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Pseudocapacitive and Ion-Insertion Materials: A Bridge between Energy Storage, Electronics and Neuromorphic Computing

Marina Mastragostino[a] and Francesca Soavi*[b]

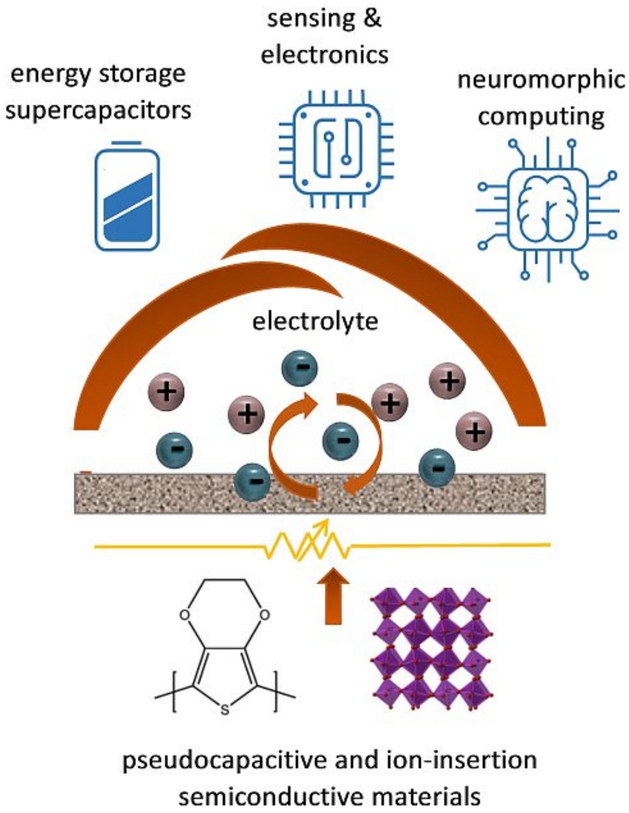
Dedication: In honour of Prof. Jean-Michel Savéant, a great scientist and innovator in molecular electrochemistry and beyond

There is considerable interest in new solid-state materials for many applications, from energy storage to electronics and neuromorphic computing. This concept paper highlights how pseudocapacitive and ion-insertion materials, for their inherent capability of storing charge and modulate electron conduction, represent a bridge between energy storage, electronics and neuromorphic computing and enable the design of new device architectures.

1. Introduction

Solid-state materials that undergo reversible and fast electrochemical processes are the key components of new generation devices that are playing a role within the new industrial revolution era. Batteries and supercapacitors, for their high energy storage/conversion efficiency, represent the enabling technologies to ensure access to affordable, reliable, sustainable and modern energy (of ONU Sustainable Development Goal n. 7). In turn, digital and information and communication technologies (internet-of-things IOT, cloud computing) are transforming services, manufacturing (Industry 4.0) and social assets, with benefits on health and environment. In IOT, energy autonomy is still a major requirement. In fact, research is needed on developing systems that harvest and store energy from the environment without wasting it under operation.[1] In this field, iontronic is emerging as a new discipline which bridges electronics, electrochemistry, solid-state physics, engineering, and biological sciences.[2,3] As an example, ion-gated transistors (IGTs) are iontronic devices, that, for their low-voltage operational characteristics, are attractive low-power electronic components for several applications, specifically sensing and bio-sensing.[4] Circuit elements whose resistive state can be electrochemically switched to store information, are also extremely attractive to develop neural network (NN) algorithms for modern computing. Even in this field, iontronic is playing a role.[5]

In addition, the integration of multiple functionalities on a single chip, i.e. Systems on Chip (SoC), like electric switch with energy harvesting and storage, is a challenging goal that can be addressed by a proper selection and combination of materials. Integrating specific device functions at materials level can open new frontiers for future development of new low energy demand and multifunction-energy storage elements.[6]



Scheme 1. Schematic illustration of applications of pseudocapacitive and ion-insertion semiconductive materials.

