boost/buck converters for the charging and discharging a meta-capacitor.

Figure 10 schematically shows an energy storage cell according to aspects of the present disclosure.

Figure 10A schematically shows a meta-capacitor with flat and planar electrodes according to aspects of the present disclosure.

Figure 10B schematically shows a meta-capacitor with rolled (circular) electrodes according to aspects of the present disclosure.

Figure 11 schematically shows an energy storage cell according to an alternative aspect of the present disclosure.

Figure 12 schematically shows an energy storage cell according to an alternative aspect of the present disclosure.

Figure 13A shows a constant voltage $V_i(t)$ feeding the input of a converter and voltage $V_c(t)$ on the capacitive energy storage device during charge as the converter transitions from buck to boost in accordance with aspects of the present disclosure.

Figure 13B shows a constant voltage $V_o(t)$ extracted from the output side of a converter and voltage $V_c(t)$ on the capacitive energy storage device during discharge as the converter transitions from buck to boost in accordance with aspects of the present disclosure.

Figure 14A shows a constant voltage $V_i(t)$ feeding the input of a converter and voltage $V_c(t)$ on the capacitive energy storage device during charge when $V_{min,op}=V_i(t)$ in accordance with aspects of the present disclosure.

Figure 14B shows a constant voltage $V_o(t)$ extracted from the output side of a converter and voltage $V_c(t)$ on the capacitive energy storage device during discharge when $V_{min,op}=V_i(t)$ in accordance with aspects of the present disclosure.

Figure 15A shows an example of a single switch buck-boost converter that may be implemented in a switch-mode voltage converter, which could be selected for use in a DC voltage conversion device in an energy storage cell according to aspects of the present disclosure.

Figure 15B shows an example of a four switch buck-boost converter that may be implemented in a switch-mode voltage converter, which could be selected for use in a DC voltage conversion device in an energy storage cell according to aspects of the present disclosure.

Figure 16 shows an example of a capacitive energy storage module having two or more networked energy storage cells according to an alternative aspect of the present disclosure.

Figure 17 shows an example of a capacitive energy storage system having two or more energy storage networked modules according to an alternative aspect of the present disclosure.

DETAILED DESCRIPTION

While various embodiments of the invention have been shown and described herein, it will be obvious to those skilled in the art that such embodiments are provided by way of example only. Numerous variations, changes, and substitutions may occur to those skilled in the art without departing from the invention. It should be understood that various alternatives to the embodiments of the invention described herein may be employed.

The present disclosure provides an energy storage cell comprising at least one capacitive energy storage device and a DC-voltage conversion device. Figure 10 schematically shows a capacitive energy storage cell 1 comprising a capacitive energy storage device 2 that includes one or more meta-capacitors 20 and a DC-voltage conversion device 3, consisting of one or more switch-mode voltage converters 100, e.g. a buck converter, boost converter, buck/boost converter, bi-directional buck/boost (split-pi) converter, Ćuk converter, SEPIC converter, inverting buck/boost converter, or four-switch buck/boost converter.

As used herein, a meta-capacitor is a capacitor comprising of a dielectric film that is a meta-dielectric material, which is disposed between a first electrode and second electrode. In one embodiment, said electrodes are flat and planar and positioned parallel to each other as shown in Figure 10A. In another embodiment, the meta-capacitor comprises two rolled metal electrodes positioned parallel to each other as shown in Figure 10B.

According to an aspect of the present disclosure a meta-capacitor may be configured as shown in Figure 10A. The meta-capacitor comprises a first electrode 21, a second electrode 22, and a meta-dielectric layer 23 disposed between said first and second electrodes. The electrodes 21 and 22 may be made of a metal, such as copper, zinc, or aluminum or other conductive material and are generally planar in shape.

The electrodes 21, 22 may be flat and planar and positioned parallel to each other. Alternatively, the electrodes may be planar and parallel, but not necessarily flat, e.g., they may be coiled, rolled, bent, folded, or otherwise shaped to reduce the overall form factor of the capacitor. It is also possible for the electrodes to be non-flat, non-planar, or non-parallel or some combination of two or more of these. By way of example and not by way of limitation, a spacing d between the electrodes 21, 22, which may correspond to the thickness of the Composite Dielectric Film layer 23, may range from about 100 nm to about 10,000 μm . As noted in Equation (4) below, the maximum voltage V_{bd} between the electrodes 21, 22 is approximately the product of the breakdown field E_{bd} and the electrode spacing d .

$$V_{bd}=E_{bd}d \quad (4)$$

For example, if, $E_{bd} = 0.1$ V/nm and the spacing d between the electrodes 1, 2 is 10,000 microns (100,000 nm), the maximum voltage V_{bd} would be 100,000 volts.

The electrodes 21, 22 may have the same shape as each other, the same dimensions, and the same area A . By way of example, and not by way of limitation, the area A of each electrode 1021, 1022 may range from about 0.01 m^2 to about 1000 m^2 . By way of example and not by way of limitation, for rolled capacitors, the electrodes may be up to, e.g., 1000 m long and 1 m wide.

These ranges are non-limiting. Other ranges of the electrode spacing d and area A are within the scope of the aspects of the present disclosure.

If the spacing d is small compared to the characteristic linear dimensions of electrodes (e.g., length and/or width), the capacitance C of the capacitor may be approximated by the formula:

$$C = \kappa \epsilon_0 A / d, \quad (5)$$

where ϵ_0 is the permittivity of free space (8.85×10^{-12} Coulombs²/(Newton·meter²)) and κ is the dielectric constant of the dielectric layer. The energy storage capacity U of the capacitor may be approximated as:

$$U = \frac{1}{2} C V_{bd}^2 \quad (6)$$

which may be rewritten using equations (4) and (5) as:

$$U = \frac{1}{2} \kappa \epsilon_0 A E_{bd}^2 \quad (7)$$

The energy storage capacity U is determined by the dielectric constant κ , the area A , and the breakdown field E_{bd} . By appropriate engineering, a capacitor or capacitor bank may be designed to have any desired energy storage capacity U . By way of example, and not by way of limitation, given the above ranges for the dielectric constant κ , electrode area A , and breakdown field E_{bd} a capacitor in accordance with aspects of the present disclosure may have an energy storage capacity U ranging from about 500 Joules to about 2×10^{16} Joules.

For a dielectric constant κ ranging, e.g., from about 100 to about 1,000,000 and constant breakdown field E_{bd} between, e.g., about 0.1 and 0.5 V/nm, a capacitor of the type described herein may have a specific energy capacity per unit mass ranging from about 10 W·h/kg up to about 100,000 W·h/kg, though implementations are not so limited.

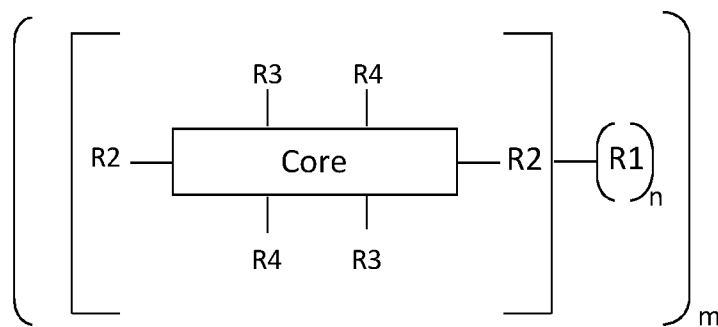
Aspects of the present disclosure include the use of meta-capacitors that are coiled, e.g., as depicted in Figure 10B. In this example, a meta-capacitor 20 comprises a first electrode 21, a second electrode 22, and a meta-dielectric material layer 23 of one or more of the types described hereinabove disposed between said first and second electrodes. The electrodes 21, 22 may be made of a metal, such as copper, zinc, or aluminum or other conductive material and are generally planar in shape. In one implementation, the electrodes and meta-dielectric material layer 23 are in the form of long strips of material that are sandwiched together and wound into a coil along with an insulating material, e.g., a plastic film such as polypropylene or polyester to prevent electrical shorting between the electrodes 21, 22. Examples of such coiled capacitor energy storage devices are described in detail in commonly-assigned U.S. Patent Application Number 14/752,600, filed June 26, 2015, which has been published as U.S. Patent Application Publication Number 2016/0379757, the entire contents of which are incorporated herein by reference.

Said meta-dielectric materials are comprised of composite molecules having supra-structures formed from polymers. Examples of said polymers include so-called Sharp polymers and so-called Furuta co-polymers and so-called para-Furuta polymers as described in detail in commonly-assigned US Patent Application Numbers 15/043,247 (Attorney Docket No. CSI-046 and 15/043,186 (Attorney Docket No. CSI-019A), and 15/043,209 (Attorney Docket No. CSI-019B), respectively, all filed February 12, 2016, the entire contents of which are incorporated herein by reference. Furuta co-polymers and para-Furuta polymers are referred to collectively as Furuta polymers.

Sharp Polymers

Sharp polymers are composites of a polarizable core inside an envelope of hydrocarbon (saturated and/or unsaturated), fluorocarbon, chlorocarbon, siloxane, and/or polyethylene glycol as linear or branched chain oligomers covalently bonded to the polarizable core that act to insulate the polarizable cores from each other, which favorably allows discrete polarization of the cores with limited or no dissipation of the polarization moments in the cores. The polarizable core has hyperelectronic or ionic type polarizability. “Hyperelectronic polarization may be considered due to the pliant interaction of charge pairs of excitons, localized temporarily on long, highly polarizable molecules, with an external electric field [.] (Roger D. Hartman and Herbert A. Pohl, “Hyper-electronic Polarization in Macromolecular Solids”, Journal of Polymer Science: Part A-1 Vol. 6, pp. 1135-1152 (1968)).” Ionic type polarization can be achieved by limited mobility of ionic parts of the core molecular fragment.

A Sharp polymer has a general structural formula:



Where Core is an aromatic polycyclic conjugated molecule comprising rylene fragments. This molecule has flat anisometric form and self-assembles by pi-pi stacking in a column-like supramolecule. The substitute R1 provides solubility of the organic compound in a solvent. The parameter n is number of substitutes R1, which is equal to 0, 1, 2, 3, 4, 5, 6, 7 or 8. The substitute R2 is an electrically resistive substitute located in terminal positions, which provides resistivity to electric current and comprises hydrocarbon (saturated and/or unsaturated), fluorocarbon, siloxane, and/or polyethyleneglycol as linear or branched chains. The substitutes R3 and R4 are substitutes located on side (lateral) positions (terminal and/or bay positions) comprising one or more ionic groups from a class of ionic compounds that are used in ionic liquids connected to the aromatic polycyclic conjugated molecule (Core), either directly, e.g., with direct bound SP2-SP3 carbons, or via a connecting group. The parameter m is a number of the aromatic polycyclic conjugated molecules in the column-like supramolecule, which is in a range from 3 to 100 000.

In another embodiment of the composite organic compound, the aromatic polycyclic conjugated molecule comprises an electro-conductive oligomer, such as a phenylene, thiophene, or polyacene quinine radical oligomer or combinations of two or more of these. In yet another embodiment of the composite organic compound, the electro-conductive oligomer is selected from phenylene, thiophene, or substituted and/or unsubstituted polyacene quinine radical oligomer of lengths ranging from 2 to 12, or combination of two or more of these. Wherein the substitutions of ring hydrogens by O, S or NR5, and R5 is selected from the group consisting of unsubstituted or substituted C₁-C₁₈alkyl, unsubstituted or substituted C₂-C₁₈alkenyl, unsubstituted or substituted C₂-C₁₈alkynyl, and unsubstituted or substituted C₄-C₁₈ aryl.

In some embodiments, the substitute providing solubility (R1) of the composite organic compound is C_XQ_{2X+1}, where X ≥ 1 and Q is hydrogen (H), fluorine (F), or chlorine (Cl). In still another embodiment of the composite organic compound, the substitute providing solubility (R1) of the composite organic compound is independently selected from alkyl, aryl, substituted alkyl,

substituted aryl, fluorinated alkyl, chlorinated alkyl, branched and complex alkyl, branched and complex fluorinated alkyl, branched and complex chlorinated alkyl groups, and any combination thereof, and wherein the alkyl group is selected from methyl, ethyl, propyl, butyl, *iso*-butyl and *tert*-butyl groups, and the aryl group is selected from phenyl, benzyl and naphthyl groups or siloxane, and/or polyethylene glycol as linear or branched chains.

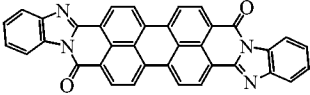
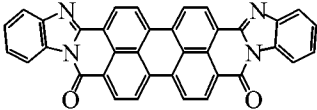
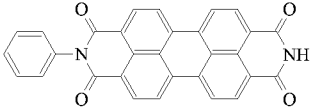
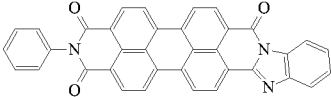
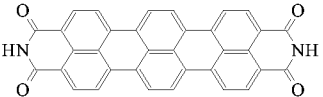
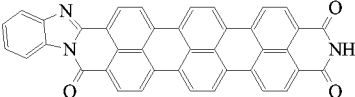
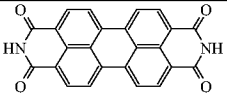
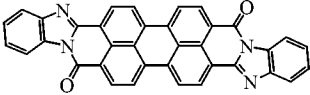
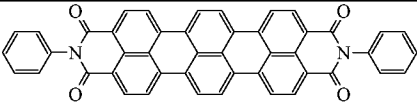
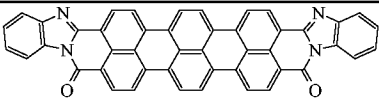
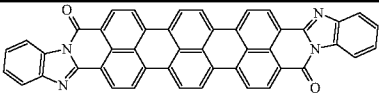
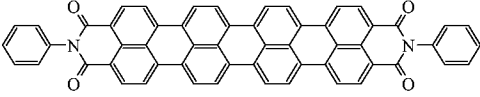
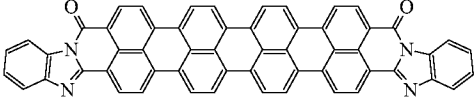
In some embodiments, at least one electrically resistive substitute (R2) of the composite organic compound is C_XQ_{2X+1} , where $X \geq 1$ and Q is hydrogen (H), fluorine (F), or chlorine (Cl). In another embodiment of the composite organic compound, at least one electrically resistive substitute (R2) is selected from the list comprising $-(CH_2)_n-CH_3$, $-CH((CH_2)_nCH_3)_2$ (where $n \geq 1$), alkyl, aryl, substituted alkyl, substituted aryl, branched alkyl, branched aryl, and any combination thereof and wherein the alkyl group is selected from methyl, ethyl, propyl, butyl, *iso*-butyl and *tert*-butyl groups, and the aryl group is selected from phenyl, benzyl and naphthyl groups. In yet another embodiment of the composite organic compound.

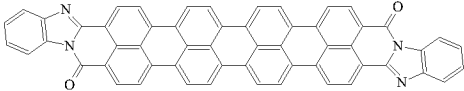
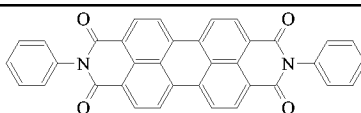
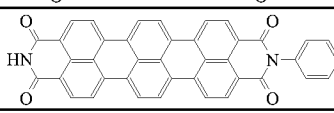
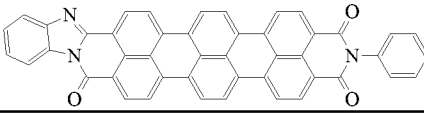
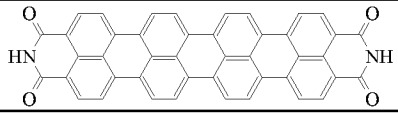
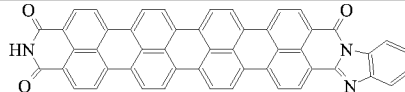
In some embodiments, the substitute R1 and/or R2 is connected to the aromatic polycyclic conjugated molecule (Core) via at least one connecting group. The at least one connecting group may be selected from the list comprising the following structures: ether, amine, ester, amide, substituted amide, alkenyl, alkynyl, sulfonyl, sulfonate, sulfonamide, or substituted sulfonamide.

In some embodiments, the substitute R3 and/or R4 may be connected to the aromatic polycyclic conjugated molecule (Core) via at least one connecting group. The at least one connecting group may be selected from the list comprising CH_2 , CF_2 , SiR_2O , CH_2CH_2O , wherein R is selected from the list comprising H, alkyl, and fluorine. In another embodiment of the composite organic compound, the one or more ionic groups include at least one ionic group selected from the list comprising $[NR_4]^+$, $[PR_4]^+$ as cation and $[-CO_2]^-$, $[-SO_3]^-$, $[-SR_3]^-$, $[-PO_3R]^-$, $[-PR_5]^-$ as anion, wherein R is selected from the list comprising H, alkyl, and fluorine.

Specifically, one aspect of the present disclosure provides a Sharp polymer in the form of a composite organic compound. In one embodiment of the composite organic compound, the aromatic polycyclic conjugated molecule (Core) comprises rylene fragments. In another embodiment of the composite organic compound, the rylene fragments are selected from structures 1 to 21 as given in Table 1.

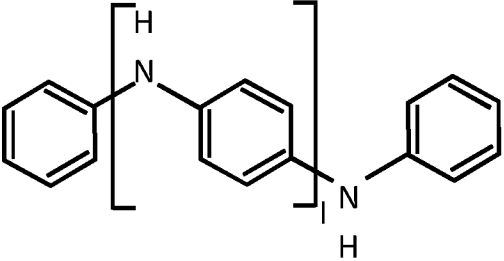
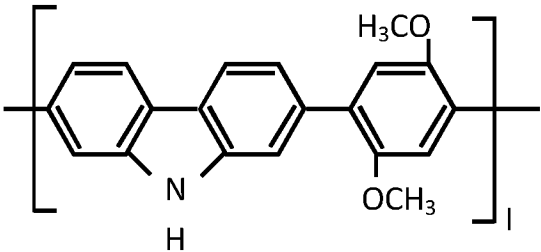
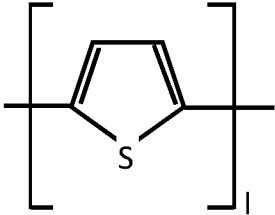
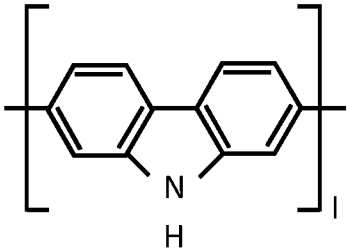
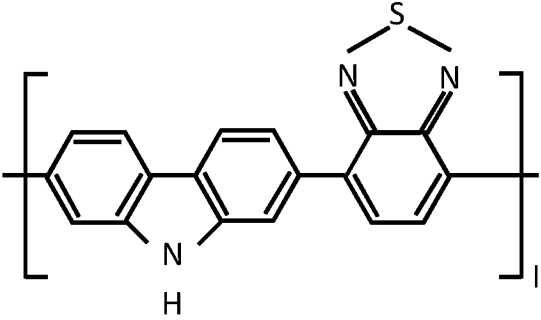
Table 1. Examples of the polycyclic organic molecule (Core) comprising rylene fragments

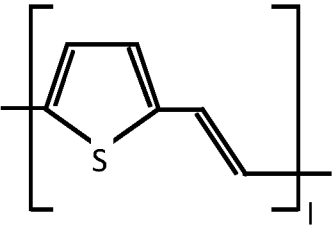
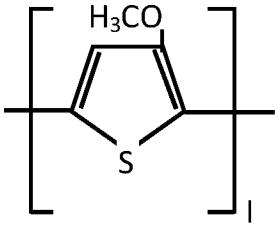
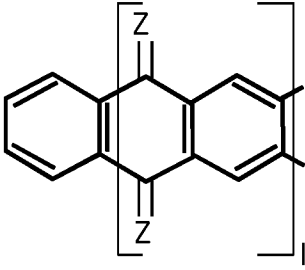
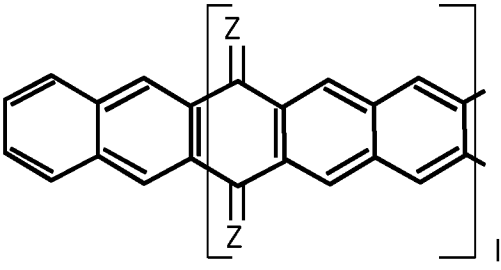
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In another embodiment of the composite organic compound, the aromatic polycyclic conjugated molecule comprises an electro-conductive oligomer, such as a phenylene, thiophene, or polyacene quinine radical oligomer or combinations of two or more of these. In yet another embodiment of the composite organic compound, the electro-conductive oligomer is selected from structures 22 to 30 as given in Table 2, wherein I = 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12, Z is =O, =S or =NR⁵, and R⁵ is selected from the group consisting of unsubstituted or substituted C1-C18alkyl, unsubstituted or substituted C2-C18alkenyl, unsubstituted or substituted C2-C18alkynyl, and unsubstituted or substituted C4-C18aryl:

Table 2. Examples of the polycyclic organic molecule (Core) comprising electro-conductive oligomer

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In some embodiments, the substitute providing solubility (R1) of the composite organic compound is $CXQ2X+1$, where $X \geq 1$ and Q is hydrogen (H), fluorine (F), or chlorine (Cl). In still another embodiment of the composite organic compound, the substitute providing solubility (R1) of the composite organic compound is independently selected from alkyl, aryl, substituted alkyl, substituted aryl, fluorinated alkyl, chlorinated alkyl, branched and complex alkyl, branched and complex fluorinated alkyl, branched and complex chlorinated alkyl groups, and

any combination thereof, and wherein the alkyl group is selected from methyl, ethyl, propyl, butyl, iso-butyl and tert-butyl groups, and the aryl group is selected from phenyl, benzyl and naphthyl groups or siloxane, and/or polyethyleneglycol as linear or branched chains.

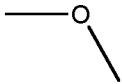
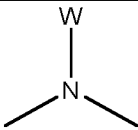
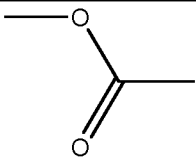
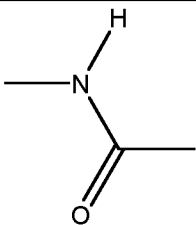
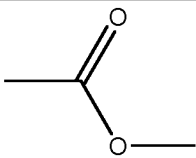
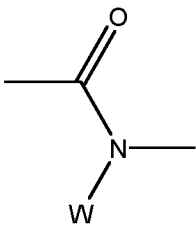
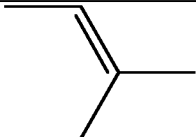
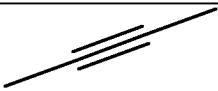
In one embodiment of the composite organic compound, the solvent is selected from benzene, toluene, xylenes, acetone, acetic acid, methylethylketone, hydrocarbons, chloroform, carbontetrachloride, methylenechloride, dichlorethane, chlorobenzene, alcohols, nitromethan, acetonitrile, dimethylforamide, 1,4-dioxane, tetrahydrofuran (THF), methylcyclohexane (MCH), and any combination thereof.

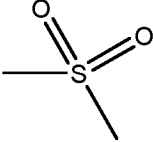
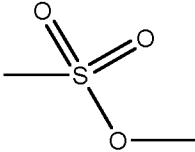
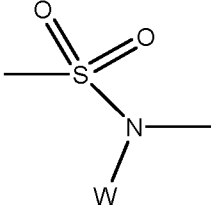
In some embodiments, at least one electrically resistive substitute (R2) of the composite organic compound is $CXQ2X+1$, where $X \geq 1$ and Q is hydrogen (H), fluorine (F), or chlorine (Cl). In another embodiment of the composite organic compound, at least one electrically resistive substitute (R2) is selected from the list comprising $-(CH_2)_n-CH_3$, $-CH((CH_2)_n-CH_3)_2$ (where $n \geq 1$), alkyl, aryl, substituted alkyl, substituted aryl, branched alkyl, branched aryl, and any combination thereof and wherein the alkyl group is selected from methyl, ethyl, propyl, butyl, I- butyl and t-butyl groups, and the aryl group is selected from phenyl, benzyl and naphthyl groups.

In some embodiments, at least one electrically resistive substitute (R2) is selected from the group of alkyl, aryl, substituted alkyl, substituted aryl, fluorinated alkyl, chlorinated alkyl, branched and complex alkyl, branched and complex fluorinated alkyl, branched and complex chlorinated alkyl groups, and any combination thereof, and wherein the alkyl group is selected from methyl, ethyl, propyl, n-butyl, iso-butyl and tert-butyl groups, and the aryl group is selected from phenyl, benzyl and naphthyl groups or siloxane, and/or polyethyleneglycol as linear or branched chains.

In some embodiments, the substitute R1 and/or R2 is connected to the aromatic polycyclic conjugated molecule (Core) via at least one connecting group. The at least one connecting group may be selected from the list comprising the following structures: 31-41 as given in Table 3, where W is hydrogen (H) or an alkyl group.

Table 3. Examples of the connecting group

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In some embodiments, the substitute R3 and/or R4 may be connected to the aromatic polycyclic conjugated molecule (Core) via at least one connecting group. The at least one connecting group may be selected from the list comprising CH₂, CF₂, SiR₂O, CH₂CH₂O, wherein R is selected from the list comprising H, alkyl, and fluorine. In another embodiment of the composite organic compound, the one or more ionic groups include at least one ionic group selected from the list comprising [NR₄]⁺, [PR₄]⁺ as cation and [–CO₂][–], [–SO₃][–], [–SR₅][–], [–PO₃R][–], [–PR₅][–] as anion, wherein R is selected from the list comprising H, alkyl, and fluorine.

