

The rise of supercapacitor diodes: Current progresses and future challenges

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TOPICAL REVIEW — Post-Moore era: Materials and device physics

The rise of supercapacitor diodes: Current progresses and future challenges

Hongyun Ma(马鸿云)[1,2,†], Lingxiao Ma(马凌霄)[1], Huasheng Bi(毕华盛)[1], and Wei Lan(兰伟)[1,‡]

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Supercapacitor has been widely known as a representative electrochemical energy storage device with high power density and long lifespan. Recently, with the deeper understanding of its charge storage mechanism, unidirectional-charging supercapacitor, also called supercapacitor diode (CAPode), is successfully developed based on the ion-sieving effect of its working electrode towards electrolyte ions. Because CAPode integrates mobile ion and mobile electron in one hybrid circuit, it has a great potential in the emerging fields of ion/electron coupling logic operations, human–machine interface, neural network interaction, and *in vivo* diagnosis and treatment. Accordingly, we herein elucidate the working mechanism and design philosophy of CAPode, and summarize the electrode materials that are suitable for constructing CAPode. Meanwhile, some other supercapacitor-based devices beyond CAPode are also introduced, and their potential applications are instructively presented. Finally, we outline the challenges and chances of CAPode-related techniques.

Keywords: supercapacitor diode, ion-sieving effect, ion/electron coupling circuit, logic operation

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1. Introduction

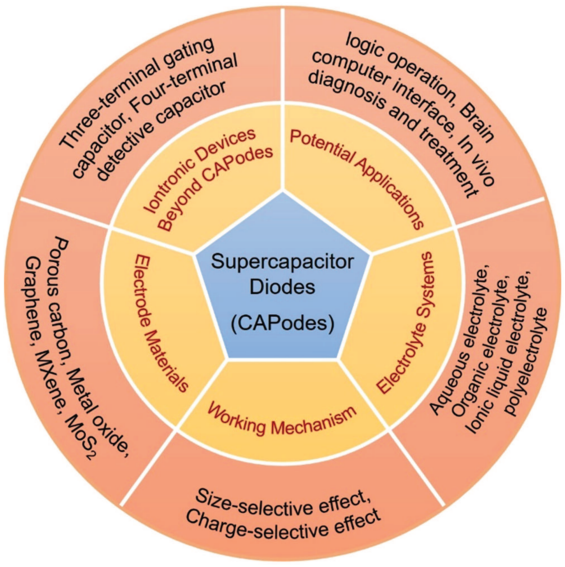
Supercapacitor diodes (CAPodes) are an emerging type of functional electrochemical devices that have a device structure similar to asymmetric supercapacitors and a unidirectional charging characteristic analogous to that of semiconductor diodes.[1,2] Considering that CAPodes integrate mobile ions and mobile electrons in the same circuit, they are recognized as the most promising components for the forthcoming ion/electron coupling circuits, thus showing a great potential in the emerging fields of human–machine interface, neural network interaction, and *in vivo* diagnosis and treatment.[3–8] The concept of CAPode was proposed by Kaskel and colleagues in 2019, and the prototype device was constructed by using a size-selective microporous carbon electrode and a tetrabutylammonium tetrafluoroborate ($TBABF_4$) electrolyte.[1] Interestingly, owing to the ion-sieving effect of the microporous carbon electrode upon the electrolyte ions (TBA^+ and BF_4^-), the as-built CAPode exhibits a unidirectional charge storage behavior, as well as a unidirectional conduction characteristic similar to that of semiconductor diode. These special properties extend the application scenarios of supercapacitors into new technique fields, endowing supercapacitors with the ability to be applied in power transmission, signal transmission, and logical operations.[9–13] As a consequence, once published, this work attracted widespread attention from both academia and industry.

Recently, Yan and colleagues developed a new ion regulation strategy that utilizes poly(ionic liquid)s as the electrolytes.[14] Owing to the blocking effect of carbon electrode towards large-size polyanions (or polycations), only small-size cations (or anions) can be normally stored in the carbon electrode. As a result, the constructed CAPodes show ideal unidirectional charging characteristics. Also, because of the utilization of polyanion or polycation electrolytes, this work achieves the constructions of both P-type and N-type CAPodes. Very recently, Yan's group reported a brand new pseudocapacitor diode that is based on spinel $ZnCo_2O_4$.[15] By utilizing the ion-selective surface redox reaction of spinel $ZnCo_2O_4$ in aqueous alkaline electrolyte, the as-built CAPode exhibits an obvious unidirectional charging behavior. On the basis of deeply analyzing and understanding the working mechanism of CAPodes, our group recently developed a molybdenum oxide based high-performance CAPode.[2] Benefiting from the unique size and charge dual ion-sieving effects of the molybdenum oxide electrode, the constructed CAPode exhibits an enhanced rectification ratio which is over 10 times higher than those of the reported systems. Such excellent rectification capability allows the as-built CAPode to work well in AND and OR logic gates, validating great potential in ion/electron coupling logic operations. More attractively, molybdenum oxide has good biocompatibility, which enables the constructed CAPode to be applied as bioelectronics without regard to biosafety, paving a new way towards forthcoming human–computer interaction.

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Though great progresses have been made, the development of CAPode is just in the infancy, and there are still many scientific and/or technological issues that need to be researched and solved. To this end, the aim of this review is to provide a holistic discussion on the electrochemical fundamental and potential application fields of CAPode (Scheme 1). Specifically, an in-depth elucidation of the working mechanism and design philosophy of CAPode is presented first. Then a comprehensive summary of the electrode materials that are suitable for constructing CAPode is provided. In the penultimate part, some other supercapacitor-based devices beyond CAPode are also introduced, and their potential applications are instructively presented. Finally, we outline the challenges and chances of CAPode-related techniques. We hope this review article can attract broad interests from the communities of material science, electrochemical energy storage, and biomimetic science, so as to further accelerate the development of CAPode.



Scheme 1. Summary of the key elements of CAPodes, including working mechanism, electrode materials, electrolyte systems, potential applications, and iontronic devices beyond CAPodes.

