

Organic Batteries

Development of sustainable processes for energy storage and supply is one of the most important world-wide concerns today. It is essential to find new, low-cost and environmentally-benign electroactive materials based on less-limited resource for electric energy storage and supply. Reversible storage materials of electric energy or charge that are currently under use in electrodes of rechargeable secondary batteries are entirely inorganic materials, such as Li ion-containing cobalt oxide, lead acid, and nickel-metal hydride, many of which come from limited resources. Tedious waste processing of used batteries is also difficult and crucial issue of the metal- and metal oxide-based conventional batteries. Electrode reactions in Li-ion batteries result in slow kinetics and heat generation during the charging and discharging processes, often producing overheating and occasional ignition. The conventional metal-based batteries involve several inherent unsolved issues from the standpoints of sustainability and safety.

Organic functional polymers have been developed as alternatives of inorganic functional materials because of their light weight, flexibility, thin film-forming ability, processability, metal-free, and benign environmental aspects, and fewer limitations of organic resources. A new trend in materials research is emerging recently, focusing on the fabrication of organic electrodes or electrodes composed of electrode-active organic compounds, characterized by the redox (oxidative/reductive or electron-releasing/gaining reaction) activity and/or electric conduction of organic molecules that typically consist of redox polymers and/or conducting polymers. The organic batteries and devices are free from using (heavy) metals and limited resources, and are potentially involved in the carbon cycle. In this lecture, the concept and outline of organic electrodes for use in rechargeable batteries is reviewed, emphasizing the material science of the organic polymers for charge-transport and storage for the development of sustainable science and engineering.

Research on organic electrode-active materials was prompted by the discovery of the electric conductivity of doped polyacetylene, which led to explore organic batteries by employing the redox capability of polyacetylene based on the reversible *p*-type and *n*-type doping/de-doping processes for the cathode and the anode, respectively, as the principal electrode reactions. Electrically conducting polymers with π -conjugated skeleton structures, such as polyaniline, polypyrrole, polythiophene, and their related derivatives, have been similarly examined as electrode-active materials, based on their reversible electrochemical doping behaviors. The limitations of the π -conjugated polymers as the electrode-active materials are based on their insufficient doping levels, the resulting low redox capacities and

fluctuation of the cell voltage through the doping/de-doping process. Chemical instability of the doped states of the π -conjugated polymers is the fatal flaw to practical application because it frequently leads to the self discharge and degradation of the rechargeable properties of the resulting batteries.

Organodisulfide compounds act as a cathode-active material with a high charge capacity through their two-electron redox reaction. Electromotive force of the redox reaction vs. Li is 2.7 – 3.0 V to give significantly high energy density. However, the redox reaction involves the formation of the disulfide polymers with the formation and cleavage of the chemical bond or the formation and the scission of the polymer chain, which renders the rate performance of the cathode low. Nasty odor of the sulfur compounds was still a problematic issue.

Another avenue toward the organic electrode-active materials is based on the sufficiently large redox capacity of aliphatic radical polymers, i.e., organic polymers densely populated with pendant redox sites. The principal finding to permit the use of the non-conjugated radical polymers is the capability of organic robust radicals, or open-shell molecules, to allow fully reversible one-electron redox reactions featuring fast electrode kinetics and reactant cyclability. The nitroxide radicals such as tetramethylpiperidineoxyl (TEMPO) derivatives and the oxygen radicals such as phenoxy and galvinoxyls are typically examined as the pendant group of the radical polymers and are persistent at ambient temperatures under air.

Nitroxide radicals are reversibly oxidized to oxoammonium cations by $1e^-$ transfer processes. Phenoxy radicals give the corresponding phenolate anion upon the electrochemically reversible $1e^-$ reactions. A variety of polymer backbones have been employed to bind the radicals, such as poly(meth)acrylates, polystyrene derivatives, polyethers, and polynorbornenes. The radical sites must be bound to polymer chains because of the need to immobilize them at current collectors for exclusion of elution into electrolyte solutions that leads to discharging, to accomplish appropriate mobility of the counterions, to make the electrode-active material amorphous and plasticized to accommodate deformation without heat generation, and to allow wet fabrication processes. Specific capacities based on the formula weight of the repeating unit are in the range of 50 – 150 mAh/g.

