

Battery Materials Design Essentials

M. Rosa Palacin

Institut de Ciència de Materials de Barcelona, ICMA-B-CSIC, Campus UAB, 08193 Bellaterra,
Catalonia, Spain.

1. INTRODUCTION

The advanced materials industry is one of the leading technology sectors worldwide. The development of such materials is at the core of the technological innovations and has been possible in the last century thanks to the transition from “observational” science to “control” science. Indeed, knowledge of the structure and dynamics of matter at different length scales has enabled replacing serendipity and edisonian trial-and-error approaches with intention and rational materials engineering and this has accelerated progresses in a wide range of technologies which are now crucial for our daily lives but could not even be imagined a century ago.

One of such examples is Li-ion batteries, which was granted the Nobel Prize in Chemistry 2019 to J.B. Goodenough, M. S. Whittingham and A. Yoshino as it enabled, in words of the Nobel Committee, “the creation of a rechargeable world”.¹ This technology is now expanding from the portable electronics realm to transportation² and even stationary grid applications.

Given the crucial relevance of all these fields of use, it seems evident that as a society we should not rely on a unique technology, neither from a sustainability nor from a geopolitical and social perspective. Despite Li-ion batteries being in itself not a single technology but a family of technologies for which several materials have been developed *ad hoc*,³ the diversification of concepts/chemistries is currently a target for battery researchers worldwide, both in academia and industry (see⁴ and references in that issue). While the quest for ever increasing energy densities has for long been the main driving force behind progress in battery technology, additional factors are now considered such as cost and sustainability. The latter comprises not only low environmental footprint in terms of toxicity and energy/water consumption but also the avoidance of critical materials.

The aim of this viewpoint is to present in a nutshell a summary of practical considerations in research for new battery materials and concepts targeting non-specialists in the field. Indeed, cross-fertilization from other research domains is, as always in science, precious, but a number of aspects need to be taken into account when entering battery research to make the best of experiments/developments and avoid biased experiment interpretations.

2. BASIC BATTERY CONCEPTS

Batteries are made of two electrodes involving different redox couples that are separated by an electronically insulating ion conducting medium, the electrolyte. The later might be a solid (inorganic⁵ or polymer⁶), despite conductivities being typically very low at room temperature (< 0.1 mS/cm),⁷ or most commonly a liquid with a certain concentration of dissolved salt. Aqueous electrolytes enable higher conductivity (~ 1 S/cm) and low cost despite a narrow stability window (1.23 V). In contrast, electrolytes based on organic solvents display a much wider stability window

(up to 4 V or even larger) but are less conductive ($< 100 \text{ mS/cm}$)⁸ and involve somewhat higher fabrication costs due to the need to assemble cells in moisture and oxygen free environments.

Upon discharge a spontaneous chemical reaction takes place ($\Delta G < 0$) and electrons transfer from one electrode to the other through the external circuit as a current I at a voltage V for a time Δt , with charges being compensated by ions' migration across the electrolyte. If the reaction is reversible, the process can be reversed applying an external current and thus batteries can be recharged. During discharge and charge, an internal battery resistance R_b to the ionic current $I_i = I$ reduces the output voltage V_{dis} from the open-circuit voltage V_{oc} by a polarization $\eta = I_{\text{dis}}R_b$ and increases the voltage V_{ch} required to reverse the chemical reaction on charge by an overvoltage $\eta = I_{\text{ch}}R_b$.⁹ As the ionic mobility in the electrolyte is much smaller than the electronic conductivity at the electrodes, thin separators are mandatory to reduce polarization as much as possible. The energy stored in each electrochemical cell is proportional to the cell capacity (usually expressed in mAh/g) and the cell voltage. Thus, it depends not only on the intrinsic properties of active electrode materials (capacity, redox potential, density) but also on the balance between the two electrodes and the total mass of “inactive weight” such as packaging, separator, electrolyte, current collectors, electrode additives (binder and carbon black) etc. which are electrochemically inactive and induce a significant decrease of energy density¹⁰ (Figure 1). Thus, care should be exercised when comparing figures of merit derived from scientific publications, often disregarding the weight/volume of such components, and practical values achieved in commercial cells (and considering the full cell or even cell modules or packs with additional components such as sensors), to avoid comparing apples and oranges.