2. Working mechanism and design philosophy

The first CAPode was developed upon the size-selective effect of microporous carbon electrode towards small anions and large cations.[1] As shown in Figs. 1(a) and 1(b), the prototype device consists of a microporous carbon (C_{micro}) working electrode, a mesoporous carbon (C_{meso}) counter electrode, and a tetrabutylammonium tetrafluoroborate ($TBABF_4$) electrolyte. The C_{micro} has a pore width of 0.87 nm, while the characteristic pore width of C_{meso} is as large as 4.8 nm, and the lateral sizes of TBA^+ cations and BF_4^- anions are 1.1 nm and 0.41 nm, respectively. It can be seen that CAPode has an identical device structure and device composition to supercapacitor, thus being an important derivative of supercapacitor. But to endow the CAPode with unidirectional conduction characteristics, one of its electrodes, i.e., working electrode, should have good ion-sieving capability. Accordingly, the unidirectional charging is realized by using the different storage behaviors of TBA^+ cations and BF_4^- anions in C_{micro} and C_{meso}, and two cases should be considered. First, when the whole device is positively charged (forward bias, Fig. 1(a)), the C_{micro} working electrode is positively polarized and the C_{meso} counter electrode is negatively polarized. In this case, BF_4^- anions will penetrate into C_{micro} working electrode and TBA^+ cations will be accommodated by C_{meso} counter electrode. As a consequence, electrode/electrolyte double layers can develop on both electrodes. Second, when the whole device is negatively charged (reverse bias, Fig. 1(b)), the C_{micro} working electrode is negatively polarized and the C_{meso} counter electrode is positively polarized. Theoretically, from the viewpoint of electrostatic interaction, TBA^+ cations should be stored in C_{micro} working electrode and BF_4^- anions should be stored in C_{meso} counter electrode. However, due to the steric hindrance effect, only BF_4^- anions can be stored in C_{meso} counter electrode, but the TBA^+ cations are too large to access the pores of C_{micro} working electrode. In this case, C_{micro} working electrode and consequently the whole device is blocked without any capacitive response. Overall, owing to the distinct size-selective effect of C_{micro} working electrode towards small anions and large cations, the whole device can only be normally operated in forward bias (Fig. 1(c)), thus being a capacitive analogue of semiconductor diodes (Fig. 1(d)). It should be noted that though CAPodes can just be operated in one (forward) bias direction, both backward and forward currents can across the CAPodes, which is completely different from semiconductor diodes. For this reason, CAPodes can not only rectify voltage but also stabilize currents. Moreover, there are two quantitative parameters to assess the rectification capability of CAPodes. They are rectification ratio I (RR_{I}) which is defined as the current ratio of forward and reverse biases, and rectification ratio II (RR_{II}) that is derived from the integral forward versus entire voltage range capacitance. These two parameters can well illustrate the rectification capability of CAPodes from different aspects.

From the above discussion, it can be seen that the unidirectional charging behavior of a CAPode mainly relies on the ion-sieving effect, i.e., asymmetric ion-storage capability towards cations and anions, of its working electrode. Therefore, the key to construct high-performance CAPode is to develop novel electrode material with excellent ion-sieving capability, or to design special electrolyte system with large electrochemical discrepancy between anions and cations. To be specific, in order to achieve higher rectification ratio, the charge storage capability of working electrode towards anions and cations should be as large as possible, and the electrochemical discrep-

ancy between anions and cations should also be large enough. Based on such working mechanism and design philosophy, more types of CAPodes can be successfully constructed. To this end, in the following section, we introduce the existing and potential electrode materials with ion-sieving effects, as well as the electrolyte systems with large electrochemical discrepancy.

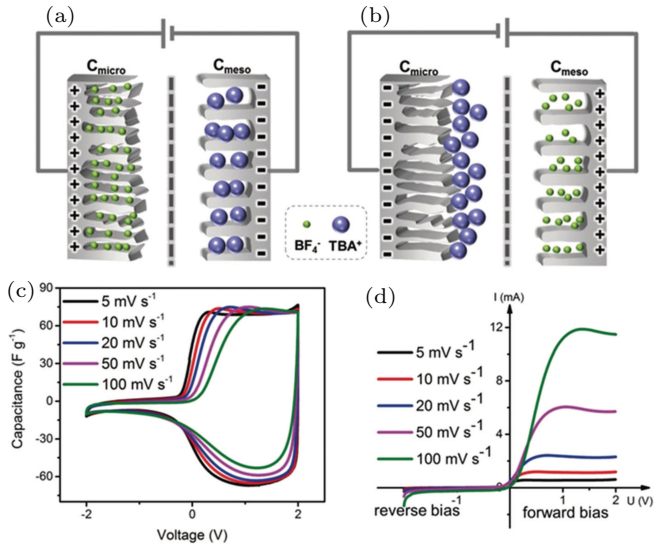


Fig. 1. Working mechanism and electrochemical behavior of the porous carbon based CAPode. (a) Forward bias, where C_{micro} is positively charged and C_{meso} is negatively charged. (b) Reverse bias, where C_{micro} is negatively charged and C_{meso} is positively charged. (c) Cyclic voltammetry of the porous carbon based CAPode at varying scan rates. (d) *I*–*U* curves of the porous carbon based CAPode at different scan rates. Reproduced with the permission from Ref. [1]. Copyright ©2019, Wiley-VCH GmbH.

3. Electrode materials and electrolyte systems with ion-sieving capabilities

As mentioned above, the rectification performance of a CAPode is mainly dependent on the ion-sieving effect of its working electrode, so developing new electrode material with enhanced ion-sieving capability is the key to constructing the next-generation CAPodes. Generally, the ion-sieving capability of one electrode material may come from two aspects: size effect and/or charge effect. For porous carbons, their pore size can be precisely tailored by various pore-structure regulation approaches. Therefore, size effect can be easily accomplished in porous carbon-based systems. However, porous carbons can be polarized positively or negatively upon electrochemical charging or discharging. Hence, almost no charge effect exists in these systems, which, to some degree, limits the rectification performances of porous carbon-based CAPodes. Apart from porous carbons, transition metal oxides such as niobium oxide (Nb_2O_5),[16] molybdenum oxide (MoO_3),[17] titanium oxide (TiO_2),[18] and tungsten oxide (WO_3)[19] are also representative supercapacitor materials. Transition metal oxides usually possess an inherent compact crystal structure that can accommodate small ions but exclude large ionic groups due to the prominent steric hindrance. Meanwhile, the ion transport channels inside transition metal oxides are surrounded by negatively charged oxygen terminals, so these kinds of electrode materials are only capable of storing cations from the viewpoint of charge effect. Therefore, it can be inferred that the rectification capability of the CAPodes will be enormously improved by taking transition metal oxides as the electrode materials, since both size effect and charge effect will synergistically contribute to these systems. This inference has been validated in our recent work, in which we take orthorhombic molybdenum oxide (α-MoO_3) as an example to demonstrate the excellent ion-sieving capability of transition metal oxides.[2]