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[a] Prof. M. Mastragostino
Accademia delle Scienze dell'Istituto di Bologna
Via Zamboni, 31 – 40126 Bologna, Italy
E-mail: marina.mastragostino@unibo.it
[b] Prof. F. Soavi
Department of Chemistry "Giacomo Ciamician"
Alma Mater Studiorum University of Bologna
Via Selmi, 2 – 40126 Bologna, Italy
E-mail: francesca.soavi@unibo.it

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In this context, pseudocapacitive and ion-insertion materials are promising candidates.

Therefore, the aim of this concept paper, that is illustrated in Scheme 1, is to highlight the role played by such materials in bridging energy storage, electronics and neuromorphic computing.

2. Pseudocapacitive and Ion-Insertion Materials

Electrode materials of batteries and electrochemical double-layer capacitors (EDLC) store charge by different processes. The battery processes are faradaic, instead the EDLC processes are electrostatic. Such different electrode behaviour, can be clearly distinguished by the shape and scan-rate (*v*) dependence of their cyclic voltammetries (CVs). Indeed, battery electrodes feature peak-shaped CV current-potential responses, proportional to v or to $v^{1/2}$, while EDLC electrodes exhibit a quasi-rectangular response with currents proportional to *v*. Pseudocapaitive materials represent a different class of electrodes. The pseudocapacitance originates from a fast faradaic process that takes place at the surface or near-surface of the electrode material and that, in parallel, gives rise to a capacitive signature, i.e. to a quasi-rectangular CV response with currents proportional to v. In addition, the galvanostatic charge/discharge (GCD) potential profile of pseudocapacitive electrodes has an almost linear dependence with the stored charge. This is indicative of fast faradic reactions that are not limited by solid state diffusion processes. Hence, overall, the pseudocapacitve electrochemical response, is similar to that of the electrical double-layer charging processes of EDLC electrodes.[7–10]

In the past, it was speculated that a quasi-rectangular CV response resembling that of a capacitive response arises from a series of faradaic redox couples with a distribution of potentials. However, this explanation was never been clearly demonstrated. Only more recently, the problem was theoretically addressed.

In [11] Constentin et al. demonstrated that whenever a quasi-rectangular CV response proportional to scan rate is observed, this behaviour must be ascribed to a real capacitive double-layer charging. In the potential domain where the material exhibits a capacitive response, it behaves like an electronic conductor forming an electrical double-layer at the contact with the electrolytic solution. This implies that the Faradaic reaction determines a variation of the electronic structure of the material which evolves from an insulating/semiconducting state to a conductive state. This is the case of some transition metal oxides, like cobalt oxide, titanium dioxide and hydrous WO_3,[10] and the conjugated conducting polymers,[12,13] i.e. the two main classes of pseudocapacitive materials. These materials show a somewhat rectangular CVs that may also display reversible redox peaks. The conducting polymers, and among them the most popular are poly(aniline), poly(pyrrole) and poly(thiophene) derivatives, store the charge by a reversible electrochemical process named doping which involves oxidation of the polymer backbone and anion's insertion from the electrolyte in the p-doping process. For the n-doping process, the polymer is reduced and cations are inserted. The p- and n-doping yield delocalized charge carriers along the polymer chain and make the polymer conductive.[13] The amount of stored charge, related to the doping level, determines the polymer conductivity, which in turn is also related to polymer conjugation length. The rate capability of pseudocapacitive materials is generally better than that of battery materials. Compared with EDLC electrodes, pseudocapacitive materials usually have larger capacitance but lower cycling stability.

The very popular lithium-ion batteries (LIBs) exploit lithium-ion insertion electrode materials. These electrodes display reversible host(crystal lattice)-guest (Li^+) reactions that take place with a negligible variation of the crystal lattice. The structure of the host should be as light as possible and able to accommodate a great amount of lithium ions to provide materials of high specific capacity. The electronic and ionic conductivity of these mixed conductors is a key characteristic and should be sufficiently high to guarantee high power performance of the battery. Lattice changes and/or amorphization phenomena can cause losses of electrical contact and could seriously affect battery cycle-life.[14]