The Sharp polymers have hyperelectronic or ionic type polarizability. “Hyperelectronic polarization may be considered due to the pliant interaction of charge pairs of excitons, localized temporarily on long, highly polarizable molecules, with an external electric field [.] (Roger D. Hartman and Herbert A. Pohl, “Hyper-electronic Polarization in Macromolecular Solids”, Journal of Polymer Science: Part A-1 Vol. 6, pp. 1135-1152 (1968)).” Ionic type polarization can be achieved by limited mobility of ionic parts of the tethered/partially immobilized ionic liquid or zwitterion (Q). Additionally, other mechanisms of polarization such as dipole polarization and monomers and polymers possessing metal conductivity may be used independently or in combination with hyper-electronic and ionic polarization in aspects of the present disclosure.

In another aspect, the present disclosure provides a meta-dielectric, wherein a meta-dielectric is a dielectric that includes one or more Sharp polymers in the form of a composite organic compound characterized by polarizability and resistivity.

Further, characteristics of meta-dielectrics include a relative permittivity greater than or equal to 1,000 and resistivity greater than or equal to 10^{13} ohm/cm. Individually, the Sharp Polymers in a meta-dielectric may form column like supramolecular structures by pi-pi interaction. Said supramolecules of Sharp polymers allow formation of crystal structures of the meta-dielectric material. By way of using Sharp polymers in a dielectric material, polarization units are incorporated to provide the molecular material with high dielectric permeability. There are several mechanisms of polarization such as dipole polarization, ionic polarization, and hyper-electronic polarization of molecules, monomers and polymers possessing metal conductivity. All polarization units with the listed types of polarization may be used in aspects of the present disclosure. Further, Sharp polymers are composite materials which incorporate an envelope of insulating substituent groups that electrically isolate the supramolecules from each other in the dielectric crystal layer and provide high breakdown voltage of the energy storage molecular material. Said insulating substituent groups are resistive alkyl or fluoro-alkyl chains covalently bonded to a polarizable core, forming the resistive envelope.

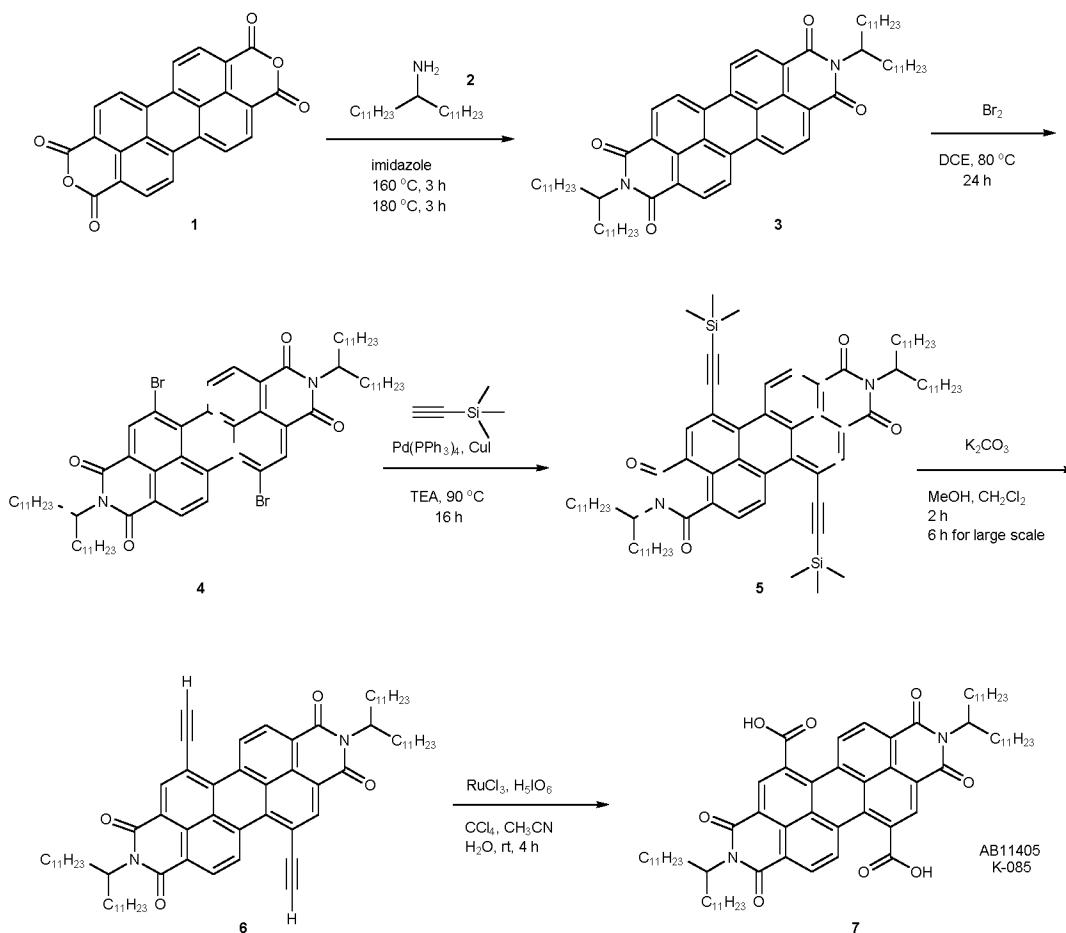
In order that the disclosure with respect to Sharp polymers may be more readily understood, reference is made to the following examples, which are intended to be illustrative of the invention, but are not intended to be limiting the scope.

Example 1

This Example describes synthesis of one type of Sharp polymer according following structural scheme:

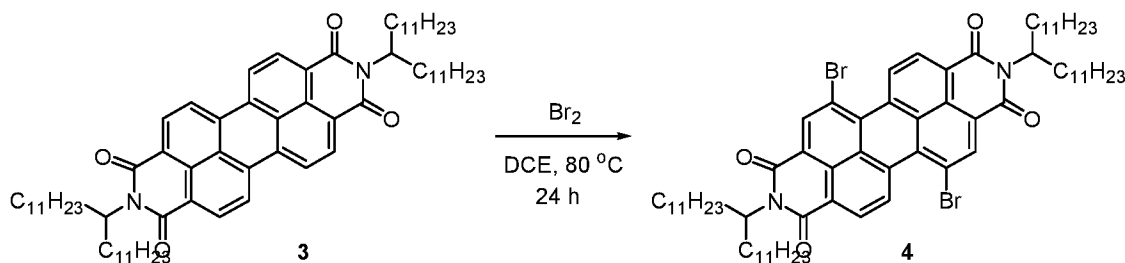
The process involved in the synthesis in this example may be understood in terms of the following five steps.

a) First step:



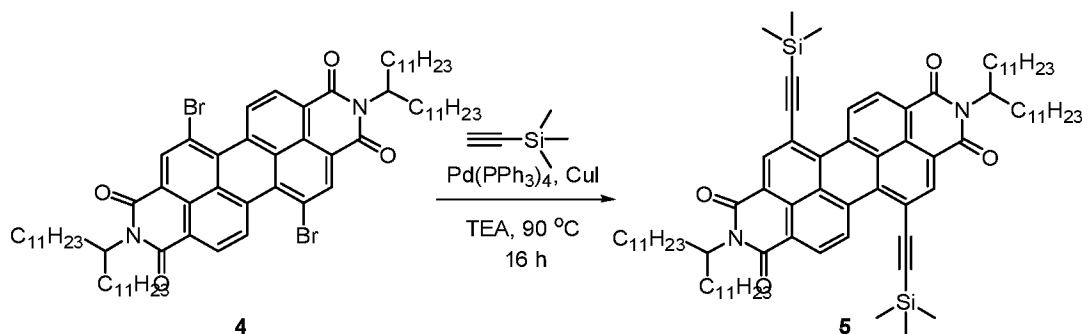
Anhydride **1** (60.0 g, 0.15 mol, 1.0 eq), amine **2** (114.4 g, 0.34 mol, 2.2 eq) and imidazole (686.0 g, 10.2 mol, 30 eq to **2**) were mixed well into a 500 mL of round-bottom flask equipped with a bump-guarder. The mixture was degassed three times, stirred at 160°C for 3 hr, 180°C for 3hr, and cooled to rt. The reaction mixture was crushed into water (1000 mL) with stirring. Precipitate was collected with filtration, washed with water (2x500 mL), methanol (2x300 mL) and dried on high vacuum. The crude product was purified by flash chromatography column ($\text{CH}_2\text{Cl}_2/\text{hexane} = 1/1$) to give 77.2 g (48.7 %) of the desired product **3** as an orange solid. ^1H NMR (300 MHz, CDCl_3) δ 8.65-8.59 (m, 8H), 5.20-5.16 (m, 2H), 2.29-2.22 (m, 4H), 1.88-1.82 (m, 4H), 1.40-1.13 (m, 64H), 0.88-0.81 (t, 12H). $R_f = 0.68$ ($\text{CH}_2\text{Cl}_2/\text{hexane} = 1/1$).

b) Second step:



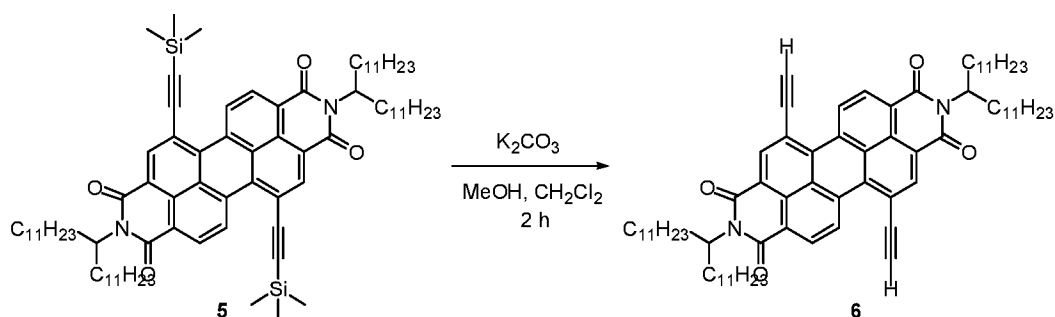
To a solution of the diimide **3** (30.0 g, 29.0 mmol, 1.0 eq) in dichloroethane (1500 mL) was added bromine (312.0 g, 1.95 mol, 67.3 eq). The resulting mixture was stirred at 80 °C for 36 hr, cooled, washed with 10 % NaOH (aq, 2x1000 mL), water (100 ml), dried over Na₂SO₄, filtered and concentrated. The crude product was purified by flash chromatography column (CH₂Cl₂/hexanes = 1/1) to give 34.0 g (98.2 %) of the desired product **4** as a red solid. ¹H NMR (300 MHz, CDCl₃) δ 9.52 (d, 2H), 8.91 (bs, 2H), 8.68 (bs, 2H), 5.21-5.13 (m, 2H), 2.31-2.18 (m, 4H), 1.90-1.80 (m, 4H), 1.40-1.14 (m, 64H), 0.88-0.81 (t, 12H). R_f = 0.52 (CH₂Cl₂/hexanes = 1/1).

c) Third step



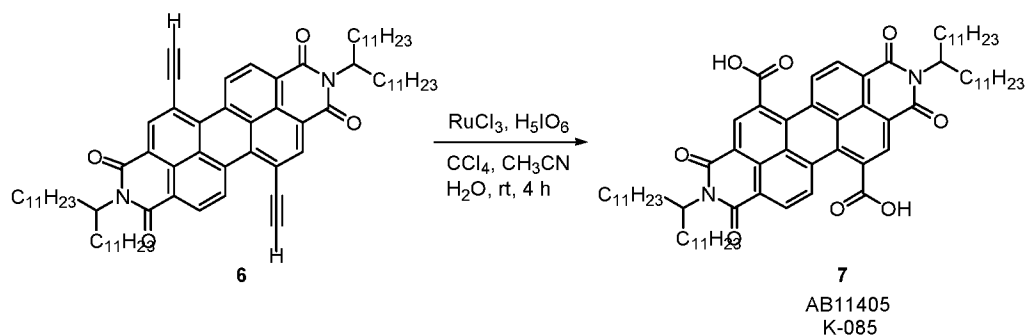
To a solution of the di-bromide **4** (2.0 g, 1.68 mmol, 1.0 eq) in triethylamine (84.0 mL) was added CuI (9.0 mg, 0.048 mmol, 2.8 mol %) and (trimethylsilyl)acetylene (80.49 g, 5.0 mmol, 3.0 eq). The mixture was degassed three times. Catalyst Pd(PPh₃)₄ (98.0 mg, 0.085 mmol, 5.0 mol %) was added. The mixture was degassed three times, stirred at 90 °C for 24 hr, cooled, passed through a pad of Celite, and concentrated. The crude product was purified by flash chromatography column (CH₂Cl₂/hexane = 1/1) to give 1.8 g (87.2 %) of the desired product **5** as a dark-red solid. ¹H NMR (300 MHz, CDCl₃) δ 10.24-10.19 (m, 2H), 8.81 (bs, 2H), 8.65 (bs, 2H), 5.20-5.16 (m, 2H), 2.31-2.23 (m, 4H), 1.90-1.78 (m, 4H), 1.40-1.15 (m, 72H), 0.84-0.81 (t, 12H), 0.40 (s, 18H). R_f = 0.72 (CH₂Cl₂/hexane = 1/1).

d) Fourth step



To a solution of diimide **5** (1.8 g, 1.5 mmol, 1.0 eq) in a mixture of MeOH/DCM (40.0 mL/40.0 mL) was added K_2CO_3 (0.81 g, 6.0 mmol, 4.0 eq). The mixture was stirred at room temperature for 1.5 hr, diluted with DCM (40.0 mL), washed with water, brine, dried over Na_2SO_4 , filtered and concentrated. The crude product was purified by flash chromatography column (CH_2Cl_2) to give 1.4 g (86.1 %) of the desired product **6** as a dark-red solid. ^1H NMR (300 MHz, CDCl_3) δ 10.04-10.00 (m, 2H), 8.88-8.78 (m, 2H), 8.72-8.60 (m, 2H), 5.19-5.14 (m, 2H), 3.82-3.80 (m, 2H), 2.31-2.23 (m, 4H), 1.90-1.78 (m, 4H), 1.40-1.05 (m, 72H), 0.85-0.41 (t, 12H). R_f = 0.62 (CH_2Cl_2).

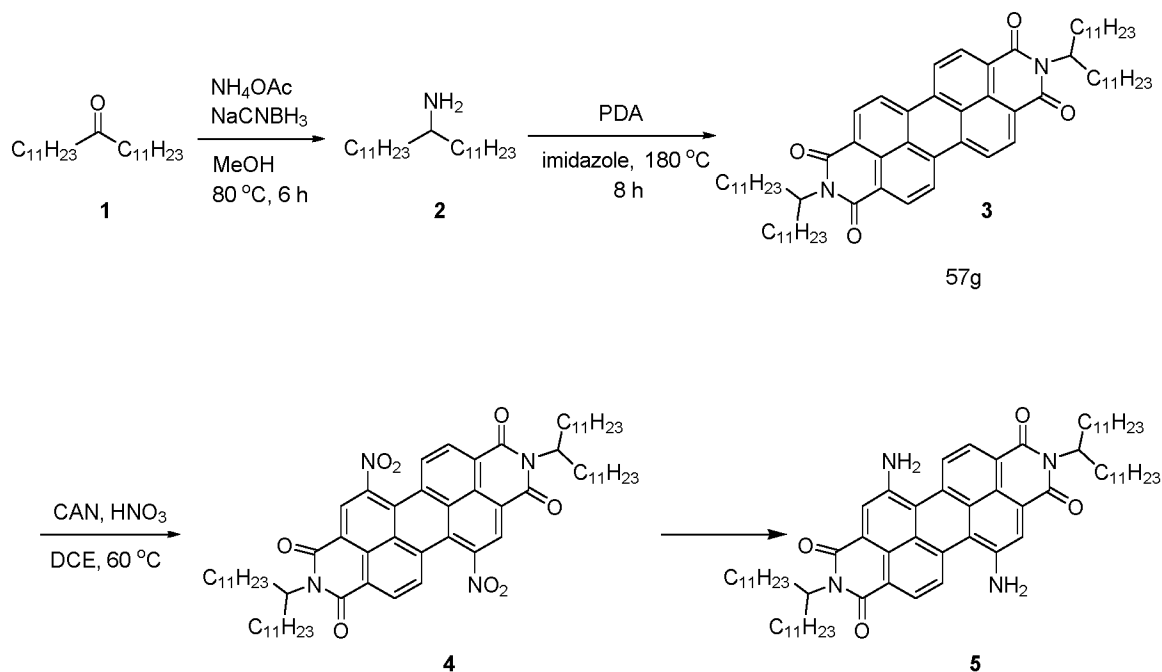
e) Fifth step



To a suspension of alkyne **6** (1.4 g, 1.3 mmol, 1.0 eq) in a mixture of $\text{CCl}_4/\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (6 mL/6 mL/12 mL) was added periodic acid (2.94 g, 12.9 mmol, 10.0 eq) and RuCl_3 (28.0 mg, 0.13 mmol, 10 mol %). The mixture was stirred at room temperature under nitrogen for 4 hours, diluted with DCM (50 mL), washed with water, brine, dried over Na_2SO_4 , filtered and concentrated. The crude product was purified by flash chromatography column (10 % MeOH/ CH_2Cl_2) to give 1.0 g (68.5 %) of the desired product **7** as a dark-red solid. ^1H NMR (300 MHz, CDCl_3) δ 8.90-8.40 (m, 6H), 5.17-5.00 (m, 2H), 2.22-2.10 (m, 4H), 1.84-1.60 (m, 4H), 1.41-0.90 (m, 72H), 0.86-0.65 (t, 12H). R_f = 0.51 (10 % MeOH/ CH_2Cl_2).

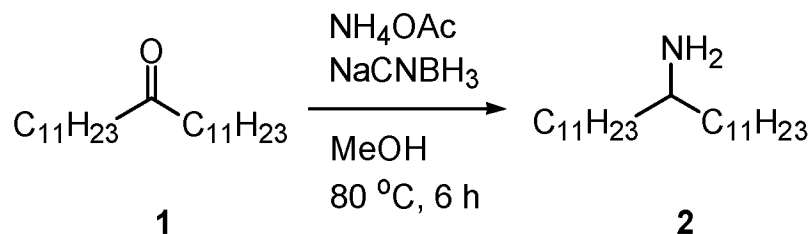
Example 2

This Example describes synthesis of a Sharp polymer according following structural scheme:



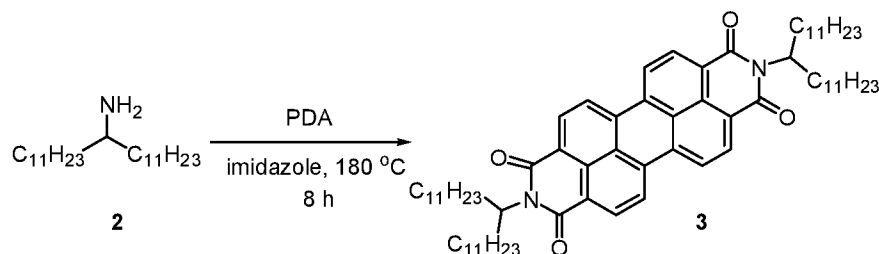
The process involved in the synthesis in this example may be understood in terms of the following four steps.

a) First step:



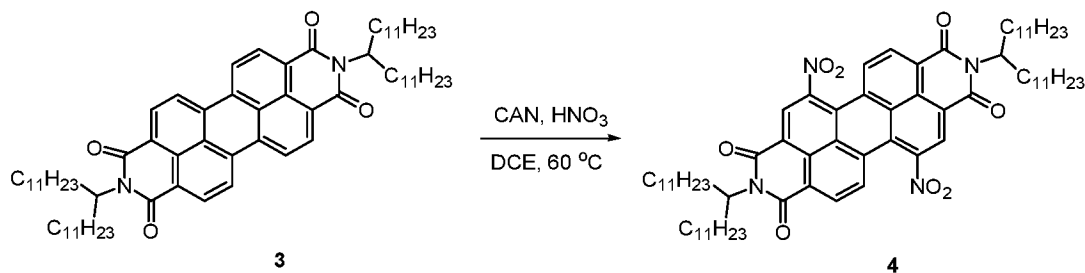
To a solution of the ketone **1** (37.0 g, 0.11 mol, 1.0 eq) in methanol (400 mL) was added ammonium acetate (85.3 g, 1.11 mol, 10.0 eq) and NaCNBH₃ (28.5 g, 0.44 mol, 4.0 eq) in portions. The mixture was stirred at reflux for 6 hours, cooled to room temperature and concentrated. Sat. NaHCO₃ (500 mL) was added to the residue and the mixture was stirred at room temperature for 1 hour. Precipitate was collected by filtration, washed with water (4 x 100 mL), dried on a high vacuum to give 33.6 g (87 %) of the amine **2** as a white solid.

b) Second step:



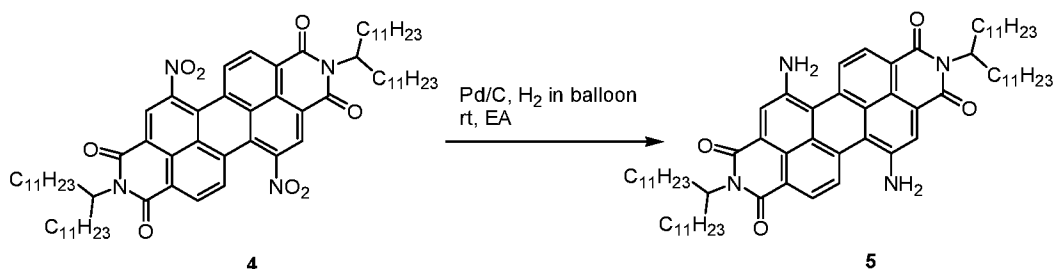
Mixed well the amine **2** (20.0 g, 58.7 mmol, 2.2 eq), 3,4,9,10-perylenetetracarboxylic dianhydride (10.5 g, 26.7 mmol, 1.0 eq) and imidazole (54.6 g, 0.80 mmol, 30 eq to diamine) into a 250 mL round-bottom flask equipped with a rotavap bump guard. The mixture was degased (vacuum and fill with N₂) three times and stirred at 160 °C for 6 hrs. After cooling to rt, the reaction mixture was crushed into water (700 mL), stirred for 1 hr, and filtered through a filter paper to collected precipitate which was washed with water (3 x 300 mL) and methanol (3 x 300 mL), dried on a high vacuum to give 23.1 g (83.5 %) of the diamidine **3** as a orange solid. Pure diamidine **3** (20.6 g) was obtained by flash chromatography column (DCM/hexanes = 1/1).

c) Third step:



To DCE (2.0 L) was added compound **3** (52.0 g, 50.2 mmol, 1.0 eq), acetic acid (500 mL) and fuming nitric acid (351.0 g, 5.0 mol, 100.0 eq) with caution. To the mixture was added ammonium cerium(IV) nitrate (137.0 g, 0.25 mol, 5.0 eq). The reaction was stirred at 60 °C for 48 hrs. After cooling to rt, the reaction mixture was crushed into water (1.0 L). The organic phase was washed with water (2 x 1.0 L), saturated NaHCO₃ solution (1 x 1.0 L) and brine (1 x 1.0 L), dried over sodium sulfate, filtered and concentrated. The residue was purified with column chromatography to give 46.7g (82%) of compound **4** as a dark red solid. ¹H NMR (300 MHz, CDCl₃) δ 0.84 (t, 12H), 1.26 (m, 72H), 1.83 (m, 4H), 2.21 (m, 4H), 5.19 (m, 2H), 8.30 (m, 2H), 8.60 - 8.89 (m, 4H).

d) Fourth step:



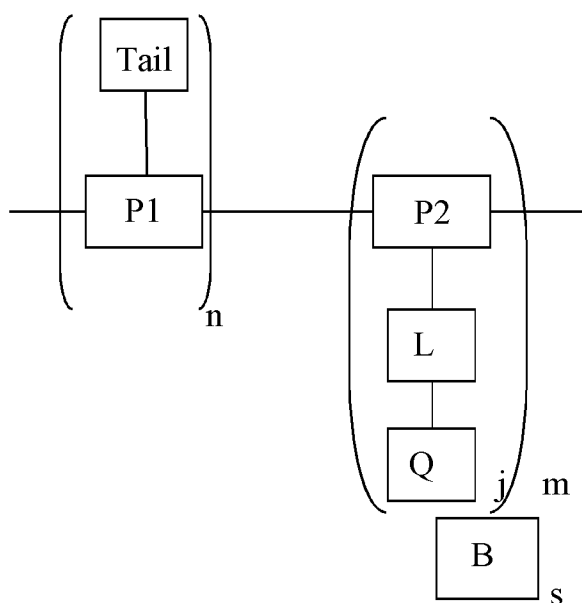
A mixture of compound **4** (25 g, 22.2 mmol, 1.0 eq) and Pd/C (2.5 g, 0.1 eq) in EtOAc (125.0 mL) was stirred at room temperature for 1 hour. The solid was filtered off (Celite) and washed with EtOAc (5 mL x 2). The filtrate was concentrated to afford the compound **5** (23.3 g, 99%) as a dark blue solid. ^1H NMR (300 MHz, CDCl_3) δ 0.84 (t, 12H), 1.24 (m, 72H), 1.85 (m, 4H), 2.30 (m, 4H), 5.00 (s, 2H), 5.10 (s, 2H), 5.20 (m, 2H), 7.91 - 8.19 (dd, 2H), 8.40 - 8.69 (dd, 2H), 8.77 - 8.91 (dd, 2H).