As shown in Fig. 2(a), α-MoO_3 has a layered structure that is composed of double-sheet MoO_6 octahedra. These MoO_6 octahedra are corner-shared along the [100] direction and edge-shared along the [001] direction, and then alternately stacked by weak van der Waals forces along the [010] direction.[20–22] This unique layered structure allows various cations to be intercalated into its interlayer or intralayer spaces upon intercalation reactions (Fig. 2(b)). Moreover, there are three types of oxygen anions in the structural framework of α-MoO_3 (Fig. 2(c)), including singly coordinated terminal oxygen (O_t), doubly coordinated asymmetrical oxygen (O_a), and triply coordinated symmetrical oxygen (O_s).[23] All these oxygen anions can be extricated from the structural framework of α-MoO_3, producing oxygen vacancies that can enhance electrical conductivity and expand interlayer distance.[24] These structural features make α-MoO_3 a very potential electrode material to construct high-performance CAPode. As shown in Figs. 2(d) and 2(e), an α-MoO_3 based CAPode was constructed by using electrochemically activated α-MoO_3 as the working electrode, activated carbon (AC) as the counter electrode, and super-concentrated $HClO_4$/$NaClO_4$ solution as the electrolyte. When the CAPode is positively charged (forward bias, Fig. 2(d)), the α-MoO_3 working electrode is negatively polarized. In this case, the H^+ and Na^+ cations in electrolyte will enter into α-MoO_3 working electrode to maintain its electrical neutrality. At the same time, the AC counter electrode is positively polarized, and the ClO_4^- anions will diffuse and adsorb into the pores of AC. As a result, the whole device can be normally operated. However, when the CAPode is negatively charged (reverse bias, Fig. 2(e)), the α-MoO_3 working electrode will be positively polarized. Since the Mo^{6+} ion in α-MoO_3 is already at its highest oxidation state, there will be barely positive charge accumulated within it. Also, the ion-transport channels inside α-MoO_3 are surrounded by negatively charged oxygen terminals, being only capable of storing cations from the viewpoint of electrostatic interaction. As a result, ClO_4^- anions just adsorb on the external surface of α-MoO_3 working electrode, but cannot access the abun-

dant active sites within α-MoO_3. Meanwhile, from the viewpoint of size effect, the large ClO_4^- ionic groups will be size-excluded by the compact crystal lattice of α-MoO_3. As a result, the whole device cannot be normally operated though the AC counter electrode has great potential to store H^+ and Na^+ cations. Overall, owing to the outstanding size and charge dual ion-sieving effects of α-MoO_3 working electrode towards electrolyte ions, the constructed CAPode can only be normally operated at the forward bias, being a capacitive analogue of semiconductor-based diodes.

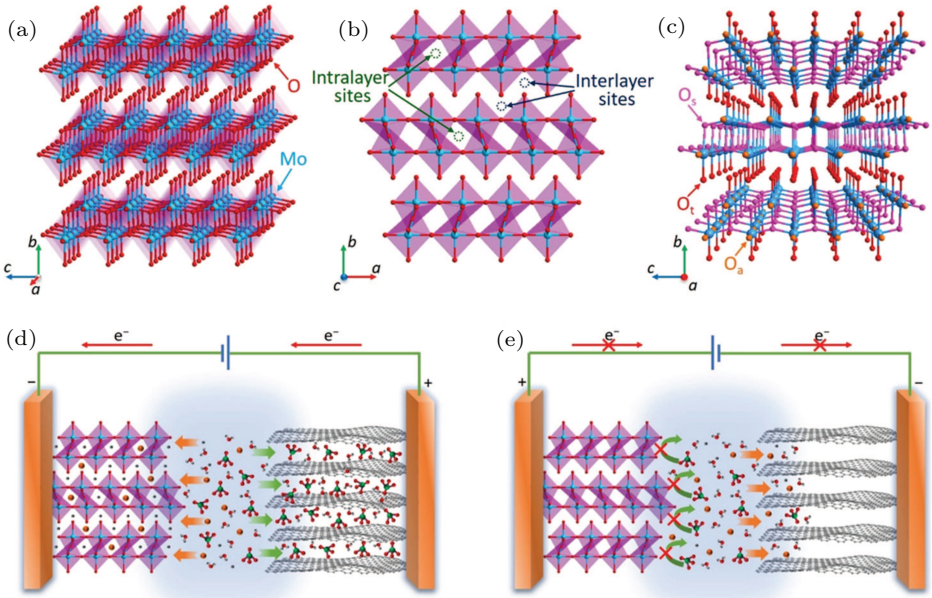


Fig. 2. Design philosophy and working mechanism of molybdenum-oxide-based CAPode. (a) Crystal structure of the layered α-MoO_3. (b) Schematic illustration of the interlayer and intralayer sites in α-MoO_3 for charge storage. (c) Schematic illustration of different oxygen anions in α-MoO_3. (d) Schematic illustration of the ion and electron fluxes in molybdenum-oxide-based CAPode at forward bias. (e) Schematic illustration of the ion and electron fluxes in molybdenum-oxide-based CAPode at reverse bias. Reproduced with the permission from Ref. [2]. Copyright ©2023, Wiley-VCH GmbH.