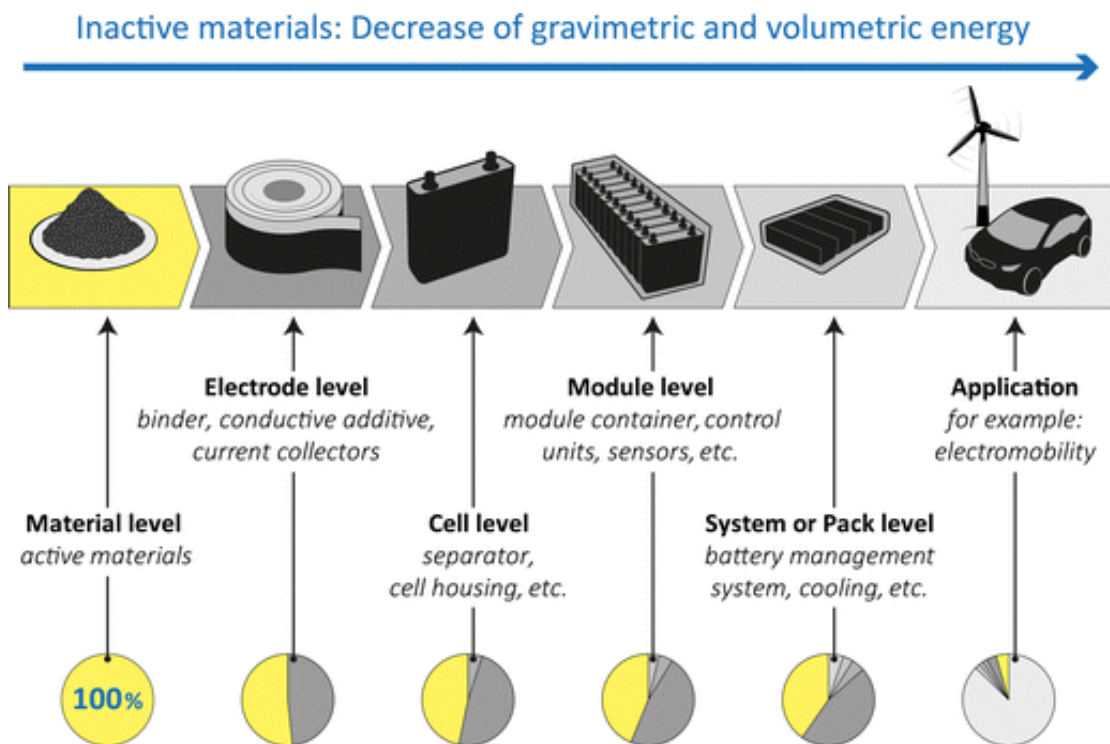


Figure 1. Schematic illustration of the battery value chain from the material level via the battery cell to the battery system level. In each step, inactive components are added which decrease the practical specific energy. Reproduced with permission from reference 10. Copyright 2017 Springer.

The electrochemical capacity of each given redox active electrode material is determined by the number of electrons exchanged per formula weight. The cell open-circuit voltage (V_{OC}) is the difference between the electrochemical potentials of the negative electrode (μ_N) and the positive electrode (μ_P) which should lie within the Electrolyte Stability Window (ESW) (Figure 2). During battery discharge, reduction and oxidation take place at the positive and negative electrodes respectively. This has prompted the generic use of the terms “cathode” and “anode” as synonyms for “positive” and “negative”, which may be confusing for a general audience. Despite the ESW commonly being related to the energy separation between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the electrolyte components, it is in fact more complex to predict, requiring consideration of all species potentially present, their

concentration, and even the surface chemistry of electrode materials.¹¹ Moreover, the “practical window” may exceed the thermodynamic value due to degradation being kinetically hindered by the formation of passivation films, as is the case for the Li-ion technology.¹²