Furuta Polymers

Furuta co-polymers and para-Furuta polymers (herein referred to collectively as Furuta Polymers unless otherwise specified) are polymeric compounds with insulating tails, and linked/tethered/partially immobilized polarizable ionic groups. The insulating tails are hydrocarbon (saturated and/or unsaturated), fluorocarbon, siloxane, and/or polyethylene glycol linear or branched chains covalently bonded to the co-polymer backbone. The tails act to insulate the polarizable tethered/partially immobilized ionic molecular components and ionic pairs from other ionic groups and ionic group pairs on the same or parallel co-polymers, which favorably allows discrete polarization of counter ionic liquid pairs or counter Q groups (i.e. polarization of cationic liquid and anionic liquid tethered/partially immobilized to parallel Furuta polymers) with limited or no interaction of ionic fields or polarization moments of other counter ionic group pairs partially immobilized on the same or parallel co-polymer chains. Further, the insulating tails electrically insulate supra-structures of Furuta polymers from each other. Parallel Furuta polymers may arrange or be arranged such that counter ionic groups (i.e. tethered/partially immobilized ionic groups (Qs) of cation and anion types (sometimes known as cationic Furuta polymers and anionic Furuta polymers)) are aligned opposite from one another.

Furuta co-polymers

A Furuta co-polymer has the following general structural formula:



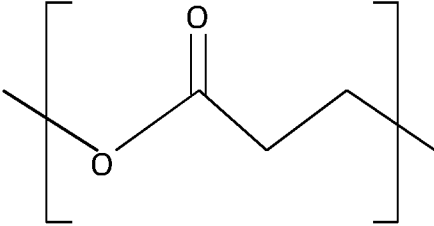
wherein backbone structure of the co-polymer comprises structural units of first type P1 and structural units of second type P2 both of which randomly repeat and are independently selected from the list comprising acrylic acid, methacrylate, repeat units of polypropylene ($-\text{[CH}_2\text{-CH(CH}_3\text{)]}-$), repeat units of polyethylene ($-\text{[CH}_2\text{]}-$), siloxane, or repeat units of polyethylene terephthalate (sometimes written poly(ethylene terephthalate)) for which the repeat unit may be expressed as $-\text{CH}_2\text{-CH}_2\text{-O-CO-C}_6\text{H}_4\text{-CO-O-}$. Parameter n is the number of the P1 structural units in the backbone structure which is in the range from 3 to 100 000 and m is number of the P2 structural units in the backbone structure which is in the range from 3 to 100 000. Further, the first type structural unit (P1) has a resistive substitute Tail which is oligomers of polymeric material with HOMO-LUMO gap no less than 2 eV. Additionally, the second type of structural units (P2) has an ionic functional group Q which is connected to P2 via a linker group L. The parameter j is a number of functional groups Q attached to the linker group L, which may range from 0 to 5. Wherein the ionic functional group Q comprises one or more ionic liquid ions (from the class of ionic compounds that are used in ionic liquids), zwitterions, or polymeric acids. Further, an energy interaction of the ionic Q groups may be less than kT , where k is Boltzmann constant and T is the temperature of environment. Still further, parameter B is a counter ion which is a molecule or molecules or oligomers that can supply the opposite charge to balance the charge of the co-polymer. Wherein, s is the number of the counter ions.

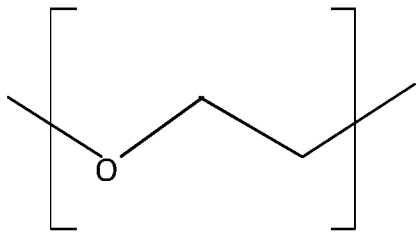
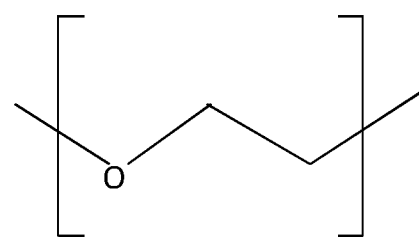
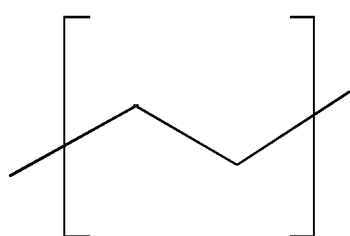
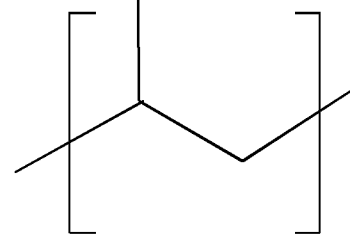
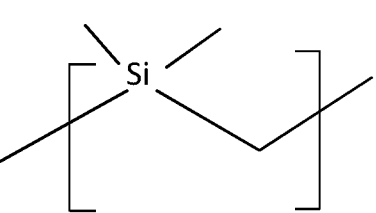
Specifically, in one embodiment, the resistive substitute Tails are independently selected from the list comprising oligomers of polypropylene (PP), oligomers of polyethylene terephthalate (PET), oligomers of polyphenylene sulfide (PPS), oligomers of polyethylene

naphthalate (PEN), oligomers of polycarbonate (PP), polystyrene (PS), and oligomers of polytetrafluoroethylene (PTFE). In another embodiment, the resistive substitutes Tail are independently selected from alkyl, aryl, substituted alkyl, substituted aryl, fluorinated alkyl, chlorinated alkyl, branched and complex alkyl, branched and complex fluorinated alkyl, branched and complex chlorinated alkyl groups, and any combination thereof, and wherein the alkyl group is selected from methyl, ethyl, propyl, butyl, *iso*-butyl and *tert*-butyl groups, and the aryl group is selected from phenyl, benzyl and naphthyl groups. The resistive substitute Tail may be added after polymerization.

In yet another aspect of the present disclosure, it is preferable that the HOMO-LUMO gap is no less than 4 eV. In still another aspect of the present disclosure, it is even more preferable that the HOMO-LUMO gap is no less than 5 eV. The ionic functional group Q comprises one or more ionic liquid ions from the class of ionic compounds that are used in ionic liquids, zwitterions, or polymeric acids. The energy of interaction between Q group ions on discrete P₂ structural units may be less than kT, where k is Boltzmann constant and T is the temperature of environment. The temperature of environment may be in range between - 60C of and 150 C. The preferable range of temperatures is between -40 C and 100C. Energy interaction of the ions depends on the effective radius of ions. Therefore, by increasing the steric hindrance between ions it is possible to reduce energy of interaction of ions. In one embodiment of the present invention, at least one ionic liquid ion is selected from the list comprising [NR₄]⁺, [PR₄]⁺ as cation and [−CO₂][−], [−SO₃][−], [−SR₅][−], [−PO₃R][−], [−PR₅][−] as anion, wherein R is selected from the list comprising H, alkyl, and fluorine. The functional group Q may be charged after or before polymerization. In another embodiment of the present invention, the linker group L is oligomer selected from structures 42 to 47 as given in Table 4.

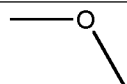
Table 4. Examples of the oligomer linker group

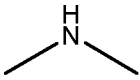
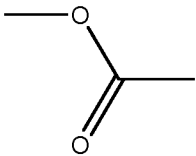
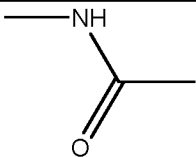
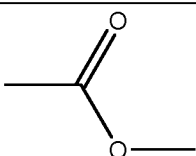
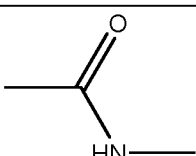
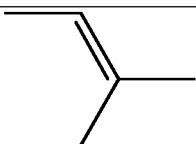
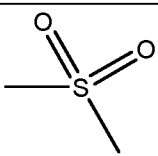
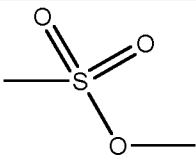
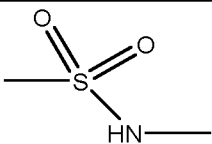
	42
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	43
	44
	45
	46
	47

In yet another embodiment of the present invention, the linker group L is selected from structures 48 to 57 as given in Table 5.

Table 5. Examples of the linker group

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	49
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	51
	52
	53
	54
	55
	56
	57

In yet another embodiment of the present invention, the linker group L may be selected from the list comprising CH₂, CF₂, SiR₂O, and CH₂CH₂O, wherein R is selected from the list comprising H, alkyl, and fluorine. The ionic functional group Q and the linker groups L may be added after polymerization.

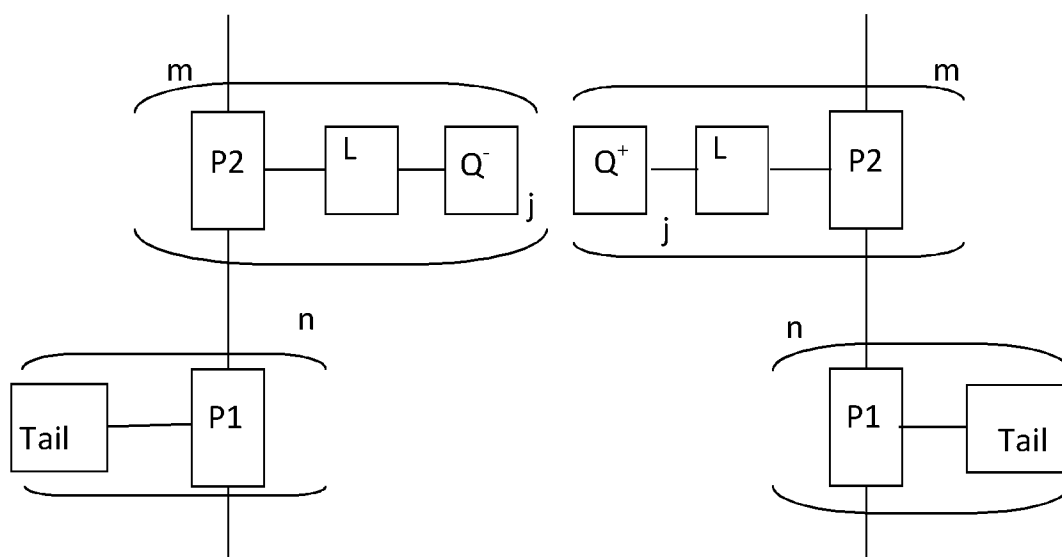
In another aspect, the present disclosure provides a dielectric material (sometimes called a meta-dielectric) comprising of one or more of the class of Furuta polymers comprising protected or hindered ions of zwitterion, cation, anion, or polymeric acid types described hereinabove. The meta-dielectric material may be a mixture of zwitterion type Furuta polymers, or positively charged (cation) Furuta polymers and negatively charged (anion) Furuta polymers, polymeric acid Furuta polymers, or any combination thereof. The mixture of Furuta polymers may form or be induced to form supra-structures via hydrophobic and ionic interactions. By way of example, but not limiting in scope, the cation on a positively charged Furuta polymer replaces the B counter ions of the anion on a negatively charged Furuta polymer parallel to the positively charged Furuta polymer and vice versa; and the resistive Tails of neighboring Furuta polymers further encourages stacking via van der Waals forces, which increases ionic group isolation. Meta-dielectrics comprising both cationic and anionic Furuta polymers have a 1:1 ratio of cationic and anionic Furuta polymers.

The Tails of hydrocarbon (saturated and/or unsaturated), fluorocarbon, siloxane, and/or polyethylene glycol linear or branched act to insulate linked/tethered/partially immobilized polarizable ionic liquids, zwitterions, or polymeric acids (ionic Q groups). The Tails insulate the ionic Q groups from other ionic Q groups on the same or parallel Furuta polymer via steric hindrance of the ionic Q groups' energy of interaction, which favorably allows discrete polarization of the ionic Q groups (i.e. polarization of cationic liquid and anionic liquid tethered/partially immobilized to parallel Furuta polymers). Further, the Tails insulate the ionic groups of supra-structures from each other. Parallel Furuta polymers may arrange or be arranged such that counter ionic liquids (i.e. tethered/partially immobilized ionic liquids (Qs) of cation and anion types) are aligned opposite from one another (sometimes known as cationic Furuta polymers and anionic Furuta polymers).

The Furuta polymers have hyper-electronic or ionic type polarizability. "Hyper-electronic polarization may be considered due to the pliant interaction of charge pairs of excitons, localized temporarily on long, highly polarizable molecules, with an external electric field [.] (Roger D. Hartman and Herbert A. Pohl, "Hyper-electronic Polarization in Macromolecular Solids",

Journal of Polymer Science: Part A-1 Vol. 6, pp. 1135-1152 (1968)).” Ionic type polarization can be achieved by limited mobility of ionic parts of the tethered/partially immobilized ionic liquid or zwitterion (Q). Additionally, other mechanisms of polarization such as dipole polarization and monomers and polymers possessing metal conductivity may be used independently or in combination with hyper-electronic and ionic polarization in aspects of the present disclosure.

Further, a meta-dielectric layer may be comprised of one or more types of zwitterion Furuta polymer and/or selected from the anionic Q^+ group types and cationic Q^- group types and/or polymeric acids, having the general configuration of Furuta polymers:



In order that the disclosure with respect to Furuta co-polymers may be more readily understood, reference is made to the following examples, which are intended to be illustrative of the invention, but are not intended to be limiting the scope.

Example 3:

Carboxylic acid co-polymer P002. To a solution of 1.02g (11.81 mmol) of methacrylic acid and 4.00g (11.81 mmol) of stearyl methacrylate in 2.0g isopropanol was added a solution of 0.030g 2,2'-azobis(2-methylpropionitrile) (AIBN) in 5.0g of toluene. The resulting solution was heated to 80 C for 20 hours in a sealed vial, after which it became noticeably viscous. NMR shows <2% remaining monomer. The solution was used without further purification in film formulations and other mixtures.

Example 4:

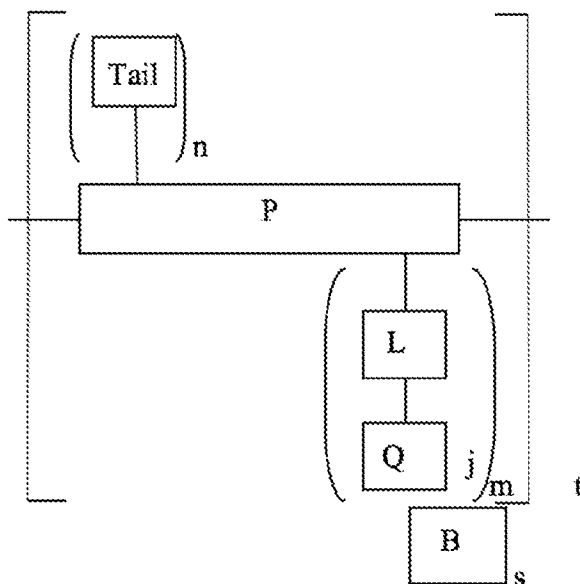
Amine co-polymer P011. To a solution of 2.52g (11.79 mmol) of 2-(diisopropylamino)ethyl methacrylate and 3.00g (11.79 mmol) of laurylmethacrylate in 2.0g toluene was added a solution of 0.030g 2,2'-azobis(2-methylpropionitrile) (AIBN) in 4.0g of toluene. The resulting solution was heated to 80 C for 20 hours in a sealed vial, after which it became noticeably viscous. NMR shows <2% remaining monomer. The solution was used without further purification in film formulations and other mixtures.

Example 5:

Carboxylic acid co-polymer and amine co-polymer mixture. 1.50g of a 42wt % by solids solution of P002 was added to 1.24g of a 56wt% solution of P011 with 1g of isopropanol and mixed at 40 C for 30 minutes. The solution was used without further purification.

Para-Furuta Polymers

A para-Furuta polymer has repeat units of the following general structural formula:



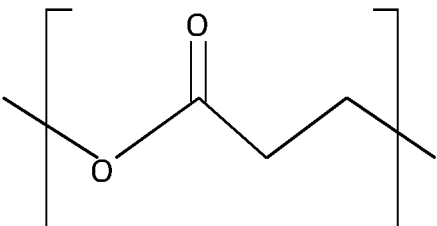
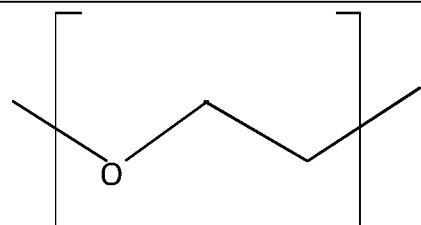
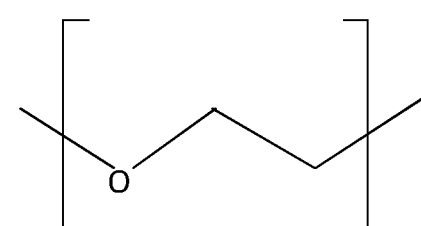
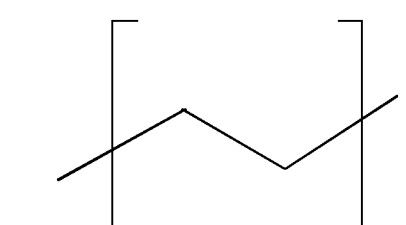
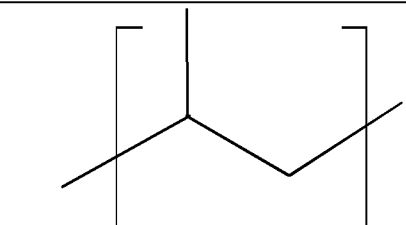
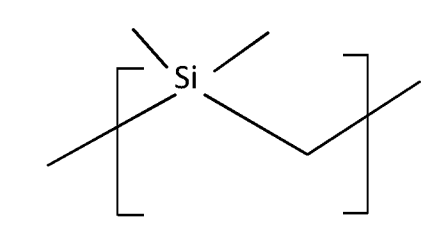
wherein a structural unit P comprises a backbone of the copolymer, which is independently selected from the list comprising acrylic acid, methacrylate, repeat units for polypropylene (PP) ($-\text{[CH}_2\text{-CH(CH}_3\text{)]-}$), repeat units for polyethylene (PE) ($-\text{[CH}_2\text{]-}$), , siloxane, or repeat units of polyethylene terephthalate (sometimes written poly(ethylene terephthalate)) for which the repeat unit may be expressed as $-\text{CH}_2\text{-CH}_2\text{-O-CO-C}_6\text{H}_4\text{-CO-O-}$. Wherein the first type of repeat unit (Tail) is a resistive substitute in the form of an oligomer of a polymeric material. The resistive substitute preferably has a HOMO-LUMO gap no less than 2 eV. The parameter n is a number of Tail repeat units on the backbone P structural unit, and is in the range from 3 to 100 000.

Further, the second type of repeat units ($-L-Q$) include an ionic functional group Q which is connected to the structural backbone unit (P) via a linker group L, and m is number of the $-L-Q$ repeat units in the backbone structure which is in the range from 3 to 100 000. Additionally, the ionic functional group Q comprises one or more ionic liquid ions (from the class of ionic compounds that are used in ionic liquids), zwitterions, or polymeric acids. An energy of interaction of the ionic Q groups may be less than kT , where k is Boltzmann constant and T is the temperature of environment. Still further, the parameter t is average of para-Furuta polymer repeat units, ranging from 6 to 200 000. Wherein B's are counter ions which are molecules or oligomers that can supply the opposite charge to balance the charge of the co-polymer, s is the number of the counter ions.

In one embodiment of the organic polymeric compound, the resistive substitute Tails are independently selected from the list comprising polypropylene (PP), polyethylene terephthalate (PET), polyphenylene sulfide (PPS), polyethylene naphthalate (PEN), polycarbonate (PP), polystyrene (PS), and polytetrafluoroethylene (PTFE). In another embodiment of the organic polymeric compound, the resistive substitutes Tail are independently selected from alkyl, aryl, substituted alkyl, substituted aryl, fluorinated alkyl, chlorinated alkyl, branched and complex alkyl, branched and complex fluorinated alkyl, branched and complex chlorinated alkyl groups, and any combination thereof, and wherein the alkyl group is selected from methyl, ethyl, propyl, butyl, *iso*-butyl and *tert*-butyl groups, and the aryl group is selected from phenyl, benzyl and naphthyl groups. The resistive substitute Tail may be added after polymerization. In yet another embodiment of the present disclosure, it is preferable that the HOMO-LUMO gap is no less than 4 eV. In still another embodiment of the present disclosure, it is even more preferable that the HOMO-LUMO gap is no less than 5 eV. The ionic functional group Q comprises one or more ionic liquid ions from the class of ionic compounds that are used in ionic liquids, zwitterions, or polymeric acids. Energy of interaction between Q group ions on discrete P structural units may be less than kT , where k is Boltzmann constant and T is the temperature of environment. The temperature of environment may be in range between - 60C of and 150 C. The preferable range of temperatures is between -40 C and 100C. Energy interaction of the ions depends on the effective radius of ions. Therefore, by increasing the steric hindrance between ions it is possible to reduce energy of interaction of ions. In one embodiment of the present invention, at least one ionic liquid ion is selected from the list comprising $[NR_4]^+$, $[PR_4]^+$ as cation and $[-CO_2]^-$, $[-SO_3]^-$, $[-SR_3]^-$, $[-PO_3R]^-$, $[-PR_3]^-$ as anion, wherein R is selected from the list comprising H, alkyl, and fluorine. The functional group Q may be charged after or before polymerization. In

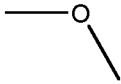
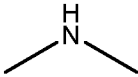
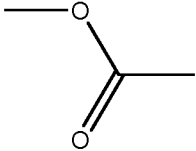
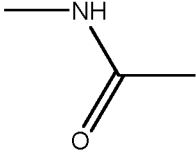
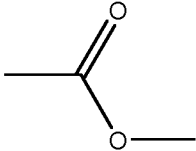
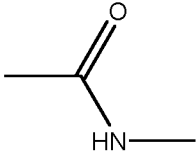
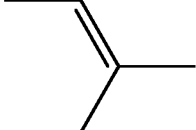
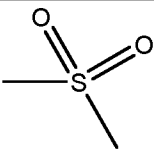
another embodiment of the present invention, the linker group L is oligomer selected from structures 58 to 63 as given in Table 6.

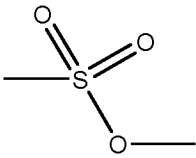
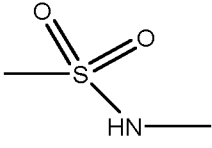
Table 6. Examples of the oligomer linker group

	58
	59
	60
	61
	62
	63

In yet another embodiment of the present disclosure, the linker group L is selected from structures 64 to 73 as given in Table 7.

Table 7. Examples of the linker group

	64
	65
	66
	67
	68
	69
	70
	71

	72
	73

In yet another embodiment of the present disclosure, the linker group L is selected from the list comprising CH₂, CF₂, SiR₂O, and CH₂CH₂O, wherein R is selected from the list comprising H, alkyl, and fluorine. The ionic functional group Q and the linker groups L may be added after polymerization.

In another aspect, the present disclosure provides a dielectric material (sometimes called a meta-dielectric) comprising of one or more of the class of para-Furuta polymers comprising protected or hindered ions of zwitterion, cationic liquid ions, anionic liquid ions, or polymeric acid types described hereinabove. The meta-dielectric material may be a mixture of zwitterion type para-Furuta polymers, or positively charged (cation) para-Furuta polymers and negatively charged (anion) para-Furuta polymers, polymeric acid para-Furuta polymers, or any combination thereof. The mixture of para-Furuta polymers may form or be induced to form supra-structures via hydrophobic and ionic interactions. By way of example, but not limiting in scope, the cation(s) on a positively charged para-Furuta polymer replaces the B counter ions of the anion(s) on a negatively charged para-Furuta polymer parallel to the positively charged para-Furuta polymer and vice versa; and the resistive Tails of neighboring para-Furuta polymers further encourages stacking via van der Waals forces, which increases ionic group isolation. Meta-dielectrics comprising both cationic and anionic para-Furuta polymers preferably have a 1:1 ratio of cationic and anionic para-Furuta polymers.

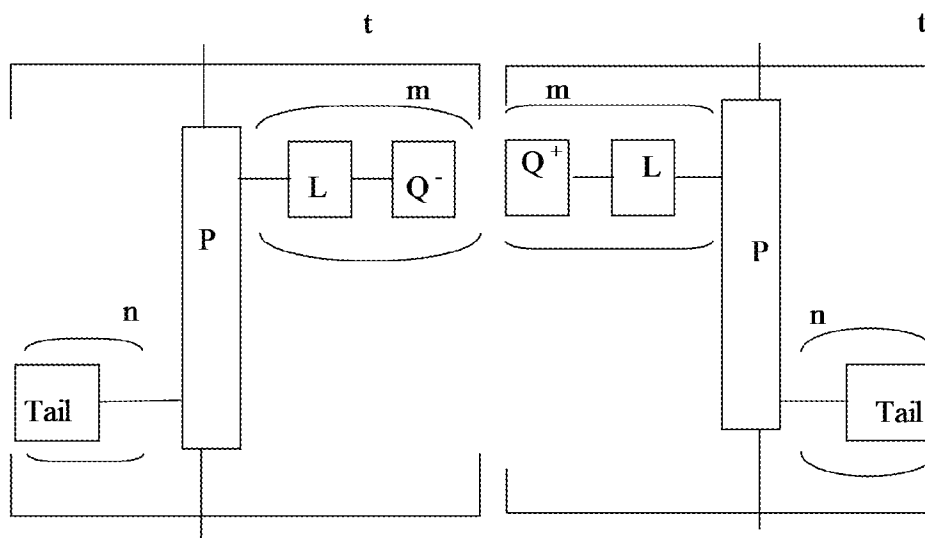
The Tails of hydrocarbon (saturated and/or unsaturated), fluorocarbon, siloxane, and/or polyethylene glycol linear or branched act to insulate linked/tethered/partially immobilized polarizable ionic liquids, zwitterions, or polymeric acids (ionic Q groups). The Tails insulate the ionic Q groups from other ionic Q groups on the same or parallel para-Furuta polymer via steric hindrance of the ionic Q groups' energy of interaction, which favorably allows discrete polarization of the ionic Q groups (i.e. polarization of cationic liquid and anionic liquid tethered/partially immobilized to parallel para-Furuta polymers). Further, the Tails insulate the

ionic groups of supra-structures from each other. Parallel para-Furuta polymers may arrange or be arranged such that counter ionic liquids (i.e. tethered/partially immobilized ionic liquids (Qs) of cation and anion types) are aligned opposite from one another (sometimes known as cationic para-Furuta polymers and anionic para-Furuta polymers).