Apart from developing novel electrode material with excellent ion-sieving capability, designing special electrolyte system with large electrochemical discrepancy between anions and cations is also an effective strategy to construct high-performance CAPodes. Recently, Yan and colleagues developed a new ion regulation strategy that utilizes poly(ionic liquid)s as the electrolytes, and two CAPodes with a charging capability in forward- or inverse-bias directions were proposed.[14] These CAPodes were assembled by taking commercially available activated carbon as the electrodes and using one of two poly(ionic liquid)s as electrolytes, that is, polycation-based PVBIm·$(TFSI)_n$ or polyanion-based $(EMIM)_n$·PSTFSI.[25,26] The cations in PVBIm·$(TFSI)_n$ and the anions in $(EMIM)_n$·PSTFSI are tethered into organic networks, but their counter ions can move freely. For the CAPode featuring the function of blocking the negative-bias charging direction (N-CAPode), PVBIm·$(TFSI)_n$ serves as the electrolyte, in which two cases should be considered. First, the working electrode is positively charged (forward bias, Fig. 3(a)): $TFSI^-$ ions with a size of 0.79 nm are absorbed in the working electrode pores, whereas $(PVBIm)^{n+}$ ions are adsorbed on the counter electrode surface with excessive activated carbon for charge balance. In this situation, the device operates normally, and its electrochemical performance is determined by the working electrode. Second, the working electrode is negatively charged (reverse bias, Fig. 3(b)): $TFSI^-$ ions enter the pores of the counter electrode for charge balance, while $(PVBIm)^{n+}$ ions are too large to enter the pores of the working electrode. In this case, the working electrode does not work properly, and thus the charge storage of the whole device is blocked. As for the CAPode possessing the ability to block the positive-bias charging direction (P-CAPode), $(EMIM)_n$·PSTFSI serves as the active electrolyte component; however, the corresponding two cases are reverse compared with those of the above N-CAPode. First, when the working electrode is under reverse bias, $EMIM^+$ ions having a size of 0.76 nm are stored in the working electrode pores, and $(PSTFSI)^{n-}$ ions approach the outer surface of the counter electrode for charge balance (Fig. 3(d)). In this situation, the device can be normally operated, and its performance is almost controlled by the working electrode. Second, when the working electrode is at forward bias, $EMIM^+$ ions enter the counter electrode pores for charge balance, meanwhile $(PSTFSI)^{n-}$ ions are adsorbed on the outer surface of the working electrode (Fig. 3(c)). Similarly, the device in this case presents a minor residual capacitance. Taken together, in an idealized CAPode system, the current can only pass across the above devices shown in Figs. 3(a) and 3(d), leading to a diode-like current response.

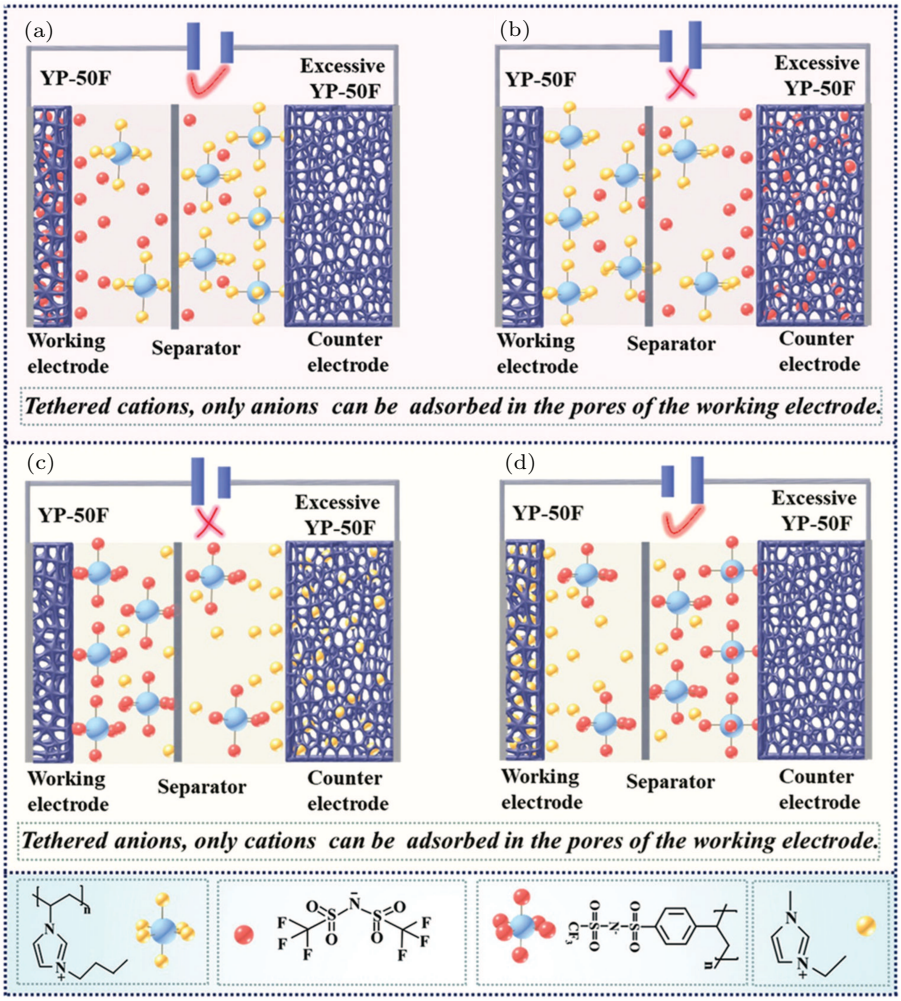


Fig. 3. Schematic illustration of the working mechanism for poly(ionic liquid)s based CAPodes. (a) Schematic illustration of the ion and electron fluxes of N-CAPode at forward bias. (b) Schematic illustration of the ion and electron fluxes of N-CAPode at reverse bias. (c) Schematic illustration of the ion and electron fluxes of P-CAPode at forward bias. (d) Schematic illustration of the ion and electron fluxes of P-CAPode at reverse bias. The bottom shows the corresponding molecular structures of $(PVBIm)^{n+}$, $TFSI^{-}$, $(PSTFSI)^{n-}$ and $EMIM^{+}$. Reproduced with the permission from Ref. [14]. Copyright ©2021, Wiley-VCH GmbH.

