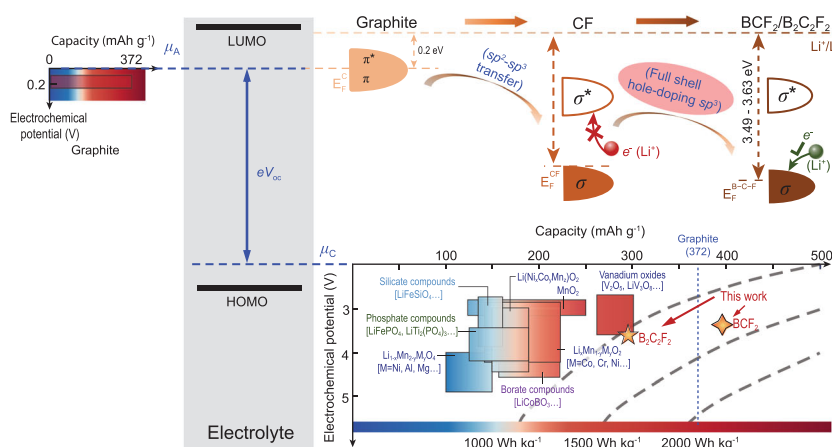PHYSICS

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

Michel Armand

Electric 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 currently available, and this value is intrinsically limited by the properties of the transition metal oxide (TMO) cathodes [1]. There are two possible strategies to overcome these limitations: i) increase the operating voltage in the >4.4 V range; and ii) attempt to use more than one electron per transition metal [2]. The first strategy faces problems of electrolyte stability limit and oxygen evolution, and thus safety hazards. The second is limited to vanadium and nickel, but using only 1.3 electrons for the former, and the latter must 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 have been countless research efforts over the past 30 years, but, to date, the current TMO cathode has practically reached its limit in terms of its theoretical specific capacity and voltage performance.

Carbon, as graphite, in a battery is synonymous to anode material because of 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 a weak π 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_8CrO_3), which could effectively 'pump' the carbon electrons into the 'd' shells of TM and therefore improve the redox potential of graphite-based electrodes. 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 were 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 breakthroughs in the design of carbonaceous materials as cathodes for rechargeable LIBs/SIBs [4]. Amazingly, they showed that electronic structure engineering via a p-type doping strategy can tune the potential of graphite derivatives to reach the requirements for

cathode application (2.7–3.7 V), leading 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 a host material devoid of any TM.

This is a new paradigm for battery design, which could address issues related to the battery energy-density limit as well as 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 could help to guide rational design of these compounds

Figure 1. Schematic open-circuit voltage (V_{OC}) of a 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].

in the future and inform prospective theoretical and experimental research in this field.

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REFERENCES

1. Armand M and Tarascon JM. *Nature* 2008; **451**: 652–7.
2. Kang B and Ceder G. *Nature* 2009; **458**: 190–3.
3. Armand M and Touzain P. *Mater Sci Eng* 1977; **31**: 319–29.
4. Wang Z, Wang D and Zou Z *et al. Natl Sci Rev* 2020; **7**: 1768–75.

CHEMISTRY

Tackling the challenge of controlling the spin with electric field

Roberta Sessoli ⬤

Electric (E) fields are commonly employed to control magnetization in some classes of materials such as multiferroics. However, the extreme confinement of the electric field, for instance under the tip of a scanning tunnel microscope, makes it an ideal tool to manipulate individual spins, generating interest in spins as potential quantum bits. Spins are in fact intrinsic quantum systems that can be manipulated easily by means of pulses of electromagnetic microwaves, as commonly done in magnetic resonance spectroscopies. Although the coupling usually involves the magnetic field of microwaves, the first experiments with E-field pulses date back to the 1970s when Mims investigated the symmetry of the lanthanide ion coordination environment [1]. A linear effect is characteristic of an acentric environment. Renewed interest in spin-electric coupling is motivated by recent advances in scanning probe spectroscopies able to perform single atom CW [2] and pulsed [3] EPR spectroscopy. These exceptional tools make possible the optimization of spin-electric coupling in the qubit and exploration of the potential for gate control. In this respect, ensemble measurements (diluted single crystals or frozen solutions) provide an immense playground. Excluding rare exceptions, spin-electric coupling is enhanced by spin-orbit coupling. Lanthanide-based materials

with the orbitally unquenched contribution of 4f electrons are promising candidates. Liu Z *et al.* recently coordinated a pulsed EPR study on Ce^{3+} ions (f^1, $S = 1/2$ and $J = 5/2$ but with a well isolated ground doublet) diluted in a polar diamagnetic crystal of yttrium aluminum garnet (YAG), as shown in Fig. 1 [4]. The standard $\pi/2 - t - \pi$ Hahn sequence generating an echo was modified by insertion of an E-field pulse. The Hahn echo

intensity was found to depend on both E-pulse intensity and length, demonstrating that the E-field is controlling the spin system. The effect, often quantified as a frequency shift per V m^{-1}, is about one order of magnitude larger than that detected in molecular qubits based on 3d ions. In the same study, the authors used the E-pulses to control evolution of the spin system through a phase gate and to implement the Deutsch–Jozsa
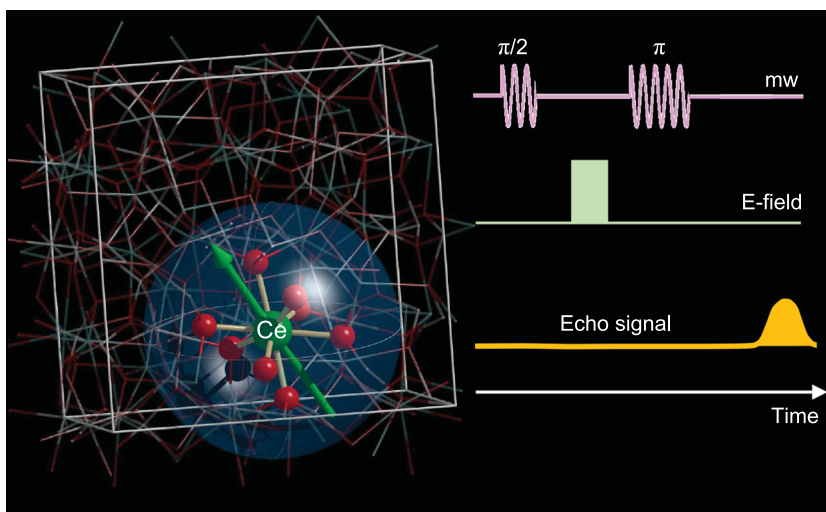
Figure 1. Diluted Ce^{3+} ions (f^1, $J = 5/2$) substituting diamagnetic Y^{3+} ions in the YAG lattice are operated as spin qubits using mw pulses, as commonly done in pulsed electron paramagnetic resonance spectroscopy (color code: Ce, green; Y, cyan; Al, grey; O, red). Liu Z *et al.* [4] have added an electric field pulse and demonstrated that it acts as a phase gate modifying the spin echo signal. The large spin-orbit coupling of Ce^{3+} ion is a key ingredient for coherent electric field control of the spin, while the rigid garnet lattice warrants long spin coherence also at moderate temperatures.