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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.

Contents

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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 ($\sim$100 Wh/kg) and relatively low power (rate of energy uptake/release) density ($\sim$1 kW/kg), while capacitors comprise media with contrary attributes, *i.e.*, relatively lower energy density ($\sim$10 Wh/kg) and higher power density ($\sim$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 $\sim$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