From the above typical examples, it can be seen that the unidirectional charging behaviors of CAPodes can be achieved from both electrode and electrolyte aspects. Therefore, to construct higher-performance CAPodes, developing unique electrode material with enhanced ion-sieving capability or special electrolyte with large anions and cations discrepancy are two feasible and effective approaches. For electrode materials, pseudo-capacitive metal oxides including Nb_2O_5, MoO_3, TiO_2, and WO_3 might be the optimal alternatives because of their unique size and charge dual ion-sieving effects. The morphologies, crystal structures, doping states and structural defects have a great effect on their ion-sieving capabilities, so future works can be carried out to tailor the above-mentioned structural parameters. Also, the emerging two-dimensional nano-materials such as graphene,[27–31] MXene,[32–35] and molybdenum disulfide (MoS_2)[36–40] are versatile building blocks. Taking them as the elementary materials and utilizing appropriate assembly approaches could construct elaborate electrode materials with ideal pore structures for selective ion storage.[31,41–45] Moreover, some unique materials with precise pore structures, such as zeolite, metal-organic frameworks (MOFs), and covalent-organic frameworks (COFs), might also be the potential electrode materials of CAPodes. By incorporating these materials with other conductive components, both high rectification ratio and high response frequency might be realized. For electrolytes, the key to achieve unidirectional charging behaviors for CAPodes is to guarantee that anions and cations have large size discrepancies. To this end, organic electrolytes might be the more promising alternatives, considering that the sizes of both anions and cations can be precisely designed.[46–49] Moreover, polyelectrolytes including ionizable polymers and poly(ionic liquid)s are also very potential candidates owing to their intrinsic large discrepancies between polyanions (or polycations) and counter cations (or anions).[50–55] Predictably, more kinds of high-performance CAPodes can be developed upon the continuous finding of excellent electrode materials and novel electrolytes.

4. Supercapacitor-based iontronic devices beyond CAPodes

Apart from CAPodes, other types of supercapacitor-based iontronic devices have recently been reported to further enrich the family of capacitive iontronic devices. For example, transistor-like gating supercapacitor (G-Cap) was successfully constructed by using a competing electro-adsorption process in a three-electrode architecture.[56] Specifically, a high-performance working supercapacitor (W-Cap) with a defined specific capacitance is gated by a third thin film porous carbon gate electrode (G; Fig. 4(a)). In this configuration, the W-Cap can be effectively switched "on" and "off" by applying an additional bias potential at the gate electrode (Figs. 4(b) and 4(c)). When the gate electrode is polarized with negative bias, the cations in the electrolyte are immediately depleted and thus the W-Cap capacitance decreases due to the deficit of charge carriers. In this case, the cations are no longer accessible for the electric double-layer formation and the W-Cap is effectively switched "off". In order to return back to the "on" state of the W-Cap, a reverse bias can be enforced on the gate electrode, which pushes the ions back into the electrolyte and the W-Cap capacitance could recover to the initial state.

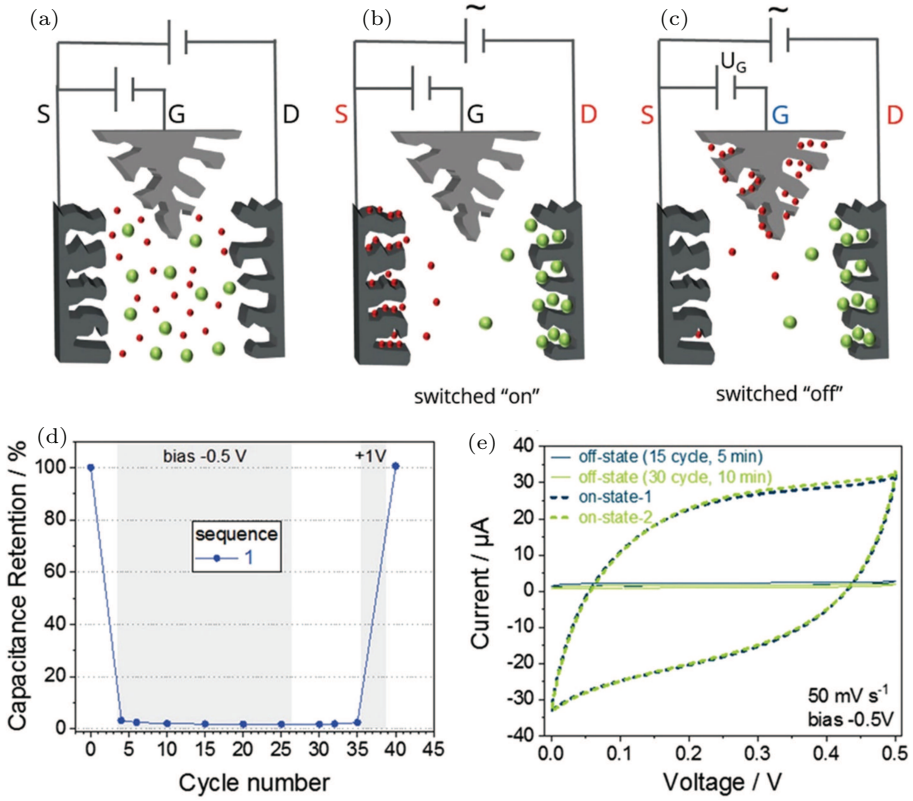


Fig. 4. Working mechanism and electrochemical behavior of the transistor-like gating supercapacitor (G-Cap). (a) Schematic illustration of the ion and electron fluxes of the G-Cap at open-circuit state. (b) Schematic illustration of the ion and electron fluxes of the G-Cap at "on" state. (c) Schematic illustration of the ion and electron fluxes of the G-Cap at "off" state. (d) Capacitance retention profile of the G-Cap upon switching the G-electrode to "on" and "off" states. (e) Corresponding CV curves of the G-Cap at "on" and "off" states. Reproduced with the permission from Ref. [56]. Copyright ©2020, Wiley-VCH GmbH.

Figure 4(d) shows the capacitance retention profile of the G-Cap. Before the G-switching, the W-Cap is cycled continuously with a capacitance of 100%. When the gate electrode is negatively polarized, the W-Cap only delivers a capacitance of 1.8%, two orders of magnitude below the initial capacitance. Interestingly, after disconnecting the G-electrode, the whole G-Cap remains polarized. Therefore, to completely switch back the G-Cap, a short positive bias needs to be applied to push the ions back into the electrolyte. Upon this procedure, the W-Cap capacitance returns to the initial "on" value of 100% after one cycle. As shown in Fig. 4(e), the CV curves in the "off" state is flat and the capacitive characteristic is effectively suppressed, demonstrating the good switchability of the G-Cap. After desorption of charge carriers from the gate electrode ("on"-state-2), the CV curves perfectly superimpose that of the initial state, indicating the high reversibility of the device. In this sense, G-Caps can be regarded as capacitive analogues of semiconductor-based transistors with intrinsic capability for energy or chemical information storage.