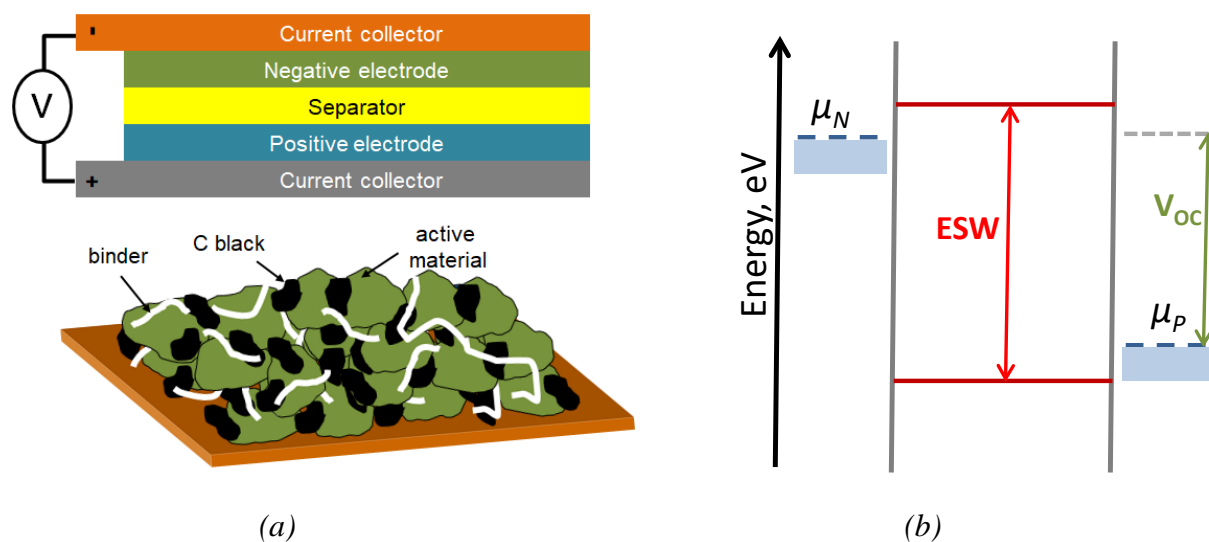


Figure 2. (a) Scheme of a battery cell (top), involving the separator in which the electrolyte is embedded and two electrodes and a conventional tape-casted composite electrode casted on a metal current collector (bottom) which consists of a mixture of active material, carbon black to enhance electronic conductivity and binder to enhance adhesion, mechanical strength and ease of processing. (b) Diagram depicting Electrolyte Stability Window (ESW) and electrochemical potentials of the negative and positive electrode materials (μ_N and μ_P respectively) falling within that window, inspired from⁹.

Battery operation upon each charge/discharge cycle brings about a change in the phases present at each electrode and modification of their physical properties. If such processes were completely reversible and no other side reaction would take place, battery service life would be unlimited. Yet, degradation upon operation is unavoidable and related to small inefficiencies and side reactions, which sometimes also involve components not expected to exhibit any redox activity, such as those related to electrolyte decomposition at extreme potentials.¹³ Some types of redox reactions (e.g. alloying, conversion reactions, etc.), involve major structural changes/reorganization. As an example, operation of Pb/acid cells involves dissolution and re-precipitation of lead sulfate or lead dioxide at each cycle. In contrast, the positive electrode

materials in Ni-based alkaline rechargeable batteries and both positive and negative electrode active materials within the Li-ion technology are based in solid-state redox reactions involving reversible topotactic de-insertion/insertion of ions (H^+ and Li^+ respectively) from the crystal structure, which remains essentially unmodified. These materials are commonly denoted intercalation/insertion compounds¹⁴ and exhibit (i) an open framework of interconnected sites (either 1D-, 2D- or 3D) wherein the inserted ion can diffuse and (ii) an electronic band structure able to reversibly accept/donate electrons.