The unpaired electron density of the radical polymers amounts to several molars in the bulk of the swollen polymer equilibrated in electrolytes. Charge propagation within the polymer layer is sufficiently fast leading to high-density charge storage. The concentration gradient-driven charge propagation is accomplished by the very fast electron self-exchange reaction, which leads to the high rate performance of the radical-based organic battery.

The radical polymers act as both cathode- and anode-active materials, depending on the redox potential. A couple of polymers, different in redox potentials, are used as the electroactive materials in the organic radical battery (Fig. 1). The charging process corresponds to the oxidation of the radical to the cation at the cathode, and the reduction of the radical to the anion at the anode. The electromotive force is close to the potential gap between the two redox couples, which typically amounts to 0.5-1.5 V.

The amorphous radical polymers allow fabrication of flexible thin-film devices (Fig. 2). A curious feature of the radical battery is the excellent rate performance to produce burst power, which also allow instant full charging (i.e. in a few seconds). Optimization of the battery have allowed retention of >90% capacity even after 1000 charging/discharging cycles. The maximum energy and power densities are 120 Wh/kg and 20 kW/kg, respectively. The resulting radical battery has allowed the rated performance of the power density of 5 kW/L for more than 10^4 times pulse charging/discharging at 100 mA, and 1 A discharging and 2 W power from only <1 mm-thick flexible battery, that is suitable for IC cards, electronic papers, and active RFIDs.

Radical batteries have proved to be a new class of organic rechargeable devices, which are characterized by the excellent rate performance and the moderate energy density as illustrated by the Ragone plots (Fig. 3). The mass-specific energy density is placed between those of polyacetylene- and disulfide-based organic batteries, but the power density is much larger and comparable to those of supercapacitors. While organic batteries have intrinsically lower volumetric energy density, this limitation can be overcome in the near future so that they can be designed to be compatible with and installable in various electronic equipments.

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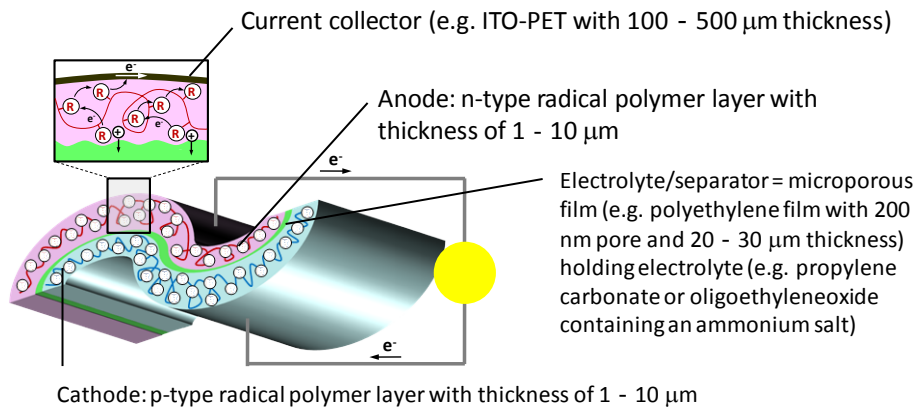


Fig. 1. Charge-storage configuration of a flexible organic radical battery.



Fig. 2. Proto-type of the thin and flexible radical battery (NEC Co.) loaded on flash devices and smart cards.

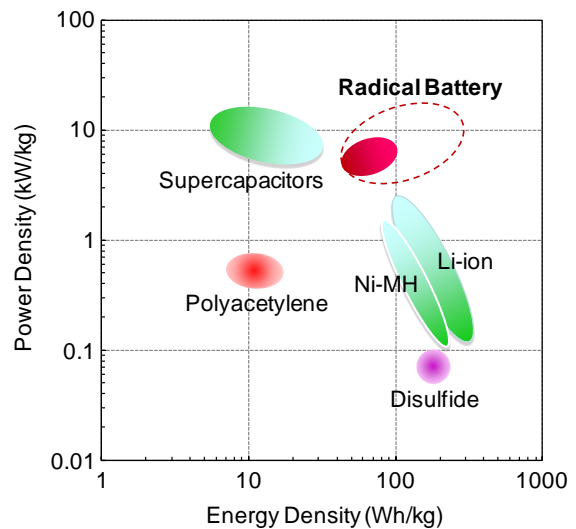


Fig. 3. Energy versus power density plots for batteries and supercapacitors.