Despite great achievements, the operation of such switchable supercapacitor was limited to toxic electrolytes, such as sulfuric acid (H_2SO_4) or tetrafluoroborates in acetonitrile (ACN).[1,56,57] In the past decades, biologically relevant ions in aqueous solutions were rarely investigated for supercapacitor applications, mainly because high energy and power density were in focus.[58–65] Nevertheless, complex biologically

active ions play a key role in health and neurological functions of humans and animals.[66,67] Specifically, the nerve system is a highly optimized operating structure which completes signal transduction by chemical transmitters.[68–71] Inspired by this, Kaskel *et. al.* demonstrated a switchable supercapacitor that was operated with functional biological ions, realizing the deliberate concentration control of biological ions at surface and in solution.[72] The proof-of-concept switchable supercapacitor is based on choline chloride (ChCl), which is an important derivative of acetylcholine that exhibits vital functions in the brain chemistry, being correlative to memory formation, learning and addictive behavior, and related to brain diseases.[73,74] As shown in Figs. 5(a)–5(c), the iontronic architecture consists of a main capacitor (M-Cap, with high mass loading and area of carbon electrode) for effective ion electrosorption and an inserted detective capacitor (D-Cap, with low mass loading and area of carbon electrode) for the detection of ion depletion. The detective effect of the 4-terminal device was demonstrated in two symmetric capacitors based on AC electrodes in 0.01 M ChCl aqueous electrolyte.

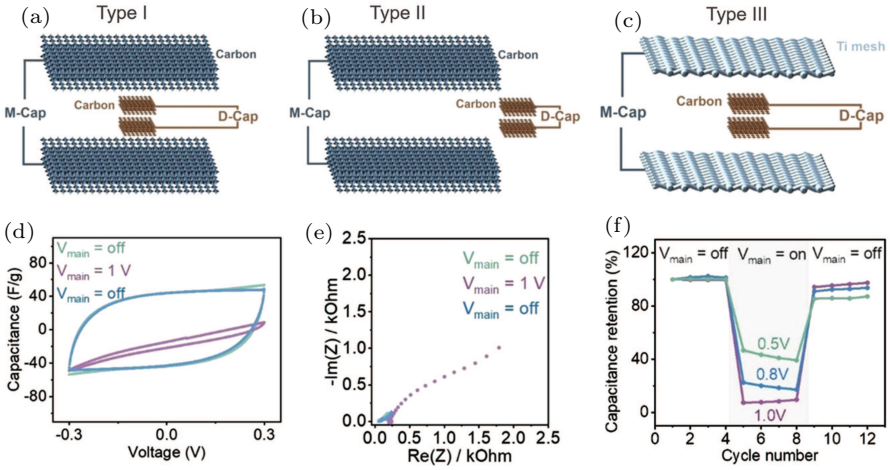


Fig. 5. Schematic diagram and corresponding electrochemical behaviors of three types of 4-terminal devices with a D-Cap and a M-Cap. (a) Type I device with a D-Cap inside a M-Cap. (b) Type II device with a D-Cap outside and near a M-Cap. (c) Type III device with a D-Cap inside a M-Cap, where M-Cap is titanium mesh without porous carbon electrode. (d) CV curves of the D-Cap in type I setup under V_{main} = on and off states. (e) The impedance spectra of corresponding D-Cap under V_{main} = on and off states. (f) The capacitance retentions of the D-Cap in type I setup under V_{main} = on and off states. Reproduced with the permission from Ref. [72]. Copyright ©2022, Wiley-VCH GmbH.

As shown in Fig. 5(d), the capacitance of the D-Cap was determined with and without applying voltage to the M-Cap (V_{main}: voltage of M-Cap, V_{main} = on, off, respectively). It can be observed that the initial capacitances of D-Cap (V_{main} = off) are significantly higher than the capacitance after turning the M-Cap "on" (V_{main} = 1 V). Moreover, the impedance of D-Cap after turning V_{main} "on" is higher than that of "off" state (V_{main} = 0, Fig. 5(e)). That is because most conducting ions were electrically adsorbed on the carbon pores of the M-Cap at V_{main} = 1 V, leading to the impedance increase for the D-Cap. Figure 5(f) shows the capacitance retentions of D-Cap by varying V_{main} values, so as to illustrate the effects of V_{main} on the starvation effect. With the increase of V_{main}, the capacitance of detective capacitors decreases correspondingly, indicating the monotonic relationship of V_{main} and electrosorption ability of M-Cap. The effect of electric field gradient inside the M-Cap on the D-Cap capacitance was further investigated by placing the D-Cap outside and near the M-Cap in a type II setup (Fig. 5(b)). In this configuration, a capacitance decrease is also observed when applying V_{main} = 1 V. However, if the porous carbon material is omitted in the M-Cap (pure titanium mesh without significant surface area, type III in Fig. 5(c)), no capacitance decrease can be detected in both "on" and "off" states. All these results demonstrate the deliberate control of ChCl concentration by porous carbon electrodes of the M-Cap, realizing the construction of switchable supercapacitors and the design of bio-interfaces for delivery control.

