Research Highlight

A new family of carbonaceous cathodes for rechargeable batteries
through electronic structure tuning engineering

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Electrical vehicles (EVs) and grid storage for renewable energies will require batteries in tens of millions of tons and thus they need to be sustainable. EVs call also for batteries with higher energy density than that of today’s and this value is intrinsically limited by the properties of the transition metal oxide (TMO) cathodes. Two strategies are followed to surpass this constraint: i) increase the operating voltage in the > 4.4 V range; ii) attempt to utilize more than one electron per transition metal. The first direction faces problems of electrolyte stability limit, oxygen evolution and thus safety hazards. The second is limited to vanadium and nickel but where only 1.3 electrons for the former, and the latter need to be diluted in 300% manganese lattice. Cobalt, used today, nickel and vanadium are metals for which shortages are foreseen with the expansion of the battery market. There has been countless research efforts in the past thirty years, and up to now, the current TMO cathode has practically reached its limit in terms of its theoretical specific capacity and voltage performance.

Carbon as graphite is in a battery synonymous to anode material due to its low electrochemical potential (< 0.5 V vs. Li/Li$^+$), determined by the high energy level $sp^{2}$-$p_z$ orbital in the form of weak $\pi$ bond. An open question is whether the electrochemical potential of carbonaceous materials can be tuned to a level comparable to that of the current widely used TMO cathodes. In the 1970s, we introduced TM salts with high valence state into graphite, e.g., graphite chromium.
oxide (C$_8$CrO$_3$), which could effectively “pump” the carbon electrons into the “d” shells of TM and therefore improve the redox potential of graphite-based electrode. The Na | β-Al$_2$O$_3$ | C$_8$CrO$_3$ cell exhibited a surprisingly high voltage of 3.9 V but the redox reactions are still pinned to the “d” orbitals of the TM.$^3$

Recently, Prof. Chuying Ouyang’s group from Jiangxi Normal University and Prof. Siqi Shi’s group from Shanghai University achieved a breakthrough in the design of carbonaceous materials as cathodes for rechargeable LIBs/SIBs.$^4$ Amazingly, they showed that electronic structure engineering via p-type doping strategy can tune the potential of graphite derivatives to reach the requirements for cathode application (2.7–3.7 V) that would lead to a record-breaking high energy density (> 1000 Wh kg$^{-1}$) (Fig. 1). This is done resorting only to light elements of the first row, as in CBF$_2$ – an example of host materials devoid of any TM.

This is a new paradigm for battery design, which is helpful in addressing issues related to the battery energy-density limit as well as the transition-metal cost and shortages. In a broader sense, the success of the full shell $p$-doping strategy to shift-down the Fermi-level of graphite may motivate more researchers to evaluate the link between the electrochemical potential and the band structure engineering of electrodes, which can help guide a rational design of these compounds in the future and inform prospective theoretical and experimental researches in this field.

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**Figure 1.** Schematic open-circuit voltage ($V_{oc}$) of battery. The energy separation of the lowest-unoccupied-molecular-orbital (LUMO) and the highest-occupied-molecular-orbital (HOMO) is the electrolyte window. Electrochemical potential vs. capacity is presented for both graphite-anode and cathodes. The cathodes are commonly transition-metal (TM) compounds which have layered, spinel, or olivine crystal structures. The figure is from [4].

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