Despite a myriad of conceivable battery chemistries resulting from combinations of any two favored redox reactions, the number of commercially important battery systems is relatively low, with rechargeable aqueous electrolyte (Pb/acid and alkaline Ni/Cd or Ni/MH)¹⁵ and Li-ion batteries¹⁶ dominating the market both in terms of size and value.¹⁷ This reduced number of technologies is related not only to figures-of-merit in terms of performance but to the general requirements imposed by practical application in terms of processability, safety, cost, reliability, environmental footprint¹⁸ etc. These are even more stringent for rechargeable systems and include also efficiency/reversibility and long-term stability.

The development of new battery chemistries is thus far more complex than the quest for a specific property and spans from electrode and electrolyte materials design (often with the help of computational tools) to synthesis and characterization, electrode fabrication and cell assembly to performance testing in laboratory prototypes which in the end will have to also include safety aspects and benchmarking against state-of-the-art technologies in terms of capacity and power, often considering application standards.

3. MATERIALS DEVELOPMENT FLOW

As far back as the 1960s, there was an adage at DARPA (Defense Advanced Research Projects Agency in the US) that said “Technology is always limited by the materials available”.¹⁹ Indeed, the cornerstone for the development of any new technology is unravelling the materials having the desired properties to make it possible.

The main fundamental challenge is therefore the successful development of compounds suitable to be used as active materials for the positive and negative electrodes within the ESW of the selected electrolyte, or in turn, the design of an electrolyte which enough ionic conductivity which remains stable during battery operation while in contact with oxidizing/reducing electrode materials.

3.1. Materials design

The driving force in battery research has always been energy density,¹⁰ which translates into a quest for electrodes with large electrochemical capacity coupled to the highest available voltage at the cell level.²⁰ As an example, Figure 3 depicts active materials considered for the Li-ion technology, with the almost empty yellow area corresponding to moderate operation values.

The potentials of the electrode materials, are determined by their respective Fermi levels and therefore dependent on their composition, crystal structure and bonding character.²¹ Typically, the highest potentials will fall on the verge of the ESW of the electrolyte, which may cause some side reactions and hence performance loss upon cycling.²² The electrochemical capacity is not at all correlated to the operation voltage but dictated by the number of exchanged electrons per formula unit and the overall formula weight. Besides requirements redox activity at suitable potentials and delivering the required capacities, active materials need to exhibit a range of

additional properties such as electronic and ionic conductivity, and be stable throughout the redox process, which should take place with appropriate kinetics.