5. Potential applications of CAPode-related iontronics

CAPodes realize the combination of electron transfer and ion diffusion in the same circuit, so they have great application potential in the ion/electron coupling circuit-based emerging fields such as logic operation, brain computer interface, neural network interaction, as well as *in vivo* diagnosis and treatment.[6–8,75–77] Though these advantages, the development and application of CAPodes are still in their early stages and various application scenarios are still been boldly imagined and actively explored. As the capacitive analogues of traditional semiconductor diodes, the simplest and most promising application scenario for CAPodes is logic operation.[2,15] As we all know, silicon-based semiconductor devices have been holding up the whole modern electronic information technology. But with the feature size of semiconductor devices in integrated circuits gradually smaller than 10 nm, the development of computer chips gradually deviates from Moore's

law.[78,79] It can be foreseen that as the size of semiconductor devices ultimately approaches 1 nm, the computing power of silicon-based computer chips will reach saturation.[80] Therefore, it is urgent to develop new materials, devices, and even logical computing architectures to satisfy the ever-increasing requirement of computational power.[81–84] Compared with computer chips, the human brain has stronger computing power and lower power consumption.[66,67,85,86] If the computing mode of the human brain can be fully replicated based on ion/electron coupling circuit, it will open up a new path for the construction of high-performance and low-power logic computing circuits in the future.[87,88] In addition, since the ion/electron coupling circuit can realize the combination of electron transfer and ion diffusion in the same circuit, the logic operation circuit based on it will provide a feasible interaction interface for the bidirectional communication of human brain and computer (Fig. 6(a)).[2,6,89,90]

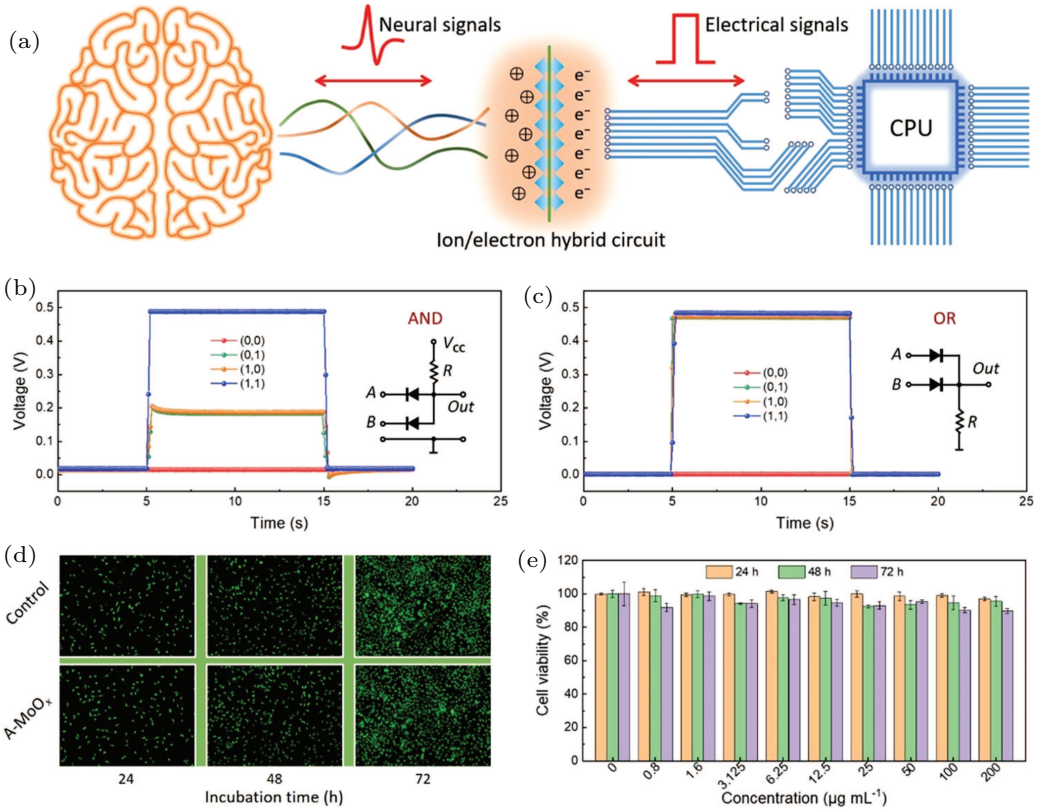


Fig. 6. The application of CAPodes in logic operations. (a) Schematic illustration of ion/electron coupling circuit as a feasible interaction interface for the bidirectional communication of human brain and computer. (b) Demonstration of an AND logic gate fabricated by integrating A-MoO$_x$-based CAPode and resistors, with insets showing the circuit diagram. (c) Demonstration of an OR logic gate fabricated by integrating A-MoO$_x$-based CAPode and resistors, with insets showing the circuit diagram. (d) Fluorescence images of the cells co-incubated with A-MoO$_x$. (e) Cell viability after co-incubated with A-MoO$_x$ with different concentrations. Reproduced with the permission from Ref. [2]. Copyright ©2023, Wiley-VCH GmbH.

Recently, Yan and colleagues reported two types of logic operation circuits, i.e., AND gate and OR gate, by using CAPodes as the basic computing units for the first time, demonstrating the huge application potential of CAPodes in logic operation circuits.[15] Our recent work also demonstrated the practical application of CAPodes in AND and OR logic operation circuits.[2] As shown in Figs. 6(b) and 6(c), two identical devices (CAPode A and CAPode B) were taken to construct AND or OR logic gates. For the AND logic gate, only when the forward-bias voltage (0.5 V, represented by "1") is applied to switch both CAPode A and CAPode B, a high output voltage can be produced (Fig. 6(b)). As long as either CAPode A or CAPode B is suppressed by a low input voltage (0 V, represented by "0"), a low output voltage is produced (Fig. 6(b)). For the OR logic gate, when the forward-bias voltage is applied to switch either CAPode A or CAPode B, a high output voltage is produced (Fig. 6(c)). Only when the low input voltage is simultaneously applied to suppress both CAPode A and CAPode B, a low output voltage can be produced (Fig. 6(c)). Benefiting from the near zero threshold voltage of the A-MoO$_x$ based CAPode, both the AND and OR logic gates exhibit an ideal logic operation behavior, which is of great worth for practical application. Moreover, when taking the *in vivo* application into account, the biocompatibility of the device is critically important. To this end, we evaluated the cell compatibilities of the main constituent material, i.e., A-MoO$_x$, by co-incubating it with the representative human endometrial adenocarcinoma cells. As shown in Fig. 6(d), the cell density is obviously increased upon increasing incubation time. More specifically, after co-incubated with

A-MoO_x extraction solutions with various concentrations for 24 h, 48 h, and even 72 h, all the experimental groups exhibit a high cell viability over 90% (Fig. 6(e)), demonstrating the good biocompatibility of the A-MoO_x electrode material. In future works, to fully achieve the goal of human–computer interaction, plenty of efforts still need to be taken to developing the CAPodes that are based on body fluid or neurotransmitters.