The para-Furuta polymers have hyperelectronic or ionic type polarizability.

“Hyper-electronic polarization may be considered due to the pliant interaction of charge pairs of excitons, localized temporarily on long, highly polarizable molecules, with an external electric field [.] (Roger D. Hartman and Herbert A. Pohl, “Hyper-electronic Polarization in Macromolecular Solids”, Journal of Polymer Science: Part A-1 Vol. 6, pp. 1135-1152 (1968)).” Ionic type polarization can be achieved by limited mobility of ionic parts of the tethered/partially immobilized ionic liquid or zwitterion (Q). Additionally, other mechanisms of polarization such as dipole polarization and monomers and polymers possessing metal conductivity may be used independently or in combination with hyper-electronic and ionic polarization in aspects of the present disclosure.

Further, a meta-dielectric layer may be comprised of one or more types of zwitterion para-Furuta polymer and/or selected from the anionic Q group types and cationic Q group types and/or polymeric acids, which may have the following general arrangement of para-Furuta polymers:



A meta-dielectric is defined here as a dielectric material comprised of one or more types of structured polymeric materials (SPMs) having a relative permittivity greater than or equal to 1000 and resistivity greater than or equal to 10^{13} ohm/cm. Individually, the SPMs in a meta-dielectric may form column like supramolecular structures by pi-pi interaction or hydrophilic

and hydrophobic interactions. Said supramolecules of SPMs may permit formation of crystal structures of the meta-dielectric material. By way of using SPMs in a dielectric material, polarization units are incorporated to provide the molecular material with high dielectric permeability. There are several mechanisms of polarization such as dipole polarization, ionic polarization, and hyper-electronic polarization of molecules, monomers and polymers possessing metal conductivity. All polarization units with the listed types of polarization may be used in aspects of the present disclosure. Further, SPMs are composite materials which incorporate an envelope of insulating substituent groups that electrically isolate the supramolecules from each other in the dielectric layer and provide high breakdown voltage of the energy storage molecular material. Said insulating substituent groups are hydrocarbon (saturated and/or unsaturated), fluorocarbon, siloxane, and/or polyethylene glycol linear or branched chains covalently bonded to a polarizable core or co-polymer backbone, forming the resistive envelope.

As depicted in Figure 10, in one embodiment of the energy storage cell 1, each of the one or more meta-capacitors 20 comprises a first electrode 21, a second electrode 22, and a meta-dielectric material layer 23 disposed between said first and second electrodes. The electrodes 21, 22 may be made of a metal, such as copper, zinc, or aluminum or other conductive material and are generally planar in shape. In one implementation, the electrodes and meta-dielectric material layer 23 are in the form of long strips of material that are sandwiched together and wound into a coil along with an insulating material, e.g., a plastic film such as polypropylene or polyester to prevent electrical shorting between the electrodes 21, 22. Examples of such coiled capacitor energy storage devices are described in detail in commonly-assigned U.S. Patent Application Number 14/752,600, filed June 26, 2015, the entire contents of which are incorporated herein by reference. Although a single meta-capacitor 20 is shown for convenience in Figure 10, aspects of the present disclosure are not limited to such implementations. As illustrated in figures 7A, 7B, 7C, 7D, those skilled in the art will recognize that the capacitive energy storage device 2 may include multiple meta-capacitors 20 connected in parallel, as in FIG. 7B, to provide a desired amount of energy storage capacity that scales roughly with the number of meta-capacitors in parallel. Alternatively, the capacitive energy storage device 2 may include two or more meta-capacitors connected in series to accommodate a desired voltage level, as in FIG. 7C. In addition, the capacitive energy storage device 2 may include combinations of three or more meta-capacitors in a capacitor network involving various series and parallel combinations, as in FIG. 7D. For example, there may be three capacitor combinations connected in parallel with each other with each combination having two capacitors connected in series.

The meta-dielectric material 23 may be characterized by a dielectric constant κ greater than about 100 and a breakdown field E_{bd} greater than or equal to about 0.01 volts (V)/nanometer (nm). The dielectric constant κ may be greater than or equal to about 100, 200, 300, 400, 500, 1000, 2000, 3000, 4000, 5000, 6000, 7000, 8000, 9000, 10,000, or 100,000. The breakdown field may be greater than about 0.01 V/nm, 0.05 V/nm, 0.1 V/nm, 0.2 V/nm, 0.3 V/nm, 0.4 V/nm, 0.5 V/nm, 1 V/nm, or 10 V/nm. By way of example, and not by way of limitation, the meta-dielectric material 23 may be characterized by a dielectric constant κ between about 100 and about 1,000,000 and a breakdown field E_{bd} between about 0.01 V/nm and about 2.0 V/nm.

In yet another implementation, the capacitive energy storage devices may comprise more than one of the meta-capacitors connected in series or parallel. In still another implementation, the capacitive energy storage device may further comprise a cooling mechanism 30. In some implementations, the cooling can be passive, e.g., using radiative cooling fins on the capacitive energy storage device 2 and DC-voltage conversion device 3. Alternatively, a fluid such as air, water or ethylene glycol can be used as a coolant in an active cooling system. By way of example, and not by way of limitation, the cooling system 30 may include conduits in thermal contact with the capacitive energy storage device 2 and DC-voltage conversion device 3. The conduits are filled with a heat exchange medium, which may be a solid, liquid or gas. In some implementations, the cooling mechanism may include a heat exchanger configured to extract heat from the heat exchange medium. In other implementations, the cooling mechanism 30 may include conduits in the form of cooling fins on the capacitive energy storage device 2 and DC-voltage conversion device 3 and the heat exchange medium is air that is blown over the cooling fins, e.g., by a fan. In another embodiment of the present invention, the heat exchanger 32 may include a phase-change heat pipe configured to carry out cooling. The cooling carried out by the phase-change heat pipe may involve a solid to liquid phase change (e.g., using melting of ice or other solid) or liquid to gas phase change (e.g., by evaporation of water or alcohol) of a phase change material. In yet another implementation, the conduits or heat exchanger 32 may include a reservoir containing a solid to liquid phase change material, such as paraffin wax.

Referring again to Figures 10, 11 and 12 the DC-voltage conversion device 3 may include a buck converter for applications in which $V_{out} < V_{in}$, a boost converter for applications in which $V_{out} > V_{in}$, or a bidirectional buck/boost converter for applications in which $V_{out} < V_{in}$ in certain situations and $V_{out} > V_{in}$ in other situations.

In still another embodiment of the energy storage cell (see, Figure 11) the DC-voltage conversion device 3 may be connected to a control board 4 containing suitable logic circuitry,

e.g., microprocessor, microcontroller, application specific integrated circuit (ASIC), field programmable gate array (FPGA), a complex programmable logic device (CPLD), capable of implementing closed loop control processes 90 and (optionally) a communication interface 5, as well as an analog to digital converter coupled to sensors on the DC-voltage conversion device 3, e.g., voltage sensors V for the input voltage V_{in} and the output voltage V_{out} , current sensors A for current I_{sd} to/from the capacitive energy storage device 2 and/or current I_{vc} to/from the DC-voltage conversion device 3, temperature sensors T on the capacitive energy storage device and/or DC-voltage conversion device. In some implementations, the control board 4 may be integrated into the DC-voltage conversion device 3. The conversion device 3 may contain a buck regulator, a boost regulator, buck and boost regulators with separate input/outputs, a bi-directional boost/buck regulator, or a split-pi converter and the control board 4 may be configured to maintain a constant output voltage V_{out} from the DC-voltage conversion device during discharge, and/or charge the capacitor at a more-or-less constant current while maintaining a stable input voltage.

By way of example, and not by way of limitation, the control board 4 may be based on a controller for a bidirectional buck/boost converter. In such a configuration, the control board 4 stabilizes the output voltage of the DC-voltage conversion device according to the following algorithm forming the control loop 90:

- a) determining a target output voltage level for the energy storage system,
- b) measuring the voltage of a capacitive energy storage device,
- c) configuring a bidirectional buck/boost converter to buck down the voltage and direct current in the output direction IF the voltage on the capacitive energy storage device is higher than the desired output voltage and the desired outcome is to discharge the device,
- d) configuring a bidirectional buck/boost converter to boost up the voltage and direct current in the output direction IF the voltage on the capacitive energy storage device is lower than the desired output voltage and the desired outcome is to discharge the device,
- e) configuring a bidirectional buck/boost converter to buck down the voltage and direct current in the input direction IF the voltage on the capacitive energy storage device is lower than the desired input voltage and the desired outcome is to charge the device,
- f) configuring a bidirectional buck/boost converter to boost up the voltage and direct current in the input direction IF the voltage on the capacitive energy storage device is

higher than the desired output voltage and the desired outcome is to charge the device,

- g) configuring a bidirectional buck/boost converter to stop outputting power if the voltage on the capacitive energy storage device falls below a predetermined level,
- h) configuring a bidirectional buck/boost converter to stop inputting power if the voltage on the capacitive energy storage device exceeds a predetermined level,
- i) repeating steps (a) through (f) (or steps (a) through (h)) as necessary.

The specifics of operation of the control board 4 are somewhat dependent on the type of buck/boost converter(s) used in the DC-voltage conversion device 3. For example, a buck/boost converter may be a single switch converter of the type shown in FIG. 15A. This type of converter includes a high-side switch SW having an input side coupled to the input voltage V_{in} and an output side coupled to one side of an inductor L, the other side of which is connected to the ground or common voltage (-). A capacitor C is coupled across the output voltage V_{out} . A pulsed switching signal S turns the switch on and off. The output voltage depends on the duty cycle of the switching signal S. By way of example, the switches may be implanted as gated switch devices, e.g., MOSFET devices, stacked MOSFET devices, IGCT devices, high drain-source voltage SiC MOSFET devices, and the like depending on the voltage and/or current requirements of the DC-voltage converter for the energy storage cell. In the case of gated switching devices, the control board provides the signals to the gate terminals of the switching devices. The control board 4 can configure this type of buck/boost converter to buck or boost by adjusting the duty cycle of the switching signal S.

Figure 15B shows an alternative four-switch buck/boost converter. In this type of converter, a first switch SW1 is connected between the high side (+) of the input voltage V_{in} and an input side of the inductor L, a second switch SW2 is connected between an output side of the inductor L and the common voltage (-), a third switch SW3 is connected between the input side of the inductor L and the common voltage, and a fourth switch SW4 is connected between the output side of the inductor and the high side (+) of the output voltage V_{out} . An input capacitor C_{in} may be coupled across the input voltage V_{in} and an output capacitor C_{out} may be coupled across the output voltage V_{out} .

The switches SW1, SW2, SW3, and SW4 change between open (non-conducting) and closed (conducting) states in response to switching signals from the control board 4. To operate in buck mode, the second switch SW2 is open and the fourth switch SW4 closed and pulsed buck mode switching signals are applied to the first switch SW1 and third switch SW3, e.g., as

described above with respect to Figure 3 and Figure 4. The control board 4 can adjust the output voltage V_{out} in buck mode by adjusting the duty cycle signal of the switching signals S1 and S3. To operate in boost mode, the first switch SW1 is open, the third switch SW3 is closed and pulsed boost mode switching signals are applied to the second switch SW2 and fourth switch SW4, e.g., as described above with respect to Figure 5 and Figure 6. The control board 4 can adjust the output voltage V_{out} in boost mode by adjusting the duty cycle signal of the switching signals S2 and S4.

By way of example and not by limitation, the DC-voltage conversion device 3 as depicted in figure 9A, 9B, 9C, 9D, 9E, 9F, 9G, 9H, 9I may include one or more switch-mode voltage converters 100, arranged to boost/or buck the input/output voltages as necessary to achieve the charge and discharge modalities depicted in figures 13A, 13B, 14A and 14B corresponding to the voltage labels $v_c(t)$, $v_i(t)$ and $v_o(t)$ on the capacitive energy storage cell 3 of figures 11 and 12. As shown in figures 9F, 9G, 9H, 9I, the input/output port may be split into a separate input and output. These separate inputs and outputs may have different bus voltages. For example, there may be an input DC bus from a solar inverter which is at a different voltage than an output DC bus meant to transmit power or feed a DC to AC converter. The switch-mode voltage converters 100 may have circuitry selected from the following list: a buck converter (as show in figure 8B), boost converter (as show in figure 8A), buck/boost converter, bi-directional buck/boost (split-pi) converter (as show in figure 8D), Ćuk converter, single-ended primary inductor converter (SEPIC), inverting buck/boost converter (as show in figure 8C), or four-switch buck/boost converters.

In figures 9A, 9B, 9C, 9D, 9E, 9F, 9G, 9H, 9I, the switch mode voltage converters 100 are connected to power ports 101, by an interconnect system 102. The power ports 101 include a positive terminal and negative terminal intended to work together to transmit power in either direction. A power port can be an input, output or bidirectional. A control interface 104 is connected to all of the control interfaces on the switch mode voltage converters 100 through a control network 103. The control network may carry target voltages, target currents, observed voltages, observed currents, temperatures and other parameters necessary to control the system. The control network 103, control interfaces 104, control board 4, and control loops 90 may or may not be combined in a single discrete physical package. For example, one implementation may have all aforementioned elements distributed throughout a system and another implementation may contain all elements in a single microprocessor unit.

In one implementation the control board 4 may control the DC-voltage converter 3 in a way that maintains the output voltage of the energy storage cell, e.g., the output voltage of the DC-voltage converter V_{out} , at a constant level during a discharge of the meta-capacitor (s) (see, Figures 13B and 14B) from an initial charge state ($V_c(t)$) to a minimum charge state ($V_c(t) = V_{min,op}$), wherein the minimum charge state ($V_{min,op}$), is defined by a voltage on the meta-capacitor (s) which corresponds to the residual energy equal to from 0% to 20% of the initial reserved energy, where the reserved energy of the meta-capacitor (s) can be calculated by $E = \frac{1}{2} CV^2$ where E is energy, C is capacitance, and V is voltage. In implementations where the control board 4 is a programmable device, the constant output voltage of the energy storage cell can be a programmable value.

In still another implementation of the energy storage cell, wherein the output voltage is made constant by the DC-voltage conversion device selected from the list comprising a buck regulator, a boost regulator, buck and boost regulators with separate input/outputs, bi-directional boost/buck regulator, split-pi converter.

In some implementations, the cell 1 includes circuitry configured to enable observation of parameters selected from the following list: the voltage on the meta-capacitor, the current going into or out of the meta-capacitor, the current flowing into or out of the DC-voltage conversion device, the output voltage of the DC-voltage conversion device, the temperature at one or more points within the meta-capacitor, the temperature at one or more points within the DC-voltage conversion device. In another implementation, the energy storage cell further comprises an AC-inverter to create AC output voltage, wherein the DC output voltage of the DC-voltage conversion device is the input voltage of the AC-inverter. In yet another implementation, energy storage cell further comprises power electronics switches which are based on Si insulated-gate bipolar transistors (IGBTs), SiC MOSFETs, GaN MOSFETs, Graphene or comprising organic molecular switches. In one embodiment of the energy storage cell, the power electronics switches comprise multiple switch elements stacked in series to enable switching of voltages higher than the breakdown voltage of individual switch components.

In another aspect of the present disclosure, a capacitive energy storage module 40, e.g., as illustrated in FIG. 16. In the illustrated example, the energy storage module 40 includes two or more energy storage cells 1 of the type described above. Each energy storage cell includes a capacitive energy storage device 2 having one or more meta-capacitors 20 and a DC-voltage converter 3, which may be a buck converter, boost converter, or buck/boost converter. In addition, each module may include a control board 4 of the type described above with respect to

Figures 10,11,12, and an (optional) cooling mechanism (not shown). The module 40 may further include an interconnection system that connects the anodes and cathodes of the individual energy storage cells to create a common anode and common cathode of the capacitive energy storage module.

In yet another aspect, some implementations, the interconnection system includes a parameter bus 42 and power switches PSW. Each energy storage cell 1 in the module 40 may be coupled to the parameter bus 42 via the power switches PSW. These switches allow two or more modules to be selectively coupled in parallel or in series via two or more rails that can serve as the common anode and common cathode. The power switches can also allow one or more energy storage cells to be disconnected from the module, e.g., to allow for redundancy and/or maintenance of cells without interrupting operation of the module. The power switches PSW may be based on solid state power switching technology or may be implemented by electromechanical switches (e.g., relays) or some combination of the two.

In some implementations, the energy storage module further comprises a power meter 44 to monitor power input or output to the module. In some implementations, the energy storage module further comprises a networked control node 46 configured to control power output from and power input to the module. The networked control node 46 allows each module to talk with a system control computer over a high speed network. The networked control node 46 includes voltage control logic circuitry 50 configured to selectively control the operation of each of voltage controller 3 in each of the energy storage cells 2, e.g., via their respective control boards 4. The control node 46 may also include switch control logic circuitry 52 configured to control operation of the power switches PSW. The control boards 4 and power switches PSW may be connected to the control node 46 via a data bus 48. The voltage control and switching logic circuitry in the networked control node 46 may be implemented by one or more microprocessors, microcontrollers, application specific integrated circuits (ASICs), field programmable gate arrays (FPGAs), or complex programmable logic devices (CPLDs). The control node 46 may include a network interface 54 to facilitate transfer of signals between the voltage control logic circuitry 50 and the control boards 4 on the individual energy storage cells 2 and also to transfer signals between the switching logic circuitry 52 and the power switches PSW, e.g., via the data bus 48.

According to yet another aspect of the present disclosure a capacitive energy storage system may include two or more networked capacitive energy storage modules, e.g., of the type shown in Figure 16. One embodiment of such a capacitive energy storage system 60 is shown in Figure 17. The system 60 includes two or more energy storage modules 40 of the type shown in

Figure 16. Each capacitive energy storage module 40 includes two or more capacitive energy storage cells 1, e.g., of the type shown in Figures 10, 11, 12, connected by an interconnection system 42 and controlled by a control node 46. Each capacitive energy storage module may also include a module power meter 44. Although it is not shown in Figure 16, each control node 46 may include voltage control logic circuitry 50 to control voltage controllers within the individual capacitive energy storage cells 1 and switching logic circuitry 52 to control internal power switches with the module, as described above. In addition, each control node 46 includes an internal data bus 48 and a network interface 54, which may be connected as described above. Power to and from capacitive energy storage modules 40 is coupled to a system power bus 62 via system power switches SPSW, which may be based on solid state power switching technology or may be implemented by electromechanical switches (e.g., relays) or some combination of the two. In some implementations, there may be an inverter (not shown) coupled between each capacitive energy storage module 40 and the system power bus 62 to convert DC power from the module to AC power or vice versa.

The system 60 includes a system controller 66 connected to a system data bus 68. The system controller may include switching control logic 70, voltage control logic 72, and system network interface 74. The voltage control logic 70 may be configured to control the operation of individual DC-voltage controllers within individual cells 1 of individual modules 40. The switching control logic 72 may be configured to control operation of the system power switches SPSW and also the power switches PSW within individual capacitive energy storage modules 40. Voltage control signals may be sent from the voltage control logic 72 to a specific DC-voltage control device 3 within a specific capacitive energy storage cell 1 of a specific capacitive energy storage module through the network interface 74, the system data bus 68, the module network interface 54 of the control node 46 for the specific module, the module data bus 48, and the control board 4 of the individual cell 1.

By way of example, and not by way of limitation, the system controller 66 may be a deterministic controller, an asynchronous controller, or a controller having distributed clock. In one particular embodiment of the capacitive energy storage system 60, the system controller 66 may include a distributed clock configured to synchronize several independent voltage conversion devices in one or more capacitive energy storage cells of one or more of the capacitive energy storage modules 40.

Aspects of the present disclosure allow for electrical energy storage on a much larger scale than possible with conventional electrical energy storage systems. A wide range of energy

storage needs can be met by selectively combining one or more meta-capacitors with a DC-voltage conversion devices into a cell, combining two or more cells into a module, or combining two or more modules into systems.

While the above is a complete description of the preferred embodiment of the present invention, it is possible to use various alternatives, modifications and equivalents. Therefore, the scope of the present invention should be determined not with reference to the above description but should, instead, be determined with reference to the appended claims, along with their full scope of equivalents. Any feature described herein, whether preferred or not, may be combined with any other feature described herein, whether preferred or not. In the claims that follow, the indefinite article “A”, or “An” refers to a quantity of one or more of the item following the article, except where expressly stated otherwise. As used herein, in a listing of elements in the alternative, the word “or” is used in the logical inclusive sense, e.g., “X or Y” covers X alone, Y alone, or both X and Y together, except where expressly stated otherwise. Two or more elements listed as alternatives may be combined together. The appended claims are not to be interpreted as including means-plus-function limitations, unless such a limitation is explicitly recited in a given claim using the phrase “means for.”

CLAIMS

What is claimed is:

1. An energy storage cell comprising:
 - at least one capacitive energy storage device; and
 - a DC-voltage conversion device;wherein the capacitive energy storage device comprises one or more meta-capacitors,
wherein the output voltage of the capacitive energy storage device is an input voltage of the DC-voltage conversion device during discharging the capacitive energy storage device,
wherein the input voltage of the capacitive energy storage device is an output voltage of the DC-voltage conversion device while charging the capacitive energy storage device.
2. The energy storage cell of claim 1, wherein the one or more meta-capacitors each include first and second electrodes and a meta-dielectric material layer disposed between the first and second electrodes, wherein the meta-dielectric material layer is comprised of one or more composite organic compounds characterized by polarizability and resistivity.
3. The energy storage cell of claim 2, wherein a resistivity of the meta-dielectric material layer is equal to or greater than 10^{13} ohm/cm.
4. The energy storage cell of claim 2, wherein a relative permittivity of the meta-dielectric material layer is equal to or greater than 100.
5. The energy storage cell of claim 2, wherein the meta-dielectric material layer includes one or more types of Sharp polymers and/or one or more types of Furuta polymers.
6. The energy storage cell of claim 5, wherein the meta-dielectric layer includes two or more Furuta polymers, including a Furuta polymer having an immobilized ion liquid group of a cationic type.
7. The energy storage cell of claim 5, wherein the meta-dielectric layer includes two or more Furuta polymers including a Furuta polymer having an immobilized ion liquid group of an anionic type.

8. The energy storage cell of any one of claims 1-7, wherein said one or more meta-capacitors have a breakdown field greater than or equal to about 0.01V/nm.
9. The energy storage cell according to Claim 1, further comprising a cooling mechanism in thermal contact with the capacitive energy storage device and/or the DC-voltage converter.
10. The energy storage cell according to Claim 9, wherein the cooling mechanism is a passive cooling mechanism. or wherein air, water or ethylene glycol can be used as a coolant.
11. The energy storage cell according to Claim 9, wherein the cooling mechanism is configured to remove heat from the capacitive energy storage device and/or the DC-voltage converter with a phase-change material.
12. The energy storage cell according to Claim 9, wherein the cooling mechanism includes a reservoir containing a solid to liquid phase change material.
13. The energy storage cell according to Claim 12, wherein the solid to liquid phase change material is paraffin wax.
14. The energy storage cell according to Claim 1, wherein the DC-voltage conversion device comprises a control board based on a buck converter, boost converter, buck/boost converter, bi-directional buck/boost (split-pi) converter, Ćuk converter, single-ended primary inductor converter (SEPIC), inverting buck/boost converter, or four-switch buck/boost converters.
15. The energy storage cell according to Claim 14, wherein the control board is configured to maintain a constant output voltage of the energy storage cell during a discharge of the one or more meta-capacitors from an initial charge state to a minimum charge state, wherein the minimum charge state is defined by a voltage on the meta-capacitor(s) which corresponds to a residual energy equal to from 0% to 20% of an initial reserved energy stored on the meta-capacitor(s).
16. The energy storage cell according to Claim 15, wherein the constant output voltage of the energy storage cell is programmable by the control board.
17. The energy storage cell according to Claim 15, wherein the DC-voltage conversion device comprises one or more switch-mode voltage converters wherein a switch-mode

voltage converter is configured as a buck converter, boost converter, buck/boost converter, bi-directional buck/boost (split-pi) converter, Ćuk converter, single-ended primary inductor converter (SEPIC), inverting buck/boost converter, or four-switch buck/boost converters

18. The energy storage cell according to Claim 15, further comprising circuitry configured to enable observation of parameters selected from the following list: a voltage on the one or more meta-capacitors, a current going into or out of the one or more meta-capacitors, a current flowing into or out of the DC-voltage conversion device, an output voltage of the DC-voltage conversion device, a temperature at one or more points within the one or more meta-capacitors, a temperature at one or more points within the DC-voltage conversion device.
19. The energy storage cell according to Claim 15, further comprising a power inverter configured to receive a direct current (DC) output voltage from the DC-voltage converter and configured to convert the DC output voltage from the DC-voltage converter to an alternating current (AC) output voltage.
20. The energy storage cell according to Claim 1, wherein the DC-voltage converter includes power electronics switches based on silicon (Si) insulated-gate bipolar transistors (IGBTs), silicon carbide (SiC) metal oxide semiconductor field effect transistors (MOSFETs), gallium nitride (GaN) MOSFETs, Graphene or organic molecular switches.
21. The energy storage cell according to Claim 20, wherein the power electronics switches comprise multiple switch elements stacked in series.
22. A capacitive energy storage module comprising two or more individual energy storage cells having anodes and cathodes and an interconnection system, wherein the interconnection system connects the anodes and cathodes of the individual energy storage cells to create a common anode and common cathode of the capacitive energy storage module, wherein each individual energy storage cell includes one or more meta-capacitors coupled to a DC-voltage conversion device, wherein each individual energy storage cell includes at least one capacitive energy storage device and a DC-voltage conversion device;
 - wherein the capacitive energy storage device comprises one or more meta-capacitors,
 - wherein the output voltage of the capacitive energy storage device is an input voltage of the DC-voltage conversion device during discharging the capacitive energy storage device,

wherein the input voltage of the capacitive energy storage device is an output voltage of the DC-voltage conversion device while charging the capacitive energy storage device.