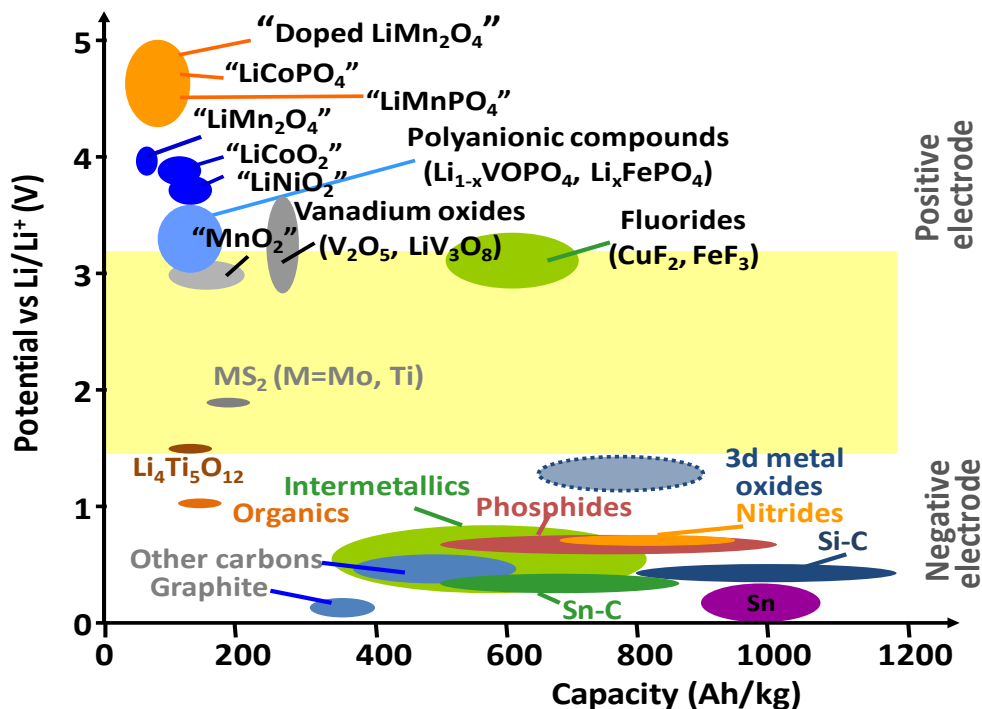


Figure 3. Potential vs. capacity for active materials considered for Li-ion technologies, either commercial or under research, where the yellow area corresponds to moderate operation potentials within the electrolyte stability window (inspired in ref.²³).

While theoretical capacity is easy to estimate and prediction of electronic conductivity relatively straightforward, ionic conductivity or kinetics are much more difficult (or even impossible) to calculate.²⁴ Experimental screening is thus still mandatory, despite computational materials science being currently an invaluable complementary tool to rationalize results and accelerate progress. Yet, open web-based approaches have been recently established enabling first-principles computing of redox potential and phase stability (amongst other properties) on thousands of known and predicted materials which will for sure accelerate materials' discovery, as they provide not only codes and workflows but also utilities for data handling and analysis.²⁵ Moreover, the scope of

During battery operation two situations arise: either the guest (charge carrier) ions are present in the initial formulation of one of the electrode materials, or else the redox mechanism is based on a dual mechanism in which the ions intercalated/de-intercalated at the positive and negative electrode are different. Note that in case these ions do have opposite sign charges, the electrolyte salt concentration will change upon operation, which should not be a major issue provided ionic conductivity is ensured, yet, fundamental issues still exist in terms of reversibility and cycle life.²⁸ Nonetheless, the simplest concepts enlist intercalation of the same ion on both sides, with the Li-ion battery technology being the paradigmatic example in which Li^+ is the charge carrier ion. The significant *know how* achieved in this field after more than 25 years' commercialization is now catalyzing the development of other concepts based on intercalation of Na^+ and K^+ while it is less useful in case of concepts involving divalent charge carrier ions (such as Zn^{2+} , Mg^{2+} or Ca^{2+}). Indeed, the latter exhibit hurdles associated to (i) their migration in the solid state and in organic electrolytes and (ii) side reactions related to competition with H^+ intercalation in aqueous systems.²⁹

One strategy to develop low cost and resource sustainable active electrode materials is to shift to metal-free organic compounds that could even be synthesized from biomass and take advantage from the well-established principles of organic synthesis and molecular engineering.³⁰ In the absence of any metal, their redox processes involve commonly both s and p orbitals and are based on either cation or anion insertion. The former (n-type) corresponds to a reversible extraction/insertion of cations balanced by electrochemical evolution of the functional group, while in the latter (p-type) the electron release/uptake is balanced by uptake/release of electrolyte anions (Figure 5). They usually demonstrate acceptable reversible capacities, but suffer from low energy density and low capacity retention due to poor electronic conductivity (and hence need to

add large amounts of carbon black to the electrode) and dissolution of the material in the electrolyte upon cycling. In this sense, the use of solid electrolyte appears as an interesting pathway to explore.