Bulky LIB electrode materials behave like battery materials, with redox CV peaks and GCD profiles typical of the lithium ion insertion-deinsertion in the host structure. However, when their particle size is reduced to a nanometric level and the materials feature very high specific surface area, the bulk redox reaction changes to a surface redox reaction and ion diffusion length in the solid phase significantly shortens. Consequently, some LIB electrode materials exhibit pseudocapacitive signature in CV and in GCD profiles. Among them, $LiCoO_2$, i.e. the cathode material adopted in the first commercialized LIBs, is an emblematic example.[15] Thus, to avoid confusion it has been suggested to indicate these materials as " extrinsic pseudocapacitive materials", because they behave as battery materials in the bulk phase, but after particle size reduction, the pseudocapacitive behavior emerges.[8]

3. Pseudocapacitive and Ion-Insertion Materials in Supercapacitors

With the challenging ambition of overcoming the energy performance of today EDLCs, pseudocapacitive, lithium ion-intercalation materials, and in general, electrodes that feature fast, reversible faradaic processes, have been exploited to demonstrate novel architectures of supercapacitors.[16] This approach requires a tailored formulation of the electrolyte. In addition to high conductivity, the electrolyte must feature high electrochemical stability at the electrode potentials set by the specific faradic reactions. The electrode/electrolyte interface kinetics and stability are also strongly affected by the electrolyte. Ionic liquids and, more recently, solvent-in-salt solutions are attracting much attention as novel class of electrolytes.[17,18]

As an example, polythiophens have been exploited to design pseudo-supercapacitors and hybrid supercapacitors, even with ionic liquid electrolytes.[19,20] In pseudocapacitors both the positive and the negative electrodes undergo fast and reversible faradic processes. Hybrid supercapacitors feature positive and negative electrode materials of different nature that are charged/discharged via different electrostatic and faradic modes.[16,19–21] The latter approach is at the basis of the called lithium-ion capacitors (LICs) that are considered the bridging technology of EDLCS and LIBs. Many combinations of electrode materials have been proposed, using activated carbon for the positive electrode and a lithium-ion intercalation negative electrode. With organic electrolytes based on lithium salts, LICs may achieve higher specific power (up to 10 $\mathrm{kW\,kg^{-1}}$) than LIBs, along with higher voltage (up to 3.8 V) and specific energy ($>10\ \mathrm{Wh\,kg^{-1}}$) than EDLCs. Moreover, the use of $Li_4Ti_5O_{12}$ (LTO) is an effective approach for LICs with long cycle life.[22]

4. Pseudocapacitive and Ion-Insertion Materials beyond Energy Storage

Beside their capability of fast and reversible charge storage that is exploited in supercapacitors and batteries, the pseudocapacitive and ion insertion materials exhibit strategic additional key properties that are extremely attractive even for other fields, of high technological impact. As an example, the specific mechanical, optical and electronic properties of pseudocapacitive polymers, like poly(pyrrole), poly(3,4ethylenedioxythiophene), poly(3- alkylthiophenes) and poly(aniline), are exploited in actuators, electrochromic devices, and sensors. Metal oxides are also widely used as mediators for electrocatalytic processes (e.g. MnO_2) and for their electrochromic and semiconductive properties (e.g.WO_3 and TiO_2).

Among the different additional features mentioned above, in many pseudocapacitive and ion-insertion materials, the faradaic reactions drive their electronic conductivity. That is to say that these materials behave like semi-conductors, with electronic structures that depend on the ion exchange between the material and the electrolyte. Specifically, in these semiconductors, conductivity can be tuned between that of a conductor (metal) and of an insulator by accumulation (or depletion) of positive (p-doping) or negative (n-doping) charge carriers, along with the accumulation (depletion) of electrolyte ions of opposite charge.