23. The energy storage module of Claim 22, wherein the interconnection system includes a parameter bus connected to the two or more individual energy storage cells by power switches.
24. The energy storage module of Claim 22, further comprising a power meter coupled to two or more individual energy storage cells.
25. The energy storage module of Claim 22, further comprising a networked control node coupled to the two or more individual energy storage cells.
26. A capacitive energy storage system comprising:
 - two or more capacitive energy storage modules, wherein each of the one or more storage modules includes two or more individual energy storage cells having anodes and cathodes and an interconnection system, wherein each of the two or more individual energy storage cells includes at least one capacitive energy storage device and a DC-voltage conversion device, wherein the capacitive energy storage device comprises one or more meta-capacitors, wherein the output voltage of the capacitive energy storage device is an input voltage of the DC-voltage conversion device during discharging the capacitive energy storage device, wherein the input voltage of the capacitive energy storage device is an output voltage of the DC-voltage conversion device while charging the capacitive energy storage device;
 - an interconnection system coupled to the two or more capacitive energy storage modules, wherein the interconnection system connects the anodes and cathodes of the individual energy storage cells to create a common anode and common cathode of the capacitive energy storage module, wherein each individual energy storage cell includes one or more meta-capacitors coupled to a DC-voltage conversion device; and
 - a power interconnection system and a system controller coupled to the two or more capacitive energy storage modules.
27. The capacitive energy storage system according to Claim 26, wherein system controller includes a deterministic controller, an asynchronous controller, or a controller having distributed clock.

28. The capacitive energy storage system according to Claim 27, wherein the distributed clock is used to synchronize several independent DC-voltage conversion devices in one or more of the individual energy storage modules.

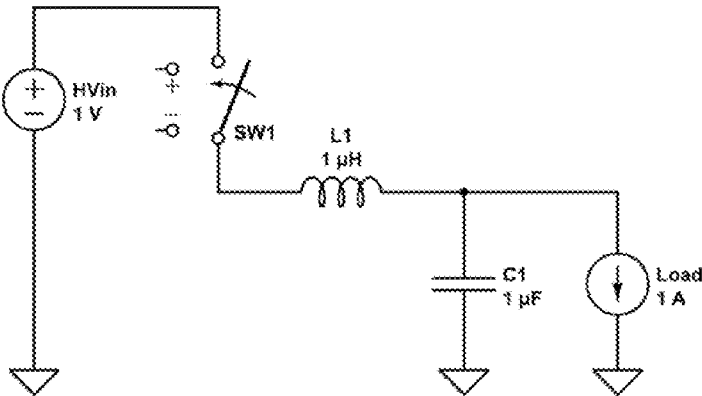


Figure 1 (Prior Art)

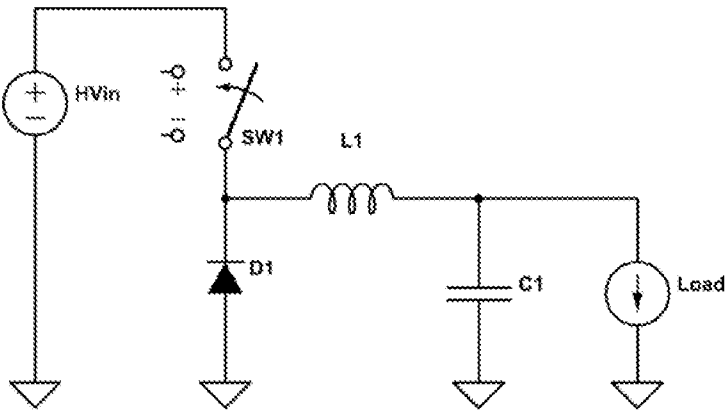


Figure 2 (Prior Art)

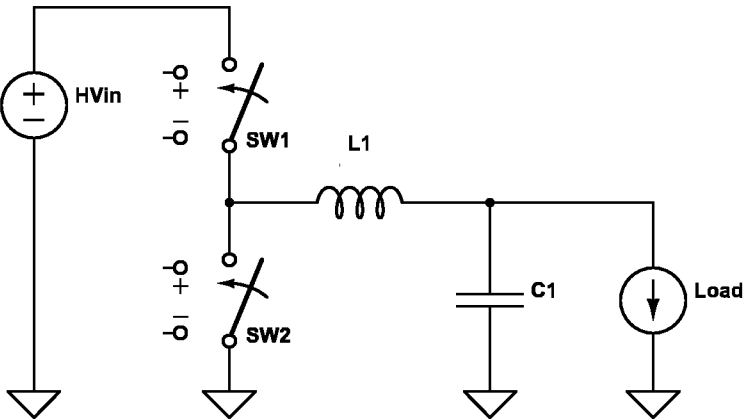


Figure 3 (Prior Art)

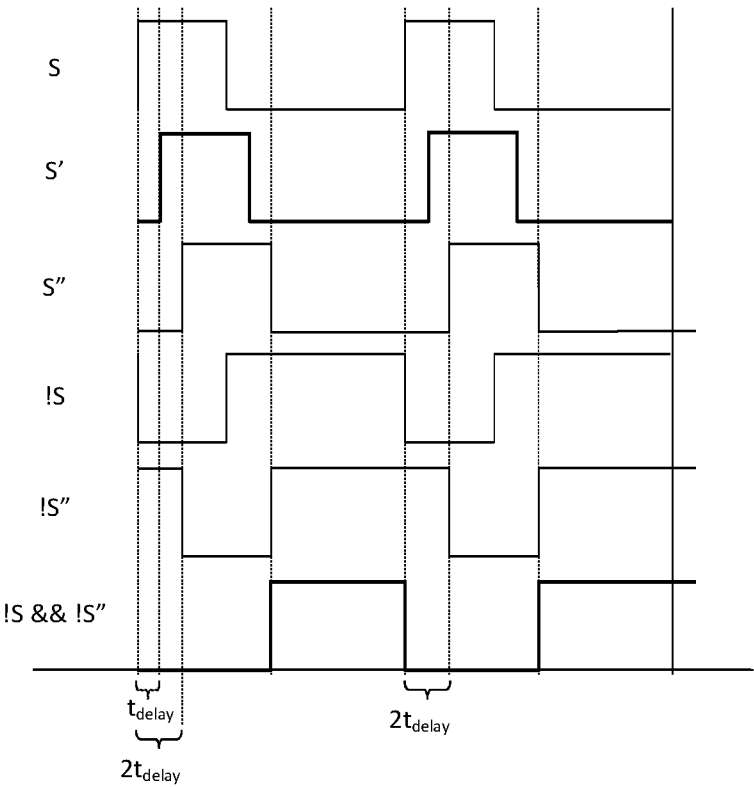


Figure 4 (Prior Art)

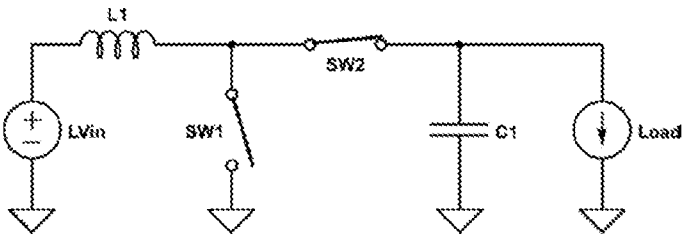


Figure 5 (Prior Art)

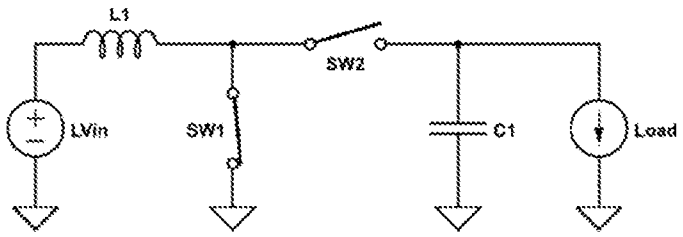


Figure 6 (Prior Art)

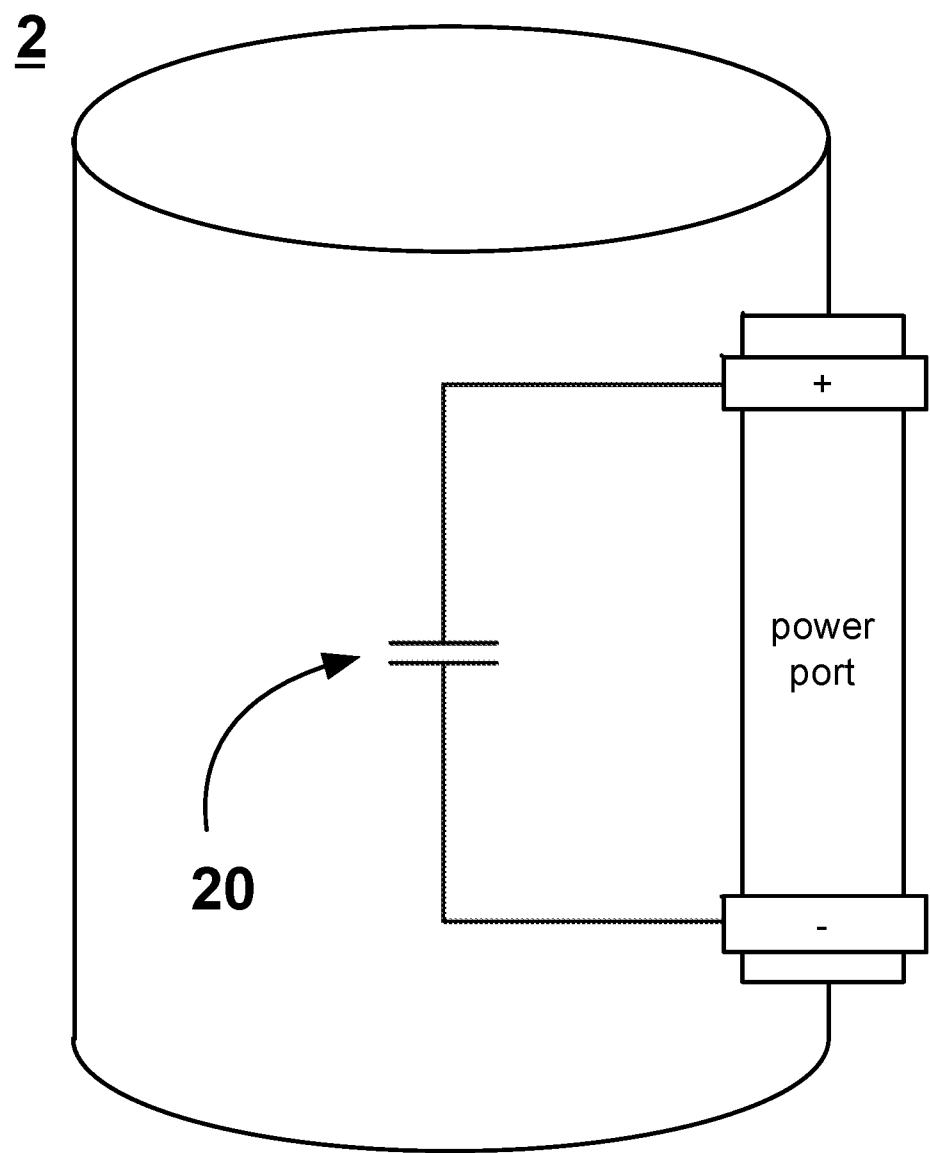


Figure 7A

2

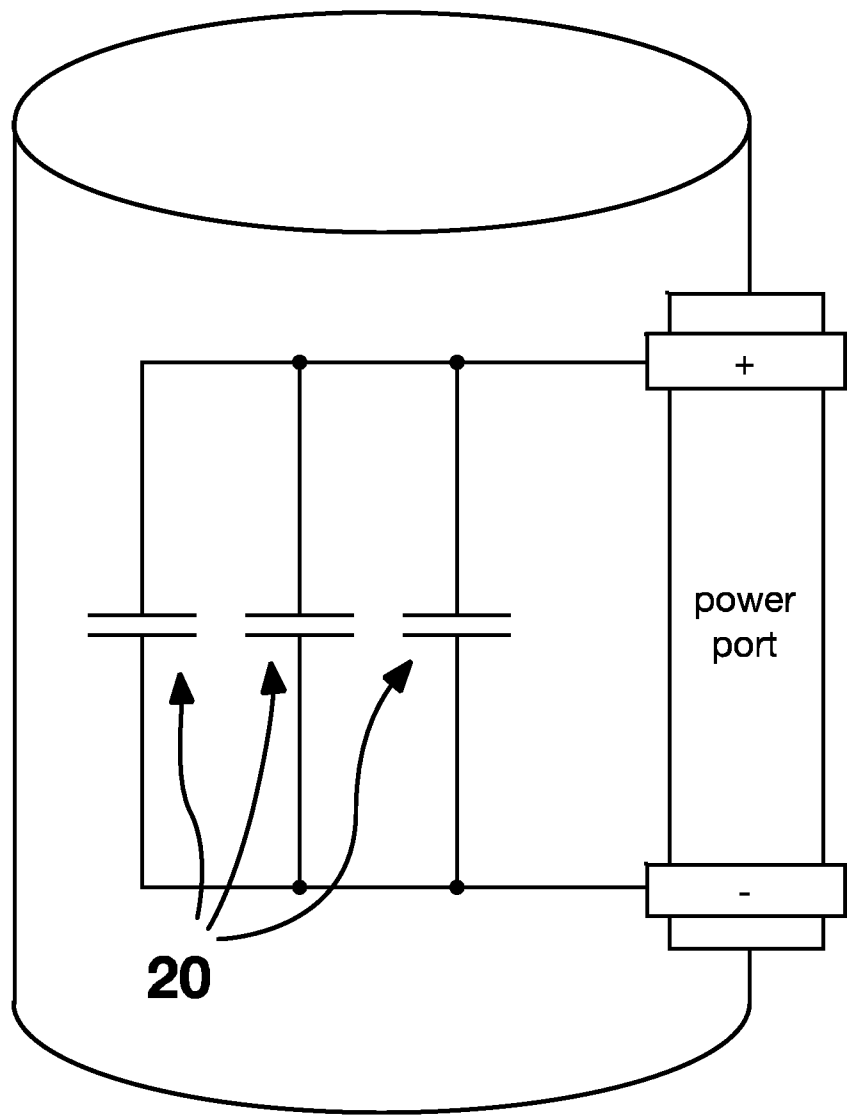


Figure 7B

2

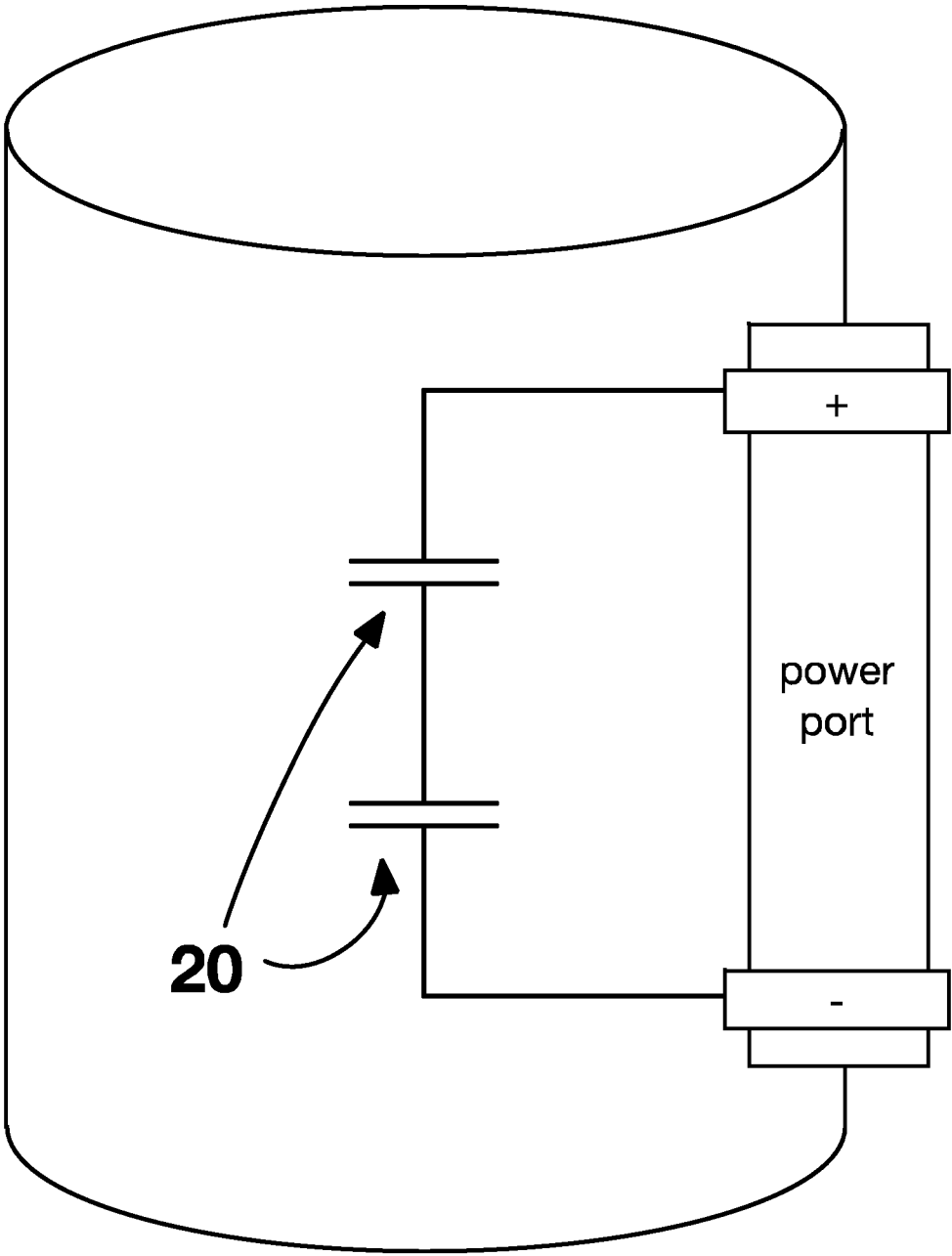


Figure 7C

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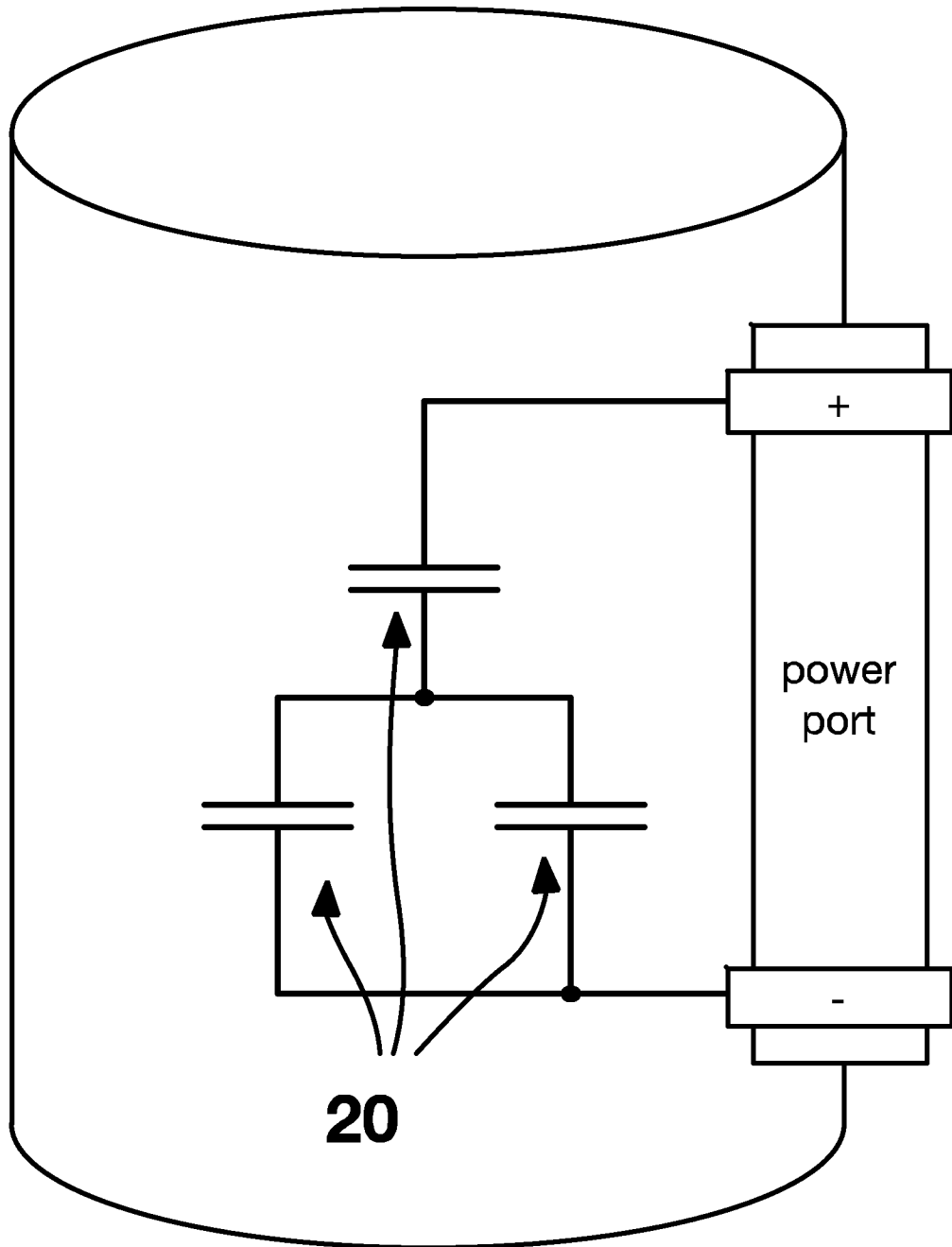
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Figure 7D

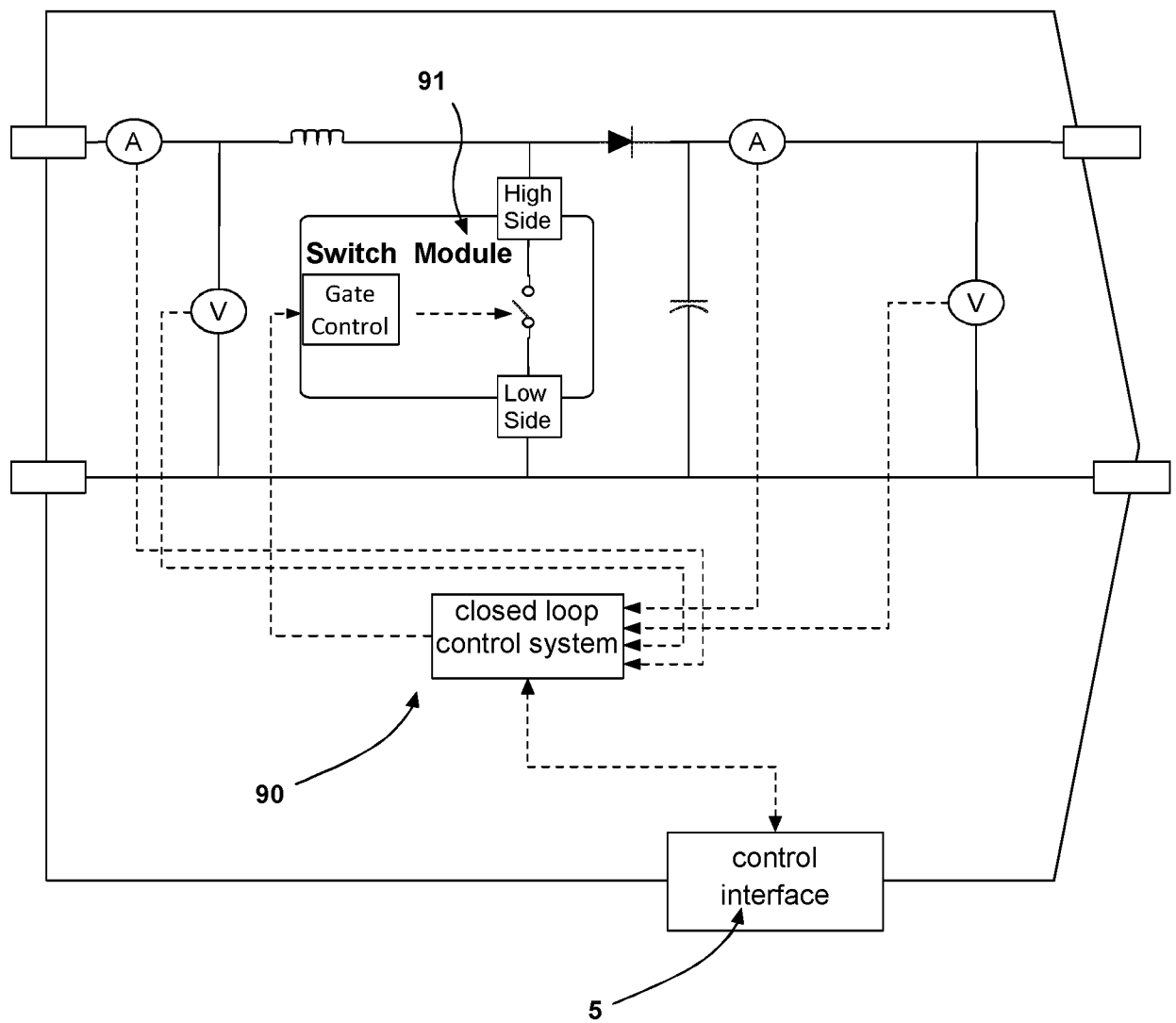
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Figure 8A

