



Charge transfer and storage in nanostructures



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ABSTRACT

Efficient storage and conversion of electrical charge in materials, to a voltage and current, provides the basis for batteries and capacitors. Given the widespread usage of portable electronics there is a continual need to further enhance the energy and power density of such devices, which could be accomplished through the use of nanostructured materials. The large surface area to volume ratio and the possibilities of new materials physics and chemistry provide the rationale for their use and is discussed. The former aspect considers the relevance to the area-dependent capacitance as well as the parasitic elements that reduce the charge and energy delivery from the theoretical maximum values. Specific instances of electrode materials, as well as the electrode–electrolyte interface and electrolyte properties, with respect to their capability and prospects are examined. Alternate internal and external surface dependent Faradaic reactions and concomitant pseudocapacitance based mechanisms, seem to have the ability to bridge the large energy densities of batteries to the power density of the capacitors perhaps helping in realizing a truly useful hybrid device. While much of the report relates to presently used devices such as Li-ion batteries and activated carbon based electrochemical capacitors, the relevant principles are shown to be valid for other types of charge conversion agents such as photoelectrochemical and dye-sensitized solar cells. The review also considers perspectives on alternate materials and architectures.

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Contents

1. Introduction	2
1.1. Characteristics of the nanoscale: classical influences	3
1.2. Characteristics of the nanoscale: quantum effects	3
2. Charge storage devices: batteries and capacitors	4
2.1. Overview	5
2.2. Energy storage in batteries: voltage and charge	6
2.2.1. Charge transfer in solids, with emphasis on reversible intercalation	7
2.2.2. Electrode materials	8
2.2.3. The influence of the electrolyte/ion-transfer medium	10
2.3. Electrochemical capacitors	11
2.3.1. The double layer	12
2.3.2. Additional capacitances modulate double layer capacitance	14
2.3.3. New electrolytes for electrochemical capacitors: ionic liquids	15
2.4. Charge capacity of electrochemical devices	15
2.4.1. State of the art and progress in enhancing charge & energy storage	15
2.4.2. Reaching the limits of charge and energy storage	17
2.4.3. Performance metrics: the proper reporting of energy density	17
3. Methodologies for measurement	18
3.1. Cyclic voltammetry (CV)	19
3.1.1. Characteristics of a typical CV plot	19
3.1.2. Reversibility, irreversibility, and quasi-reversibility	21

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3.2.	Chronopotentiometry	22
3.3.	Electrochemical impedance spectroscopy (EIS)	23
3.3.1.	An EIS application: self-discharge in electrochemical capacitors	24
3.3.2.	Components of the impedance	25
3.3.3.	Capacitive dispersion	26
4.	Influence of the electrodes in charge transfer	27
4.1.	Charge carrier concentration in the electrode	28
4.2.	The thermodynamics of charge transfer in a redox couple	28
4.3.	The electrical current between the electrode and the electrolyte	30
4.4.	Surface processes vs. drift-diffusion based processes	31
4.5.	The practical surface state of an electrode, e.g., the SEI (Solid Electrolyte Interface)	33
4.6.	Charge transfer in semiconductors	34
4.6.1.	Charge configuration at a semiconductor interface	35
4.6.2.	Charge transfer through the semiconductor–electrolyte interface	36
4.7.	Charge transfer induced by photons: photoelectrochemical cells	37
4.8.	Specific characteristics of nanostructured electrodes	38
4.8.1.	Nanostructured carbons	38
4.8.2.	Non-ideality: charges at defects	39
4.8.3.	Influence of defects on bandstructure and charge capacity	42
4.8.4.	Wetting and roughness of the electrodes	43
4.9.	Porosity in electrodes: a metric for high capacitance density	44
4.9.1.	Anomalous variation of capacitance	45
4.10.	Chemical capacitance in nanostructures: applications in dye sensitized solar cells	46
4.11.	Quantum capacitance	48
5.	Faradaic charge transfer processes	51
5.1.	Pseudocapacitance	51
5.1.1.	Criteria for maximal pseudocapacitance	53
5.1.2.	Underlying mechanisms of adsorption pseudocapacitance	54
5.1.3.	The relation of pseudocapacitance to battery-like behavior	55
5.1.4.	Intercalation pseudocapacitance (inner and outer electrode areas?)	56
5.2.	Faradaic energy storage in nanoscale confined electrolytes	59
6.	Materials trends and prospects	61
6.1.	Electroactive polymers for high charge density and capacitance	61
6.1.1.	Lignin modified electrodes	62
6.1.2.	Polymer – inorganic oxide hybrids	63
6.2.	Developing novel architectures for charge and energy storage	64
7.	Summary	65
	Acknowledgements	66
	References	67

1. Introduction

Human prosperity has been directly linked to the ability to efficiently use energy, and requires both energy generation and storage. Concerns related to the environmental impact as well as the possible resource crunch underlying fossil-based fuels has been a major motivator for the development of alternative, renewable, energy sources. To enhance the viability of such sources, as well as to increase the utility of conventional energy sources, it is necessary to provide compatible materials and devices that can store the energy for later use. In this context, recent advances in nanoscience and technology have been explored to gauge whether their use could facilitate improvements in the energy storage capacity. Given that most energy is utilized in the form of electricity and that the source of energy often resides at the level of chemical interactions involving electrons and ions, the notion of charge transfer and charge based energy storage is prominent.

Broadly, energy storage in the electrochemical sense has been conventionally classified into (a) batteries or (b) capacitors, in terms of whether electrical charge is harnessed mostly in a *thermodynamic sense* (in terms of a net free energy change, of the material undergoing an electrochemical reaction) or in a *kinetic sense* (in terms of transducing the charge at an interface into an electrical current). From a practical perspective, batteries incorporate devices with high energy density (~ 100 Wh/kg) and relatively low power (rate of energy uptake/release) density (~ 1 kW/kg), while capacitors comprise media with contrary attributes, *i.e.*, relatively lower energy

density (~ 10 Wh/kg) and higher power density (~ 10 kW/kg) [1,2] (for an excellent perspective on the meaning of such numbers, consider the book: *Sustainable Energy* [3], *e.g.*, the hydrocarbon based fuel for cars has a calorific value of ~ 8 kWh/kg or that the typical power consumed by a 100 W light bulb (say, 50 g in weight) would be of the order 2 kW/kg). The overarching technological imperative in energy storage is then to devise *intermediate* devices, combining the best of both batteries and capacitors. Indeed, there has been frequent utilization of mutual principles, *e.g.*, the invoking of an intercalation pseudocapacitance (see Section 5.1.4) for the fabrication of electrochemical capacitors.

We will then consider the major technological imperatives for the scientific study of charge storage, *viz.*, through exploring the principles of batteries and capacitors. We broadly survey and understand the scientific rationale behind the modalities of charge creation and manipulation for electrochemical energy storage in nanostructures. We will attempt to understand the aspects that are unique to the nanoscale for it is to be expected that the relevant length scales bridge atomistic aspects to macro-scale utilization. It is also aimed to comprehend (a) where the charge is stored *i.e.*, on the surface or in the volume/bulk, and (b) the specific reaction sites for charge transfer in an electrochemical device, and their relevance for energy storage. Insights into the mechanism of charge transfer may be obtained through a consideration of the combined as well as separate influences of (a) adsorption, (b) accumulation, and (c) electrochemical reaction processes. The nature and origin of the reaction sites in materials will then be

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