While this phenomenon has been reported as one of the reasons that explains the pseudocapacitive electrochemical finger print of pseudocapacitive materials,[11] it is also deeply investigated within an emerging interdisciplinary discipline, termed iontronic. Indeed, iontronic investigates and design systems where electronic properties of electrode materials are controlled by ion arrangement/adsorbtion and viceversa. Examples are delivery devices, where charged molecules are released at specific locations at specific times by the application of selected potential biases, iontronic resistors, resistance random-access memory, diodes, transistors, and memristive-based neuromorphic computing hardware. All these elements can be implemented into iontronic circuits. Compared to traditional electronics, iontronic enables the design of flexible electronic and of bio-compatible devices.[2–6]

In particular, ion gated transistors (IGTs) are attractive for their low-voltage operation characteristics (<1 V) that permit the design of low-power electronics.[4,6] In IGTs, the channel is a semiconducting material and the gating medium is an electrolyte (liquid solutions, gel, polymer, ionic liquids). The selection of the electrolyte, that can be aqueous or organic, is strongly related to the nature of the channel. Indeed, the electrolyte has to be electrochemically stable at the working potentials of the channel.

IGTs exploit the capacitive behaviour of the channel. Indeed, a high capacitive channel enables high charge carrier density at operating voltages as low as 0.5 V. Polymer, organic and inorganic channel materials and electrolytes have been used in IGTs.[4] Even for the gate electrode, high capacitive features are beneficial for low voltage operation. Indeed, high capacitance gates, like high surface area carbons, are capable to supply, within a narrow potential excursion, the charge required to dope IGT channels.[23] In addition, the pseudocapacitive channel/ionic medium/high surface area carbon stacking of IGTs is analogous to that of a hybrid supercapacitor where channel and gate electrodes are charged/discharged by a faradic and an electrostatic process, respectively, while the channel conductivity is modulated. This results in a monolithically integrated IGT-supercapacitor system. This means that energy used to dope, i.e. to open, the channel is stored and then is ready to be delivered when the IGT channel is closed and the channel is de-doped. In addition, the charge storage capability of the channel and the gate permits to keep the transistor channel open even when the transistor is not connected to a power supply The integration of a transistor and a capacitor provides a very efficient and low-cost energy system of great interest for autonomous SoC, flexible/stretchable electronics and bioelectronics. This new concept, termed TransCap, demonstrates that capacitive materials can be used to process sub-1 V IGT components and to design novel architectures for new multifunction energy storage elements. This concept has been demonstrated by IGT making use of channels based on conducting polymers (MEH-PPV, PEDOT:PSS) and ionic liquid electrolytes.[6,24,25]

Finally, it is worth noting the great opportunities that pseudocapacitive and ion-insertion materials are having in an emerging sector, like neuromorphic computing. Today electronics is considered to be still inefficient to support fast-response neuromorphic hardware that mimics the brain. Circuit elements that store data by changing their resistive state by fast, reversible, and finely adjustable switching are highly desirable.[1,2,5,26]

Li-ion intercalation oxides have been recently proposed as a new class of functional materials for memristive devices. Indeed, their specific crystalline structures are designed to provide fast and reversible lithium-ion diffusion in the host lattice. In addition, some oxides are known to change their electronically conductivity in function of the degree of lithiation. Examples are Li_xCoO_2 and LTO.[15,26]

The use of Li-ion insertion materials in iontronic will benefit of the great achievements in crystal engineering, electrolyte formulation, electrode/electrolyte interface modelling produced in more than 20 years of research in lithium-ion batteries. In turn, a clear understanding of the relation between electronic properties and state of charge of lithium ion insertion materials will provide valuable information to be exploited for the evaluation of the state-of-health and state-of-charge of batteries.

Nevertheless, understanding the interplay between the electrode/electrolyte interface structure and the electronic and electrochemical properties of pseudocapacitive and lithium ion insertion materials, could represent a strategic, fundamental opportunity for the design of novel components of emerging technologies.

5. Conclusions

This concept paper aims at emphasizing that pseudocapacitive and ion-insertion materials have guided important developments in energetics and electronics, that are key pillars of today social development. They have the potentiality to bridge energy storage, electronics and neuromorphic computing and will have a great impact for future development of next generation technologies. Indeed, solid-state pseudocapacitive and ion-insertion materials that simultaneously feature semiconductive properties and charge storage capability, can be considered as building blocks of novel, low-power or autonomous iontronic devices.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: pseudocapacitance · ion insertion · supercapacitor · iontronic · ion gated transistor

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