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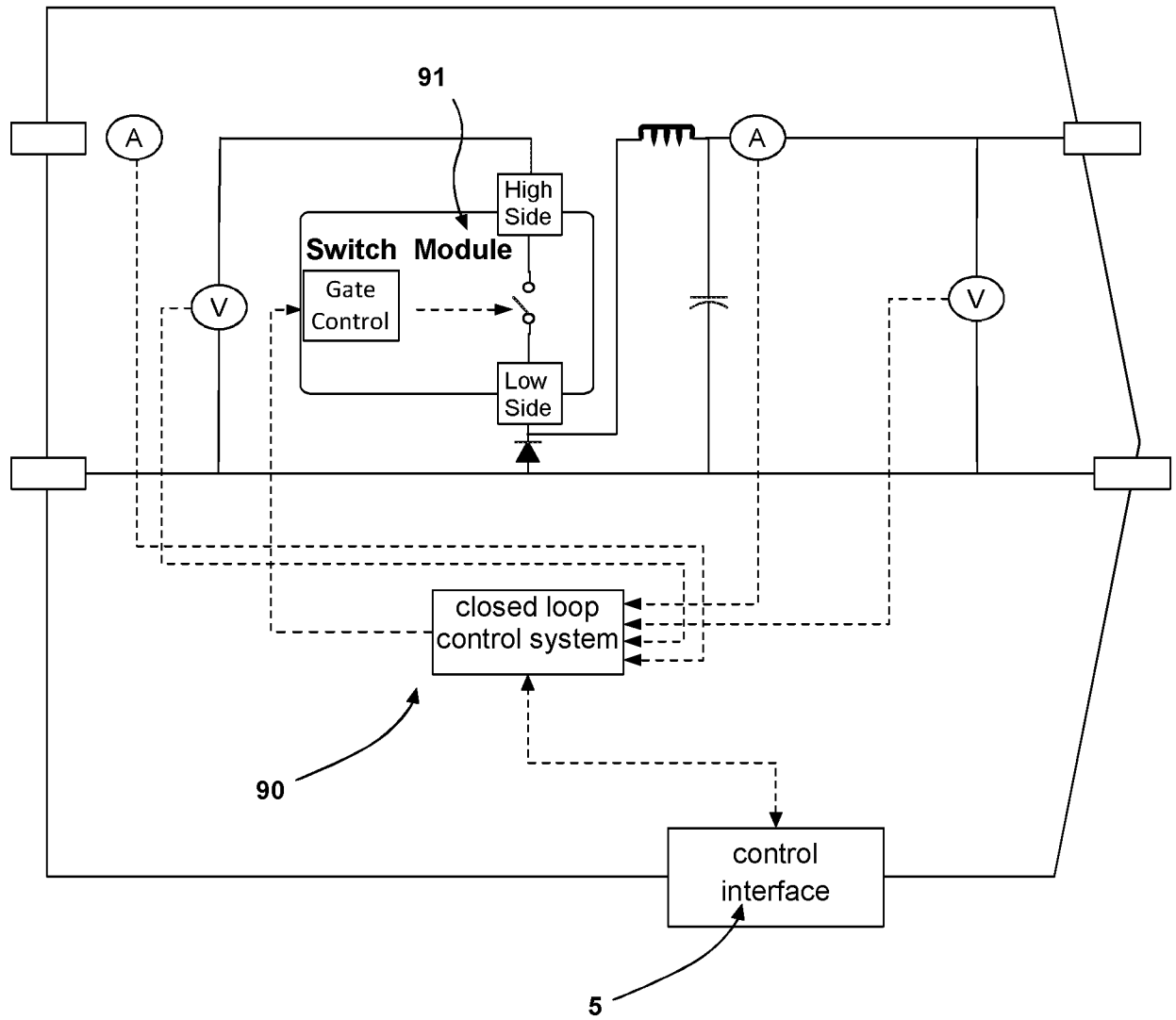
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Figure 8B

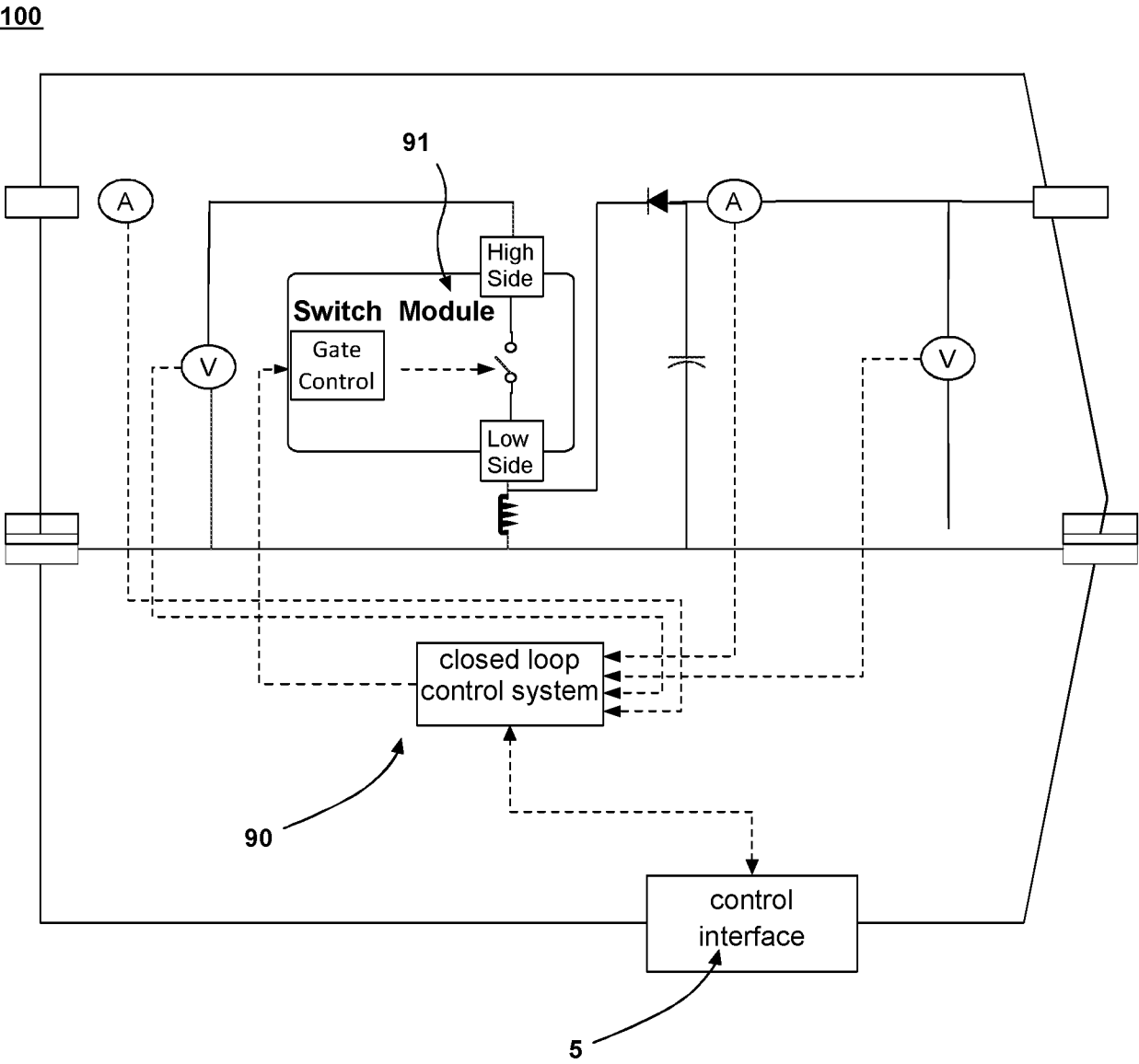


Figure 8C

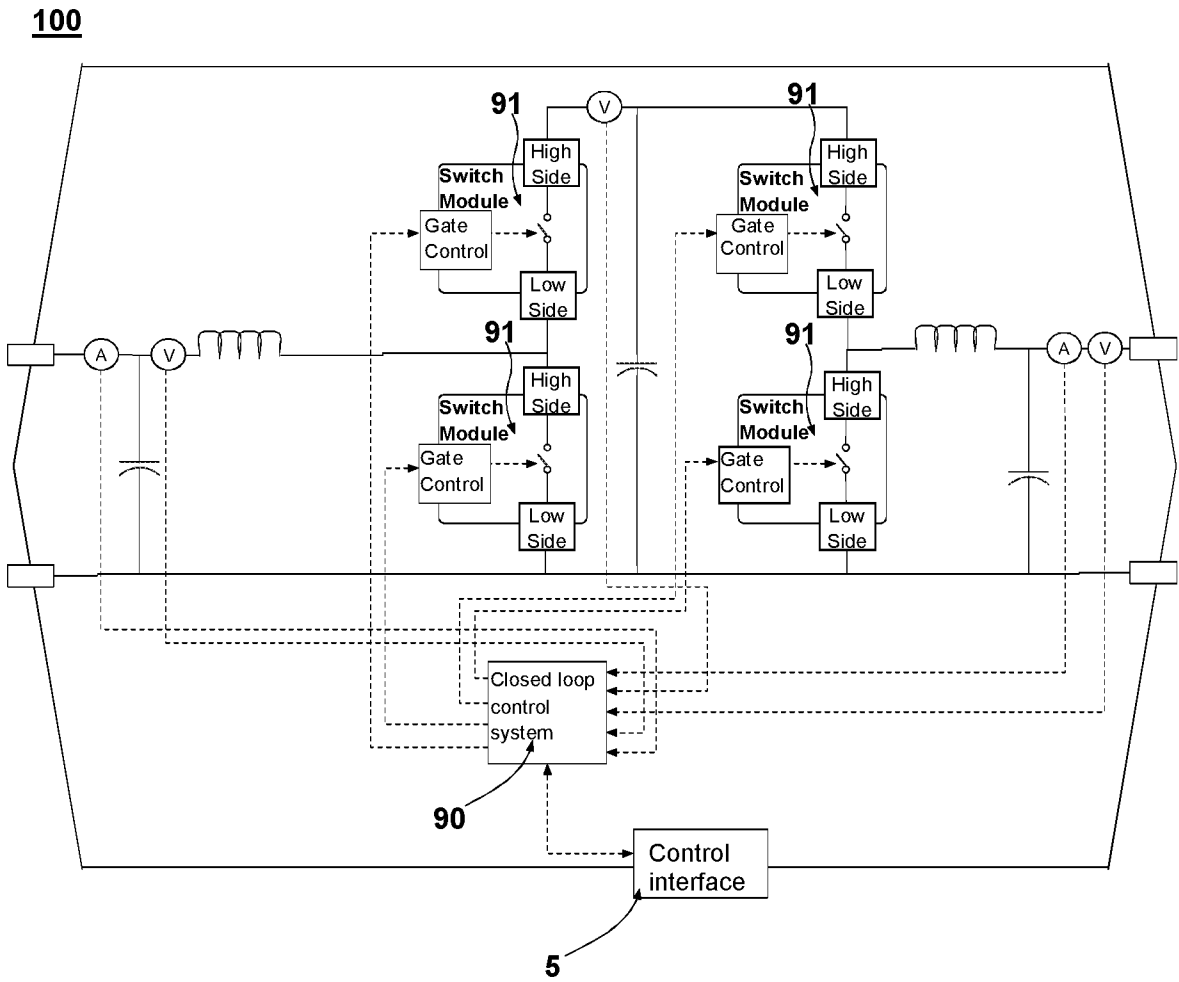


Figure 8D

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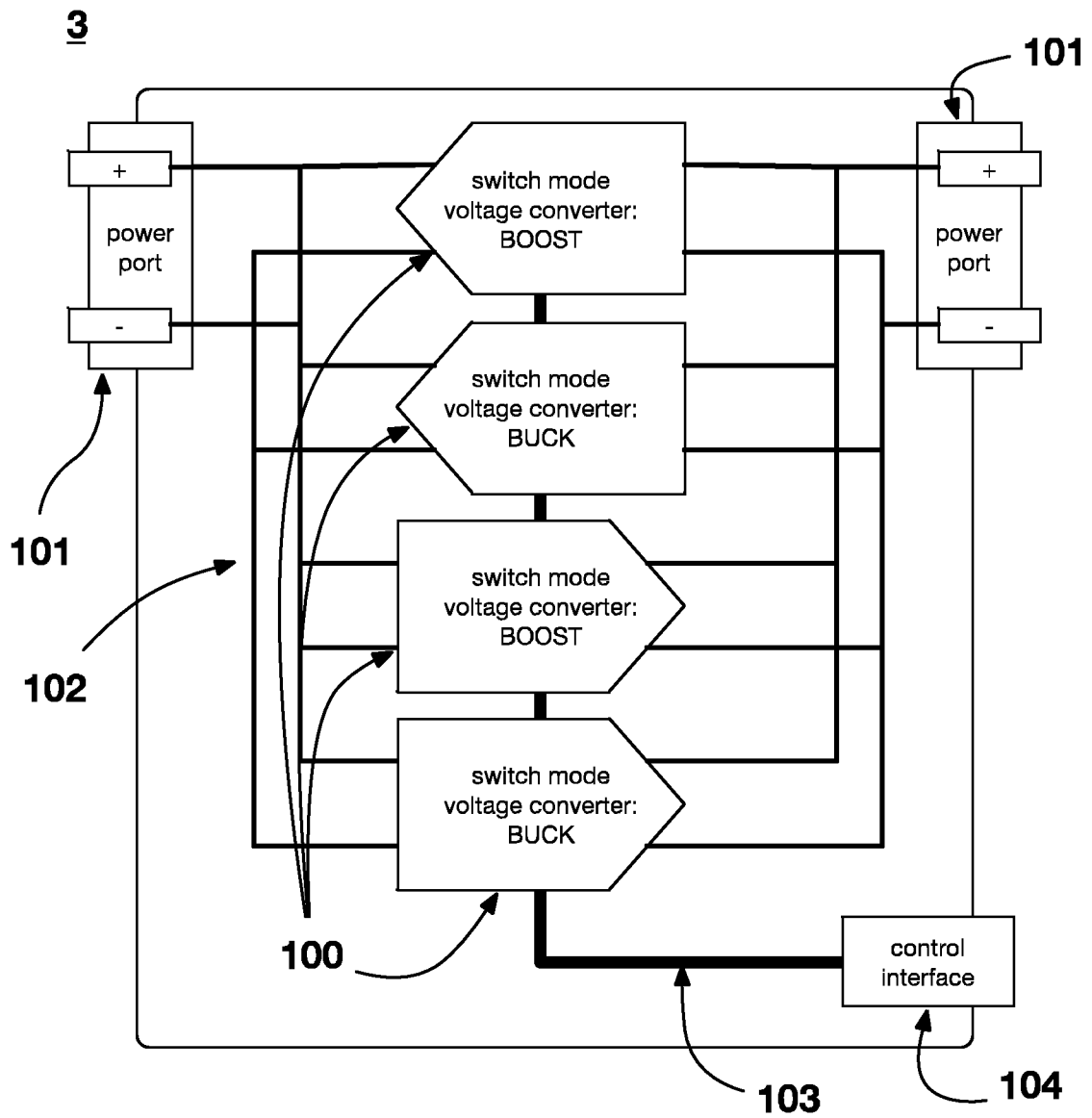


Figure 9A

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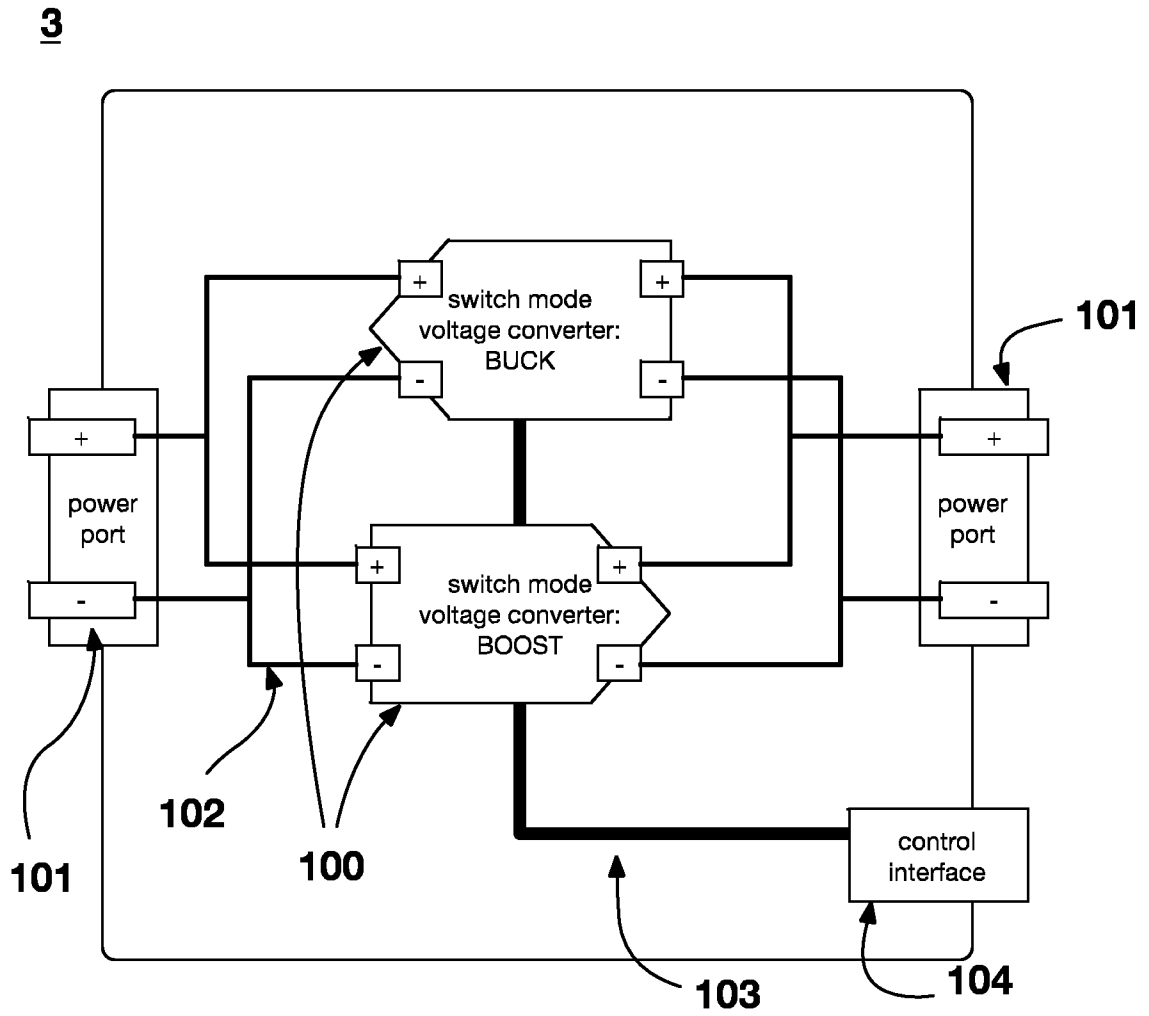


Figure 9B

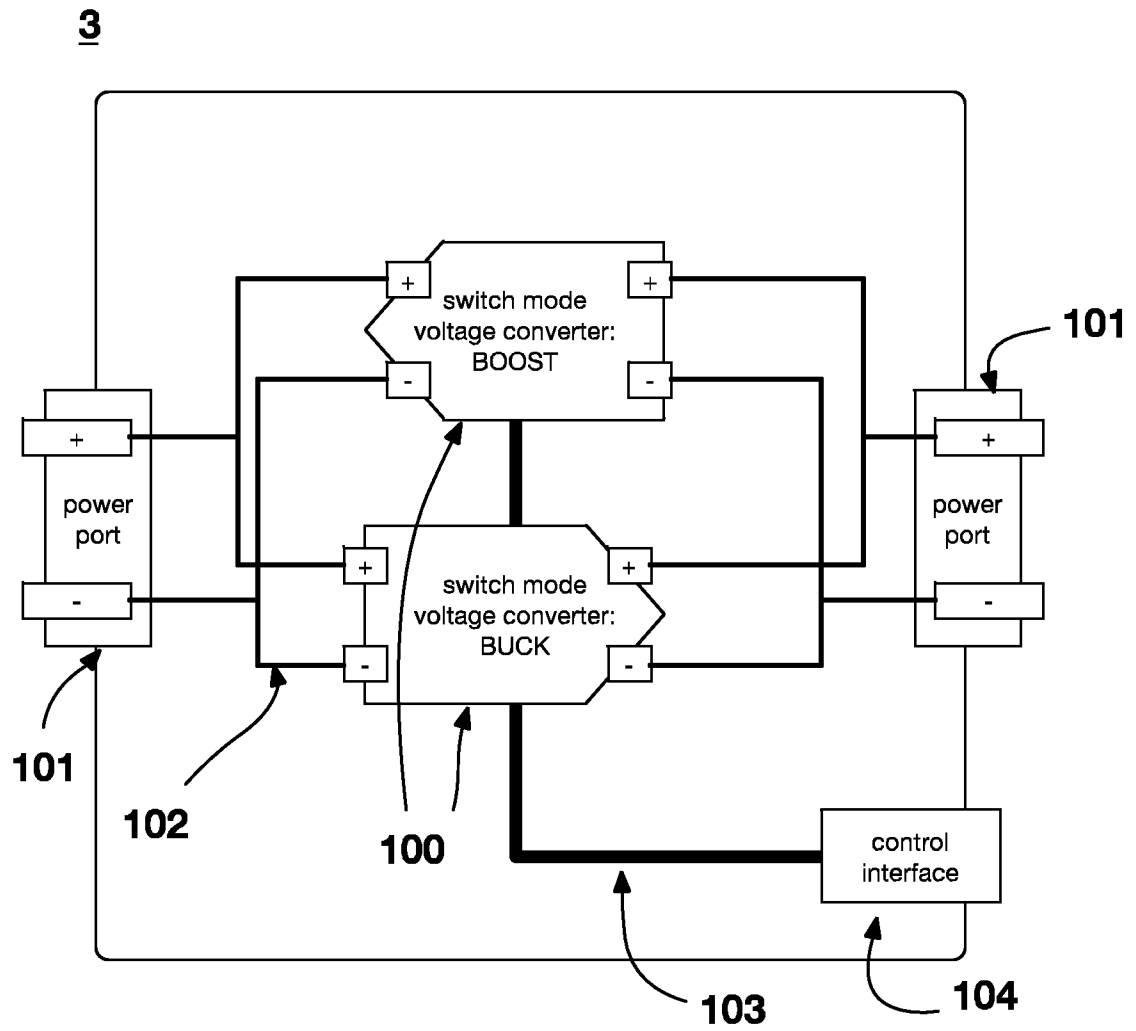


Figure 9C

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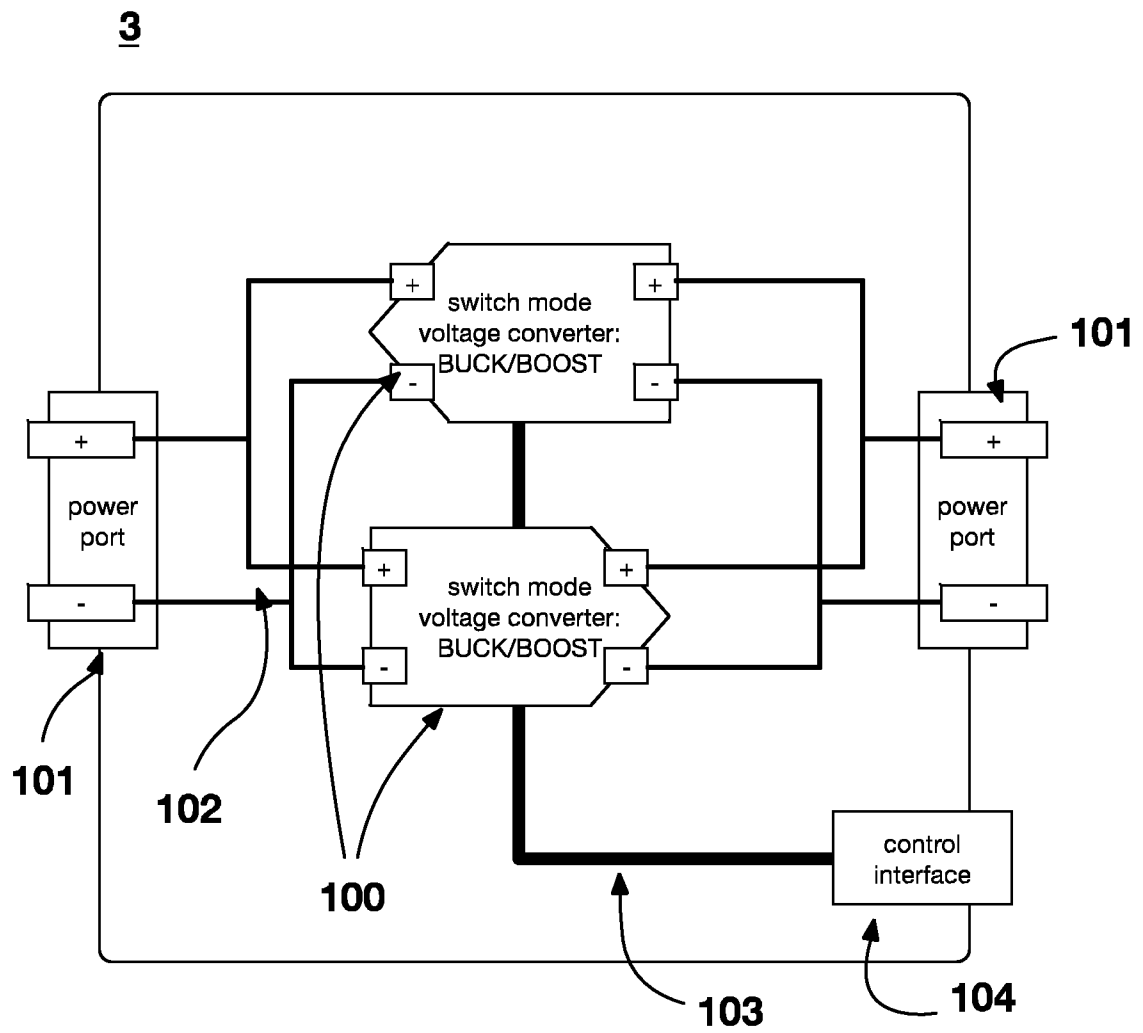