The above results indicate that CAPodes not only have the energy storage function of supercapacitors, but also have the rectification characteristics of diodes. Therefore, CAPodes can be used as logic computing elements in integrated circuits with energy storage capabilities. In addition, by connecting the CAPodes with other electronic components such as transistors, resistors, capacitors and inductors, it is believed that more complex yet more powerful logic operation circuits can be built, such as "NAND gate", "XOR gate", "NOR gate", "XNOR gate", and then used for power management of electronic equipment.[91–93] Although they have very broad practical application prospects, there are still a series of scientific problems and technical difficulties to be solved in the development of CAPodes. Firstly, CAPodes are dual functional devices that integrate the characteristics of traditional electrochemical capacitors and diodes. But the interaction mechanism between the energy storage and rectification characteristics is still unclear, and further in-depth research is needed. Secondly, the current development of CAPodes adopts the device structure of supercapacitors, which are equivalent in size to button batteries. Considering that the future application field of CAPodes will mainly focus on integrated circuits, the design and construction of miniaturized devices are another challenge. Finally, based solely on CAPodes, only the simplest logic operation circuits of AND gate and OR gate can be realized in theory. To achieve more complex logic operation functions based on ion/electron coupling circuits, it is inevitable to develop other basic components such as ionic transistors, ionic resistors, ionic capacitors and ionic inductors, which requires the broad cooperation of researchers in more fields.

6. Conclusion and outlook

Overall, CAPodes are an emerging type of functional electrochemical devices that integrate mobile ions and mobile electrons in the same circuit, thus being recognized as the most promising components for the forthcoming ion/electron coupling circuits. To further accelerate the development of CAPodes and attract broad interests from the communities of material science, electrochemical energy storage, and biomimetic science, we herein comprehensively summarize the key fundamentals of CAPodes. Specifically, we elucidate the working mechanism and design philosophy of CAPodes, and summarize the electrode materials that are suitable for constructing CAPodes. Meanwhile, some other supercapacitor-based devices beyond CAPode are also introduced, and their potential applications are instructively presented. As mentioned above, the working mechanism of CAPodes, i.e., the unidirectional charging behavior, is highly dependent on the ion-sieving effects of their working electrodes. Therefore, the key to construct high-performance CAPode is to develop novel electrode material with excellent ion-sieving capability. To this end, transition metal oxides should be the more competent electrode materials than porous carbons because of their unique size and charge dual ion-sieving effects. Apart from developing novel electrode materials, designing special electrolytes with large anions and cations discrepancy is also an effective strategy to construct high-performance CAPodes. To achieve this goal, organic electrolytes might be the more promising alternatives, since both the anions and cations of organic electrolytes can be precisely designed. Moreover, polyelectrolytes are also very potential candidates owing to the intrinsic large discrepancies between polyanions (or polycations) and counter cations (or anions). Based on the above working mechanism and design philosophy, it can be expected that more CAPodes can be successfully constructed.

To further enrich the family of capacitive iontronic devices, other types of supercapacitor-based iontronic devices have also been designed and developed. The representative devices are transistor-like gating supercapacitors (G-Caps), in which a working supercapacitor (W-Cap) with a defined specific capacitance is gated by a third gate electrode. In this configuration, the W-Cap can be effectively switched "on" and "off" by applying an additional bias potential at the gate electrode. In this sense, G-Caps can be regarded as capacitive analogues of semiconductor-based transistors. Despite great achievements, the operation of such switchable supercapacitor was limited to toxic electrolytes, and biological ions that play key roles in health and neurological functions of humans and animals were often ignored. To fill this blank, a choline chloride (ChCl) based switchable supercapacitor was recently developed, achieving the deliberate concentration control of biological ions at surface and in solution by electrically-driven processes. These achievements greatly promoted the development of switchable supercapacitors and the related technical fields. When taking practical application into consideration, the simplest and most promising application scenario for CAPodes is logic operation. Till now, several works have demonstrated the AND and OR logic gates by taking CAPodes as the basic computing units, reflecting the huge application potential of CAPodes in future logic operation circuits.

Though significant achievements have been made in the past few years, the developments of CAPodes and CAPodes-related techniques are still in their infancy. In future works,

lots of efforts should be made to fully accomplish the goal of high efficiency ion/electron coupling circuit-based logic operations. First, considering that the unidirectional charging behaviors of CAPodes are mainly based on the ion-sieving effects of their working electrodes on the electrolyte ions, more high-performance electrode materials and unique electrolytes should be investigated and developed to enrich the material systems and improve the rectification capabilities of CAPodes. Second, the electrical and electrochemical performances of CAPodes, especially rectification ratio and response frequency, should be further improved by optimizing the device structures. These parameters have great impacts on the accuracy, speed, reliability, and stability of ion/electron coupling logic operation circuits. Third, CAPodes are dual functional devices that integrate the characteristics of traditional electrochemical capacitors and ionic diodes, but the interaction mechanism between the energy storage and rectification characteristics is still unclear. Therefore, further in-depth researches should be carried out to elucidate the relationship and interaction between the energy storage and rectification characteristics. Also, simultaneous information storage and logic operation are a crucial element of neuromorphic computing architectures. The in-depth understanding of the multifunctionality of CAPodes may provide the possibility for realizing the simultaneous information storage and logic operation. Fourth, almost all the current CAPodes adopt the sandwich-type or coin-type configurations, which have an adverse effect on their response speeds. Since the application field of CAPodes mainly focuses on integrated circuits, more efforts need to be devoted to developing micro-devices, considering that the speeds of charge migrations in micro-devices are faster than those in routine sandwich-type or coin-type devices. Future works can take the state-of-the-art processing technologies including screen printing, laser processing, photolithography, and three-dimensional printing to achieve the compact integration of CAPodes. Finally, based solely on CAPodes, only the simplest logic operation circuits of AND gate and OR gate can be realized in theory. To achieve more complex logic operation functions such as “NAND gate”, “XOR gate”, “NOR gate”, and “XNOR gate”, substantial efforts need to be devoted to developing other ionic components including ionic transistors, ionic resistors, ionic capacitors and ionic inductors. In brief, to further accelerate the development of CAPodes and finally realize the goal of highly efficient ion/electron coupling circuit-based logic operations, it is indispensable to gather the sincere cooperations from the fields of materials science, electrochemistry, integrated circuit, brain science, flexible electronics, and big data analytics.

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