Figure 9D

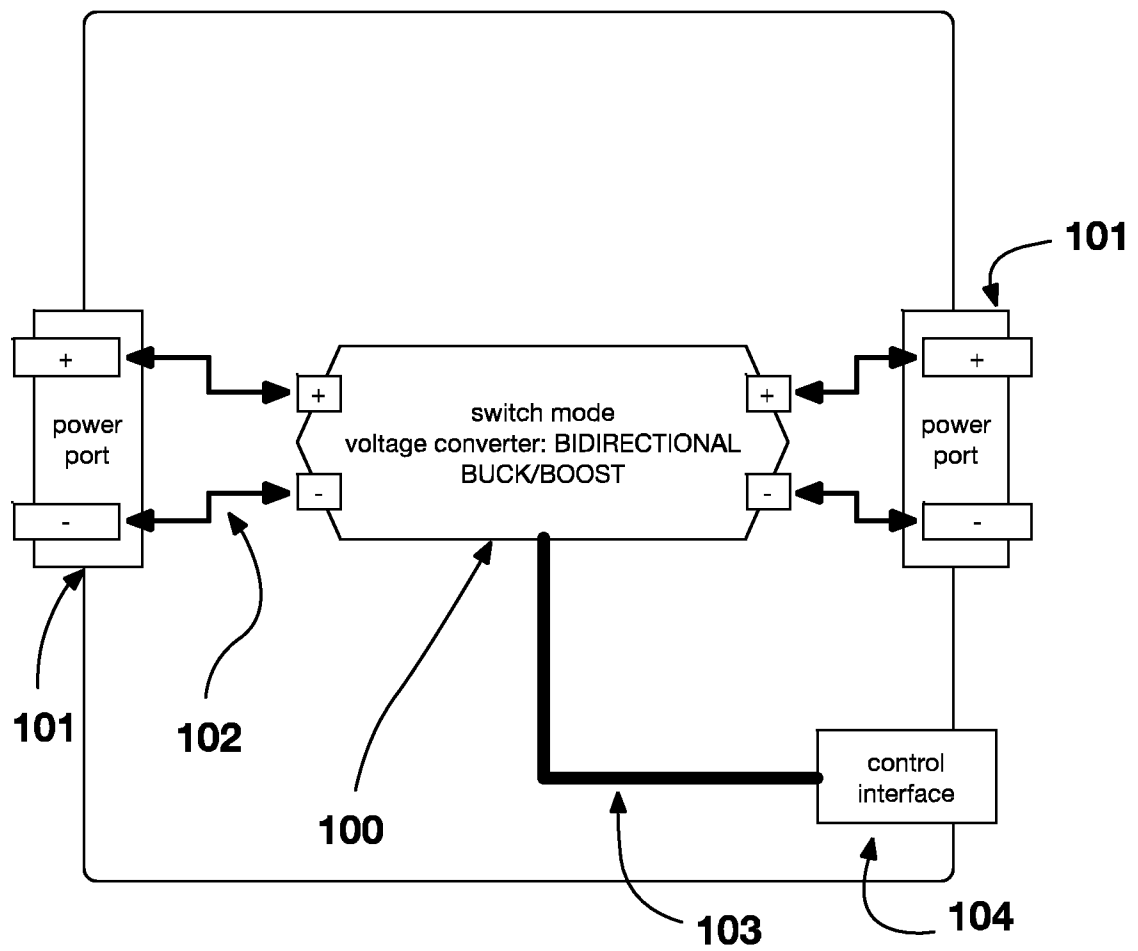
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Figure 9E

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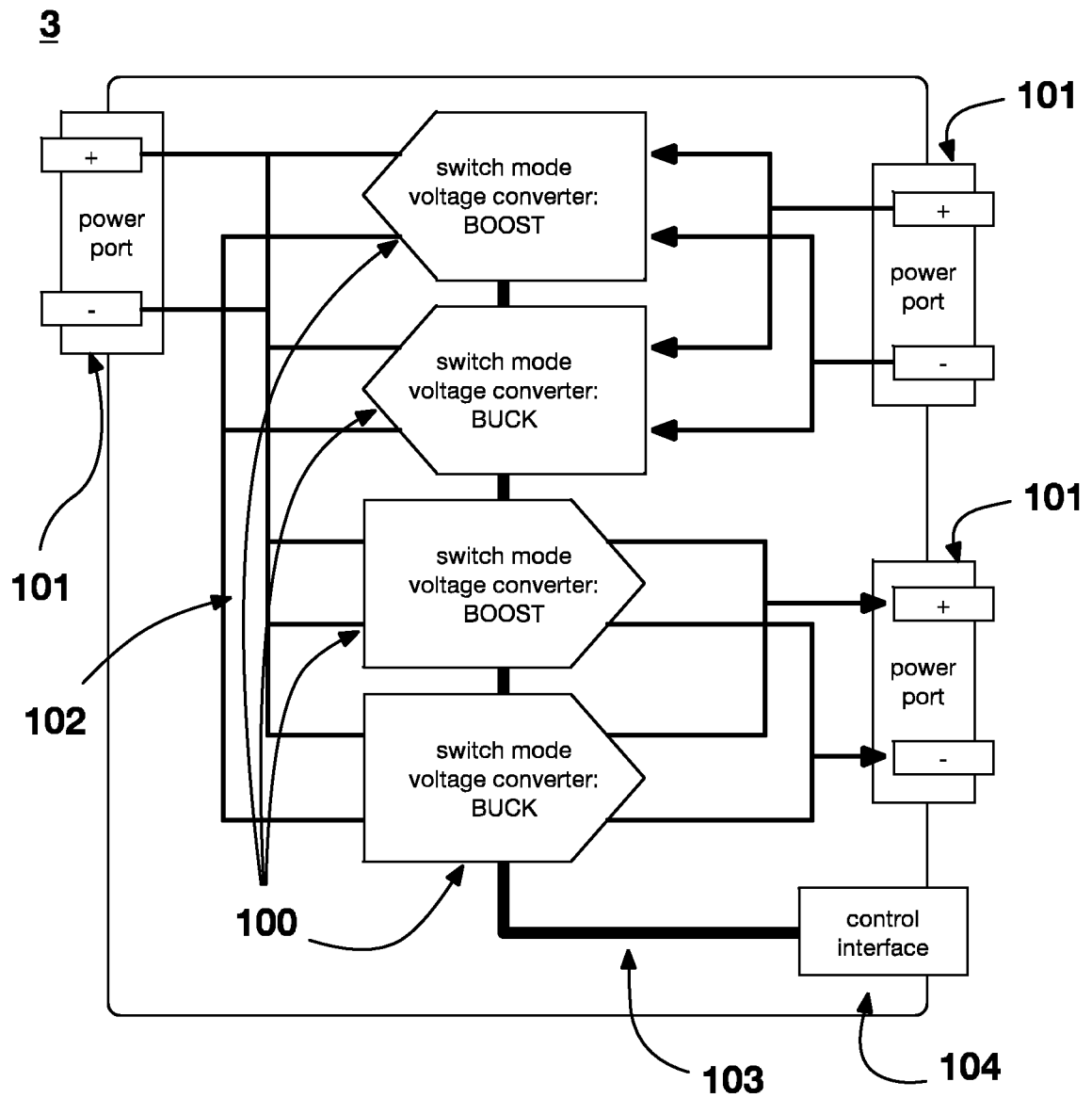


Figure 9F

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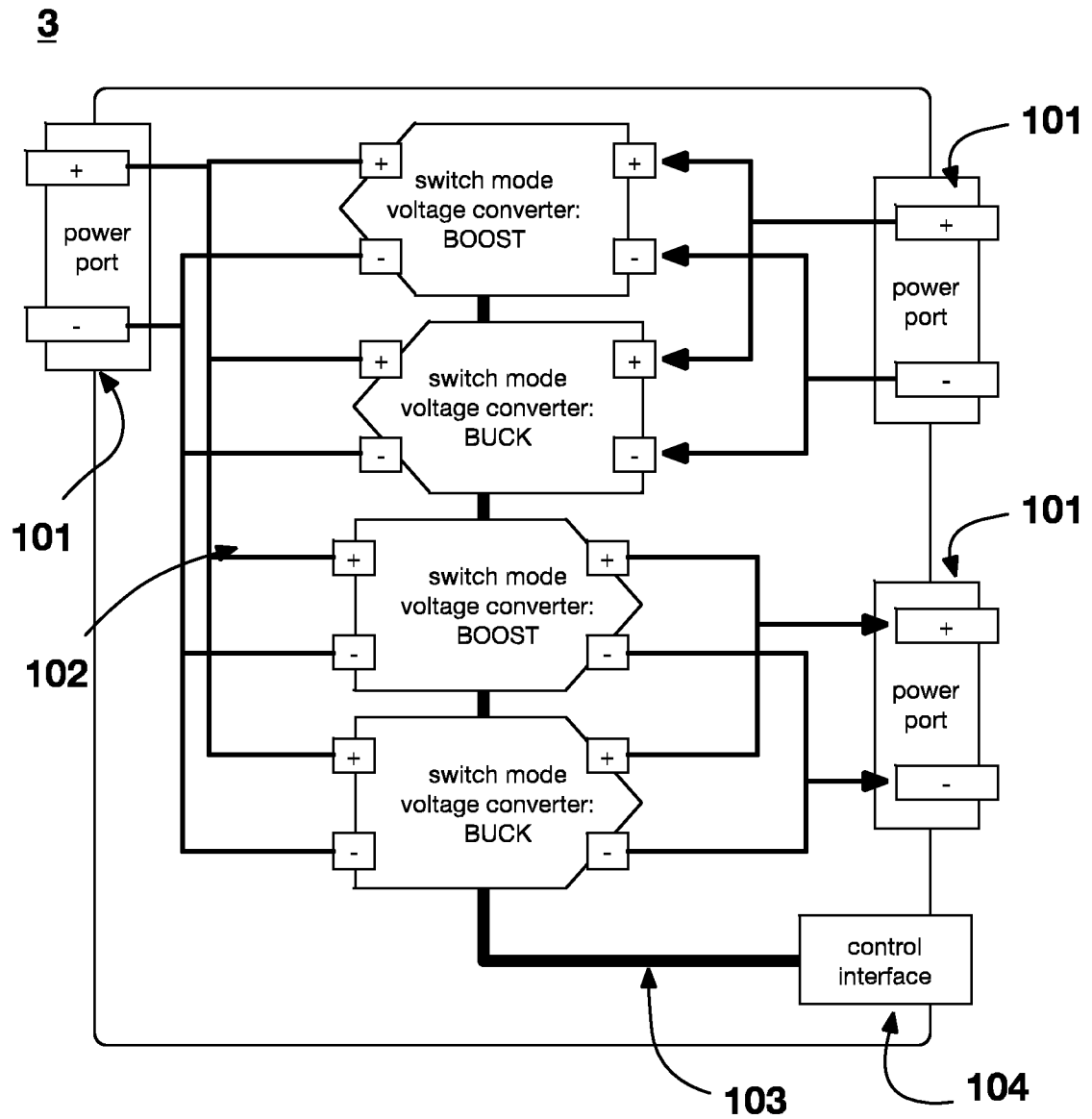


Figure 9G

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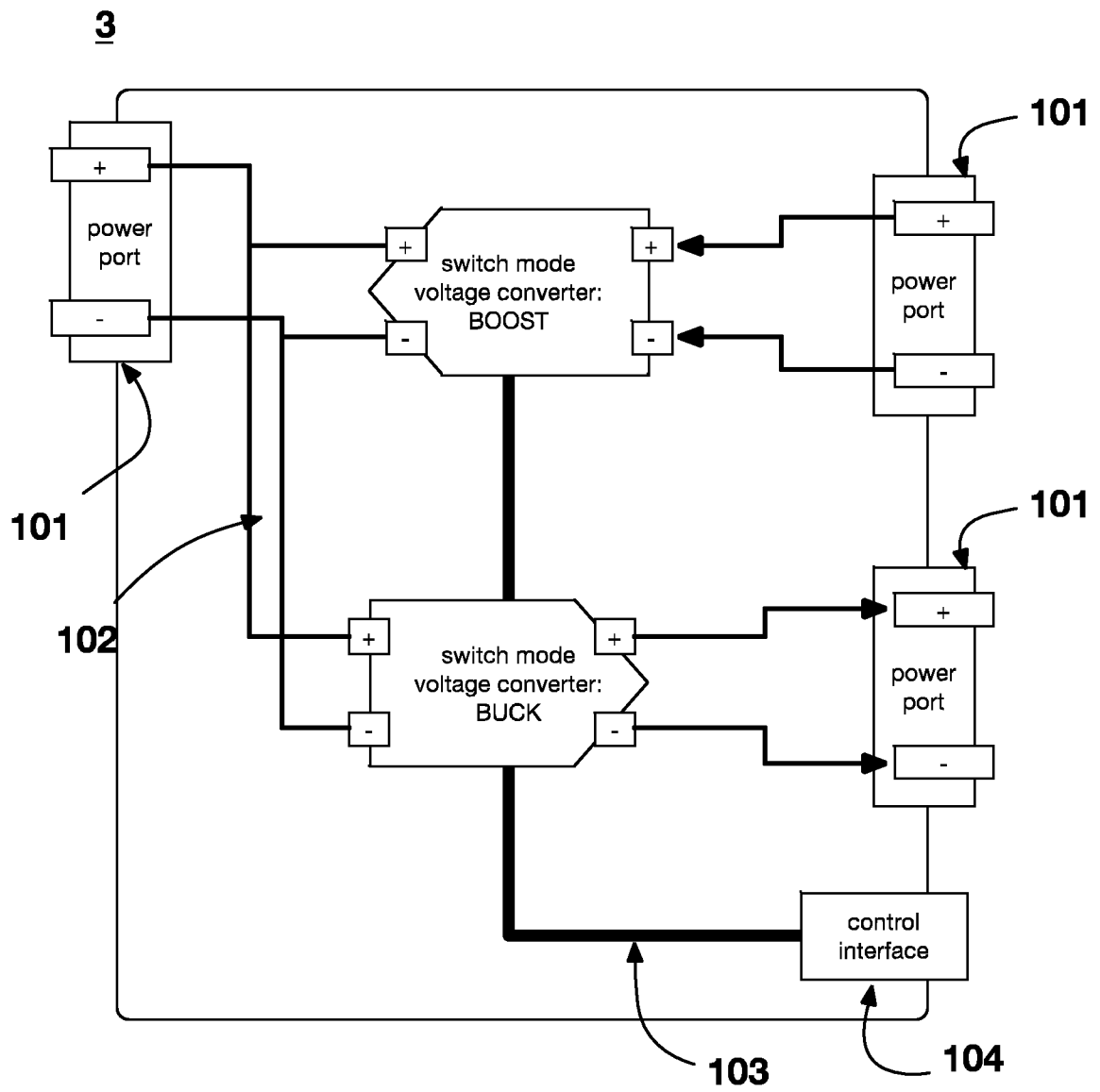


Figure 9H

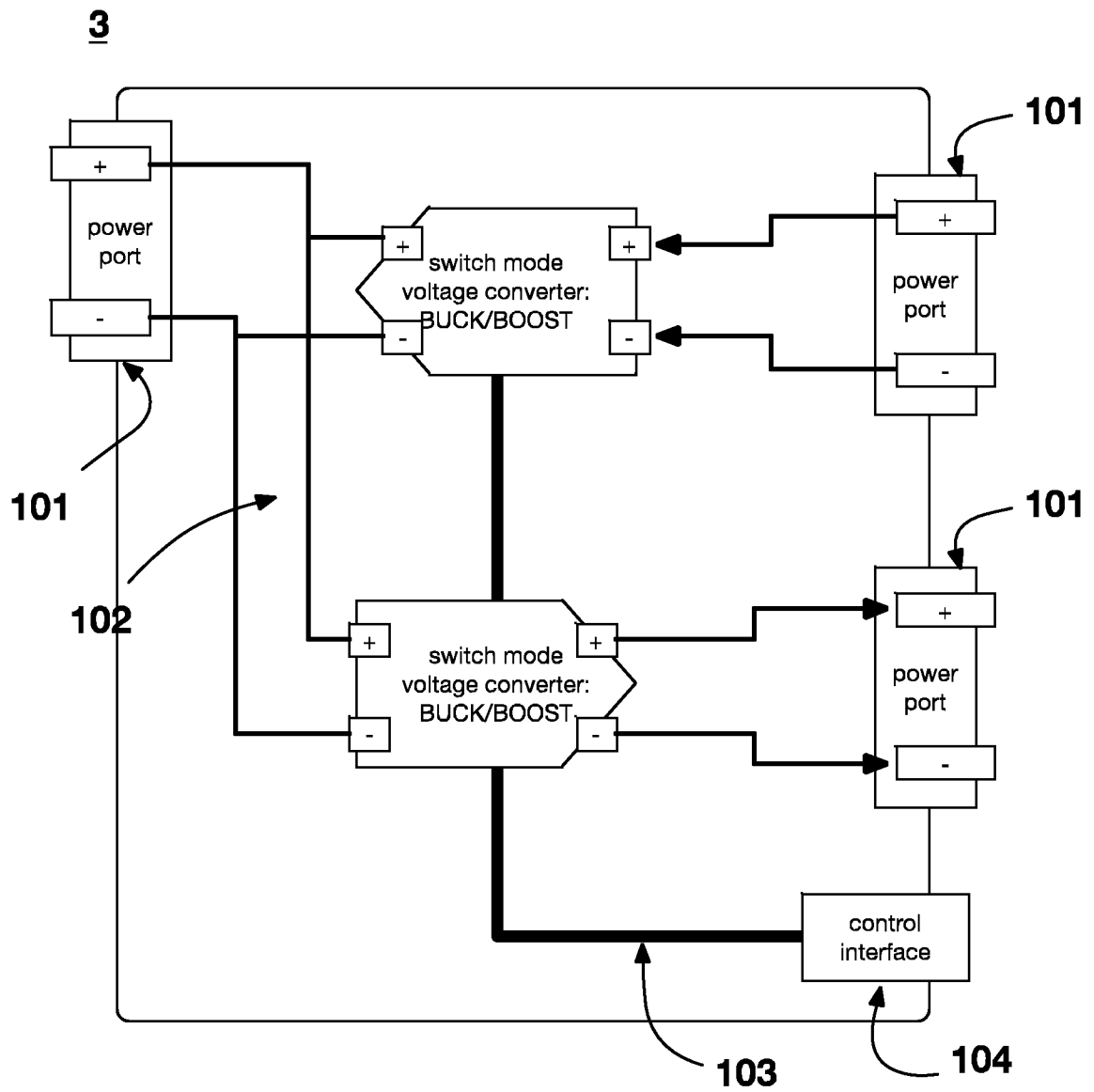


Figure 9I

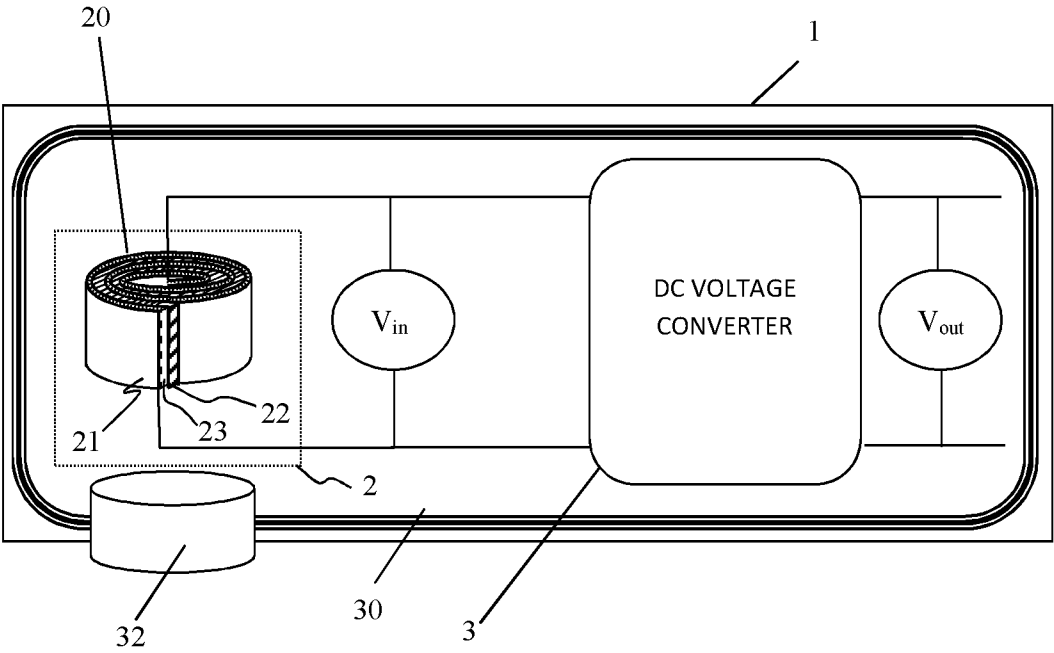


Figure 10

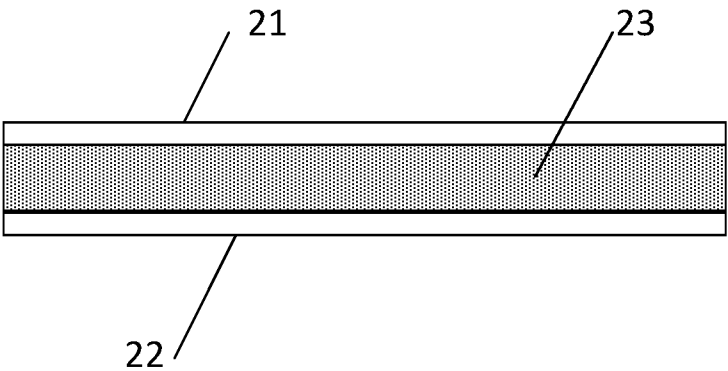


Figure 10A

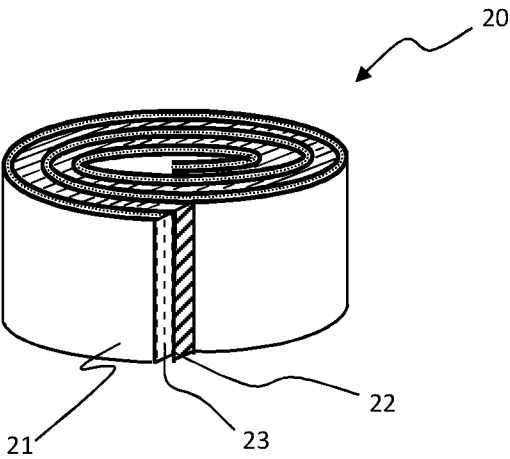


Figure 10B

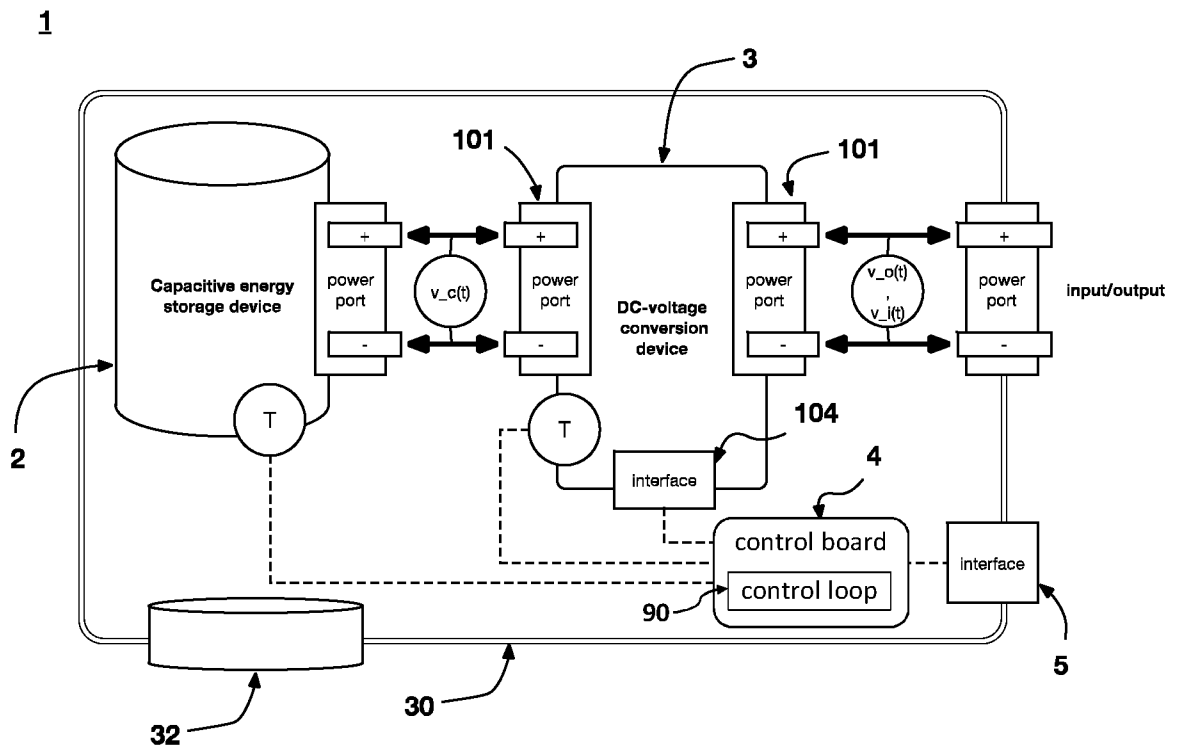


Figure 11

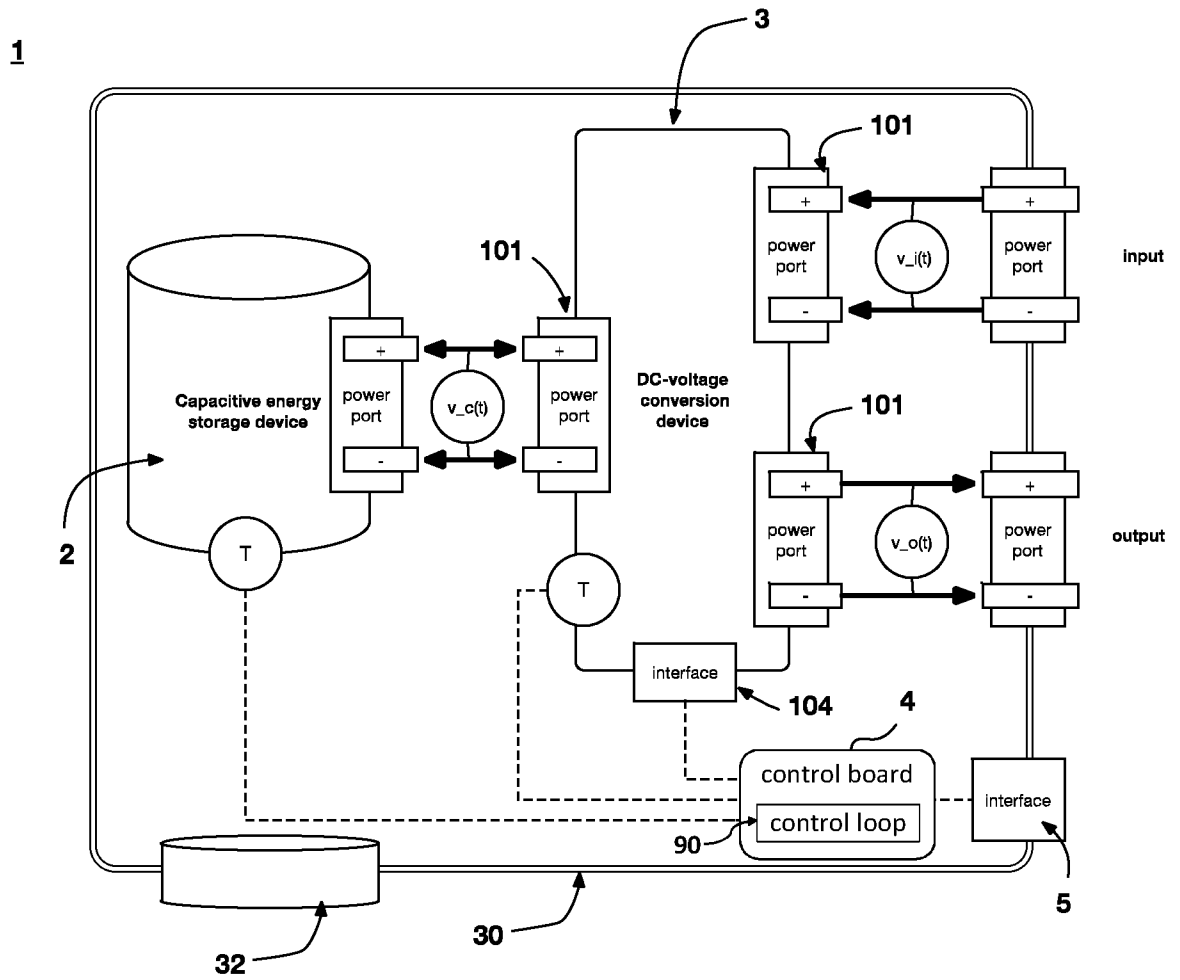


Figure 12

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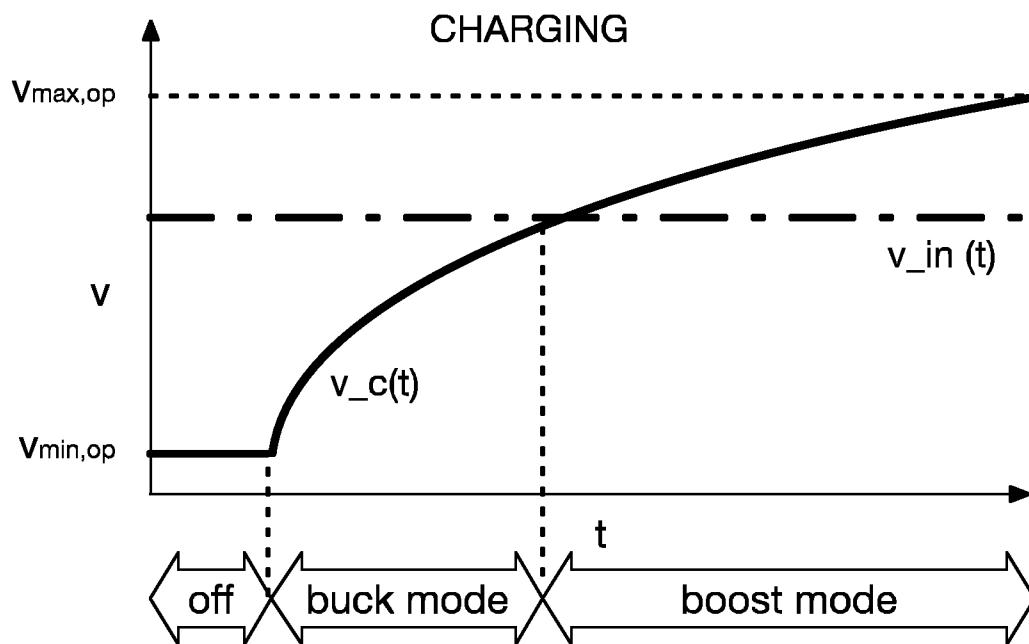


Figure 13A

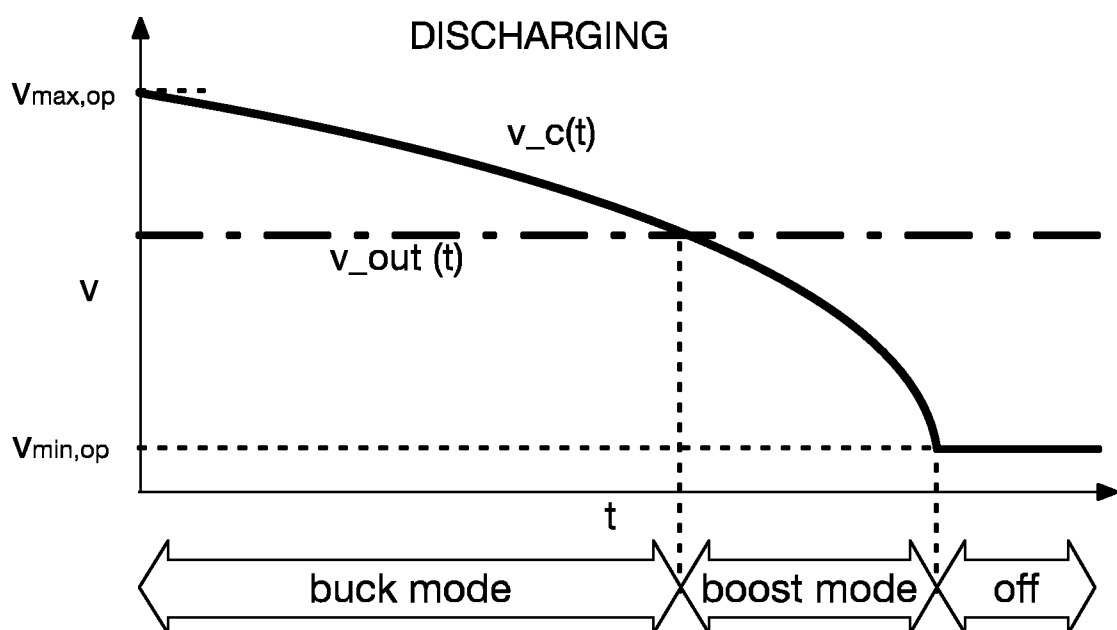


Figure 13B

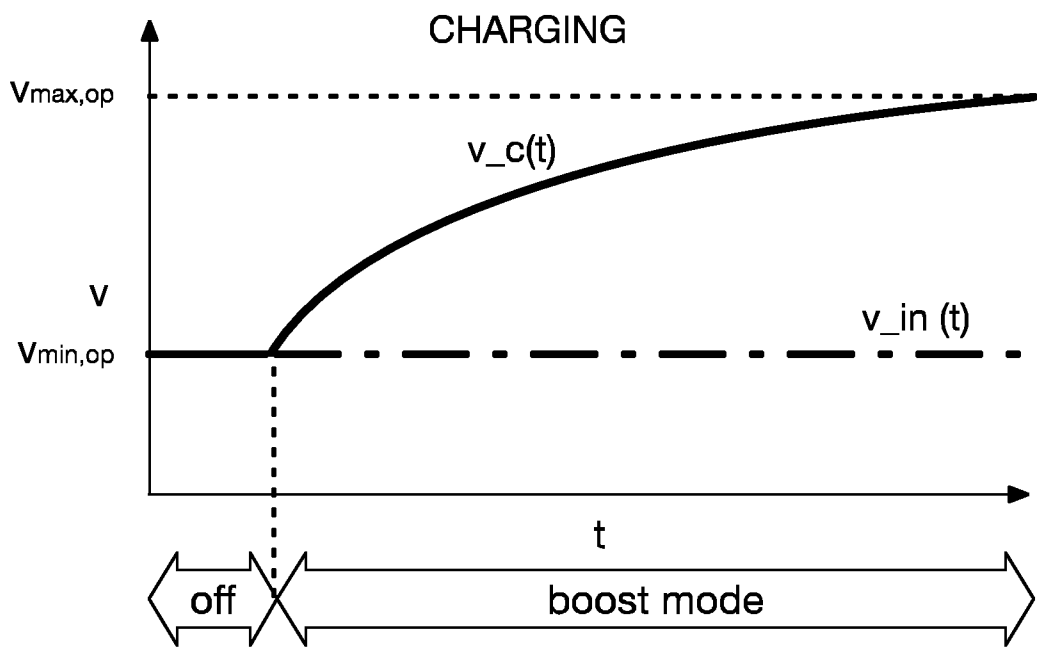


Figure 14A

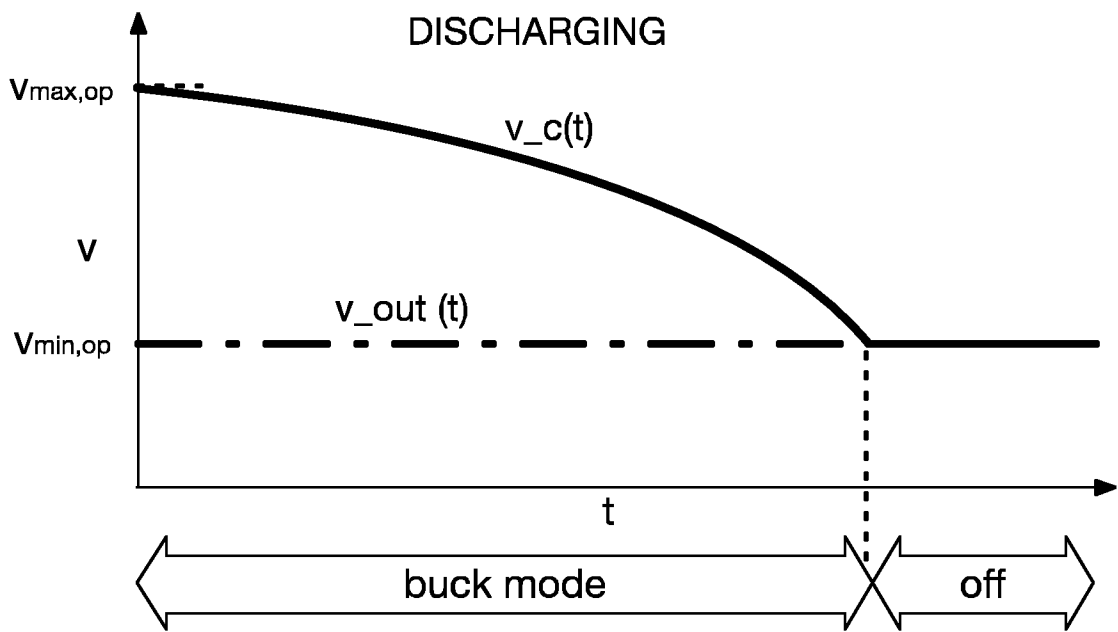


Figure 14B

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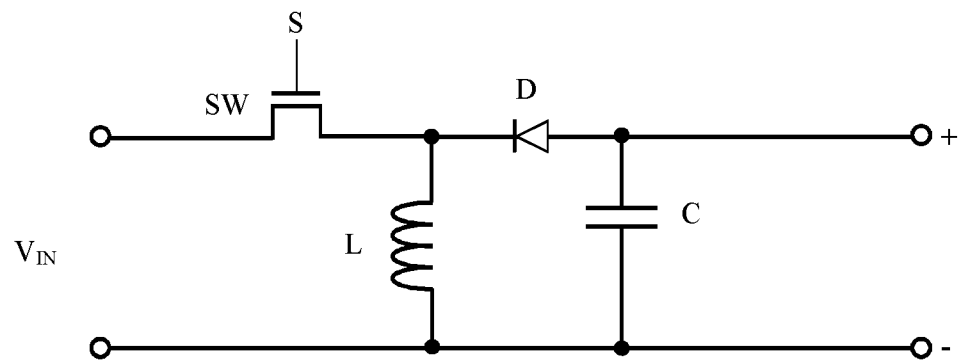


Figure 15A

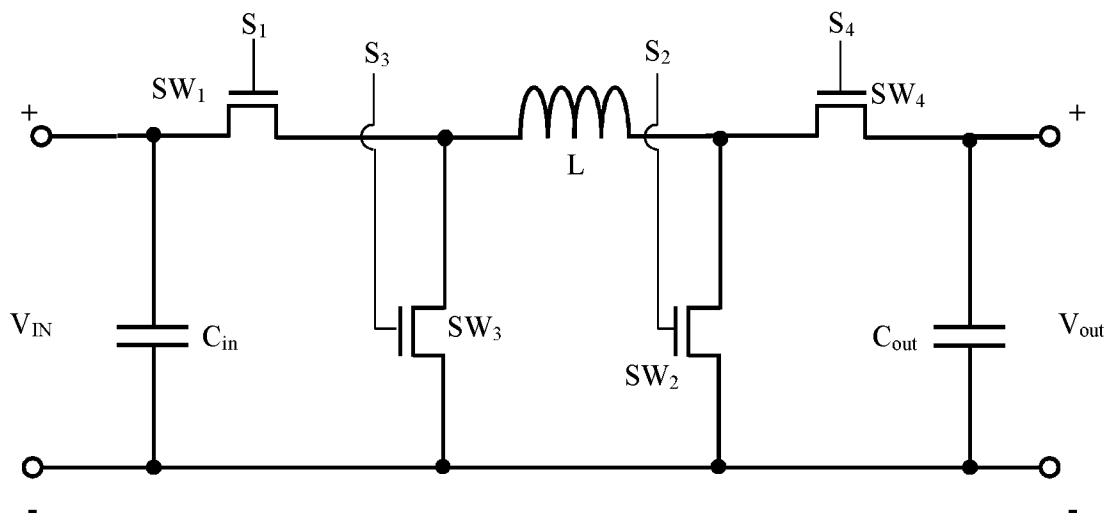


Figure 15B

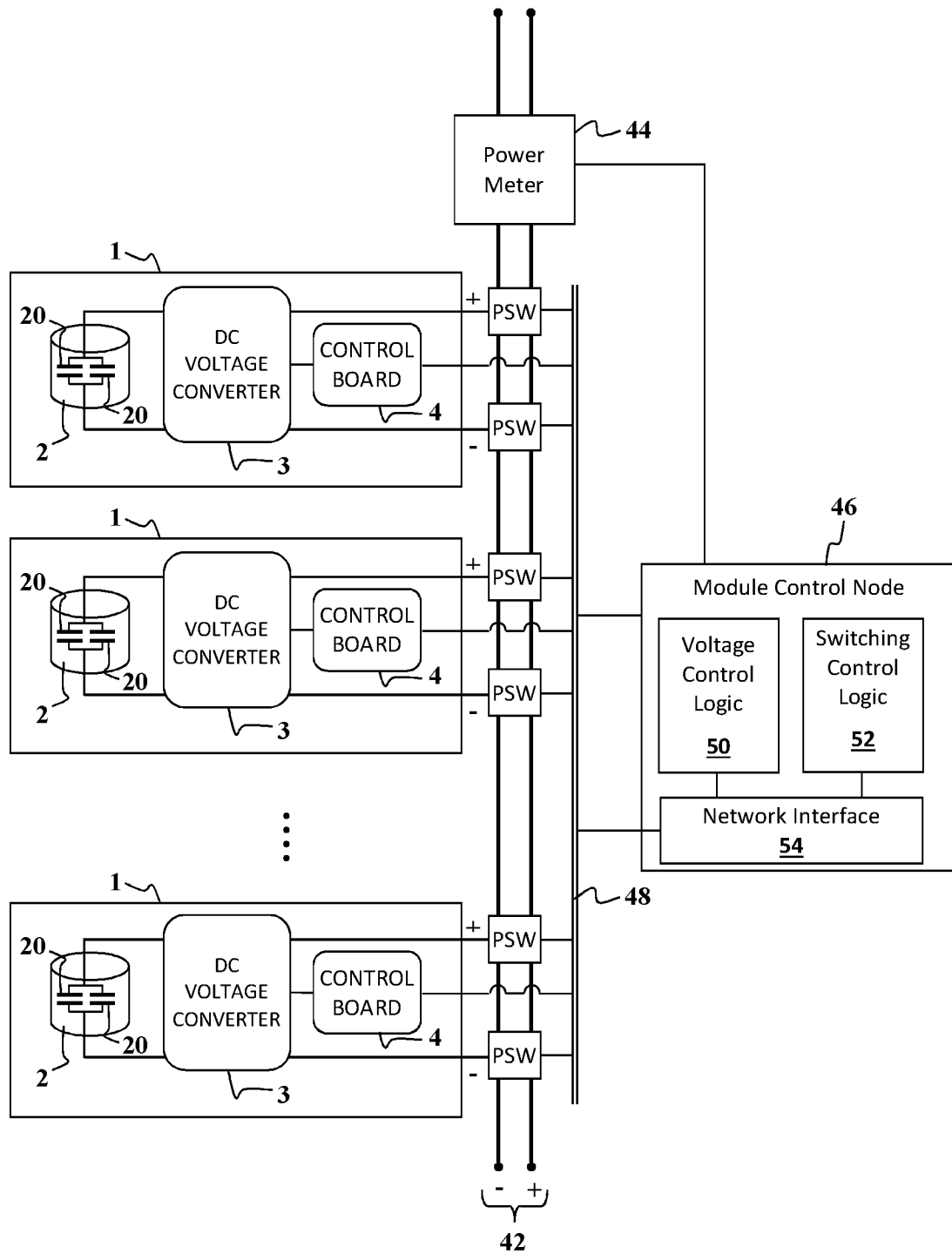


Figure 16

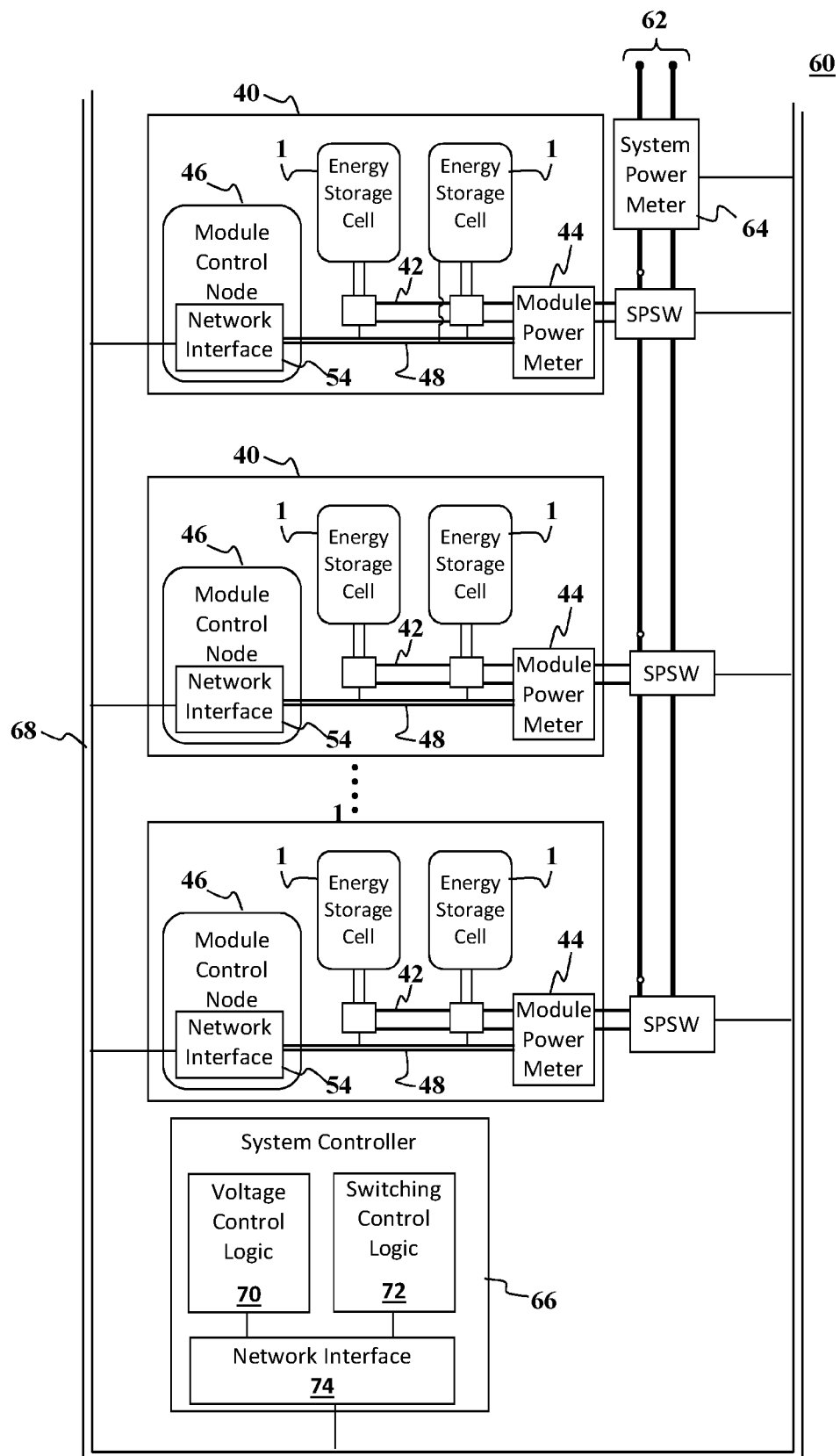


Figure 17