Reversible redox-active moiety	Classification	General redox mechanism	Example of electrode reaction
Conjugated carbonyl	n-type		
Organodisulfide	n-type		
Conjugated azo group	n-type		
Conjugated nitrile	n-type		
Conjugated amine	p-type		
Conjugated etheroxide	p-type		
Conjugated thioether	p-type		
Nitroxide radical	n/p-type (bipolar)		

Figure 5. Examples of redox active organics and the corresponding mechanisms. Reproduced with permission from reference 30. Copyright 2020 American Chemical Society (ACS). PBQS: poly(benzoquinonyl sulfide); PDTTA: poly(5,8-dihydro-1H,4H-2,3,6,7-tetrathia-anthracene); ADALS: azobenzene-4,4'-dicarboxylic acid lithium salt; TCNQ: tetracyanoquinodimethane; PPy: polypyrrole; DBMMB: 2,5-di-tert-butyl-1-methoxy-4-[2'-methoxyethoxy]benzene; PT: polythiophene; PTMA: poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate).

3.2. Materials characterization

Once designed and prepared, the compounds under study need to be characterized with conventional means (diffraction, microscopy, spectroscopies, etc.), bearing in mind that microstructure (crystallite/particle size, specific surface, defects, etc.) can have a significant influence on the electrochemical behavior.³¹

Assessment of redox activity should ideally be carried out in three-electrode cells, but in practice often two electrode cells are employed. Regardless of the presence of a reference electrode, the

use of the so-called *half cell* configuration is advisable. In this case the working electrode contains the active material under study, which can be simply mixed with 15-30% carbon black to enhance electronic conductivity, and the selected counter electrode should not be limiting neither from the point of view of capacity nor due to kinetics. Typical counter electrode choices are metals which operate through a well-known mechanism with constant potential, such as Pt in aqueous medium, or lithium metal in organic electrolytes. Activated carbon counterelectrodes operating through a capacitive instead of a faradaic redox mechanism are a suitable choice in absence of better alternatives and often used with organic electrolytes when exploring new battery chemistries. This requires careful control of cell balancing and the use of a reference or at least pseudo-reference electrode (e.g. a silver wire), with calibration of its redox potential being advisable.³²

Stability of the investigated compounds in the electrolyte needs to be confirmed prior to any test. Despite seemingly trivial, the choice of the electrolyte is extremely relevant, as its ESW must comprise the potential at which redox activity is expected to take place. One of the issues preventing breakthroughs in energy density in the field of Li-ion batteries is the development of electrolytes with ESW > 5V, which despite challenging, would enable the use of materials operating at extreme potentials and hence significantly increase the potential at cell level. For tests carried out in aqueous media, the influence of pH can be significant and some basic considerations can be extracted from Pourbaix diagrams.³³ Alternatively one of the most used solvents in organic electrolytes is propylene carbonate (PC), due to its high dielectric constant ($\epsilon \sim 64$) coupled to a wide electrochemical stability window.

The variation of potential during operation is related to the redox mechanism taking place at each electrodes. Considering simple insertion reactions, when it is homogeneous (i.e., formation of solid solution), a constant evolution of electrode potential is observed concomitant to the change

in the electrode chemical composition. If heterogeneous (i.e., first order phase transition) nucleation of a second phase takes place, and the relative amount of each phase is modified as the redox process proceeds, but the electrode potential is constant.³⁴ Most active materials, especially if exhibiting a wide compositional range during operation (i.e. large capacity), may exhibit a complex redox mechanism enlisting multiple redox steps, both homogeneous and heterogeneous. Since the overall cell voltage is the difference between the potentials of the negative and positive electrodes, these dictate the behavior at the full cell level. Note that upon real applications involving battery packs, the battery management system³⁵ will likely rely on the measure of cell potential to assess state of charge.

Most active materials being likely crystalline throughout the full redox process, *operando* and *ex situ* diffraction are expected to play a major role in the elucidation of the redox mechanisms.^{36, 37, 38} Yet, other bulk- and surface-sensitive techniques, including microscopy (SEM, TEM) and spectroscopies (XPS, NMR, IR, EDX, EELS, Mössbauer) are expected to provide very useful additional complementary insights.³⁹ These are now also nicely complemented by imaging techniques.⁴⁰

Characterization of redox mechanism is of the utmost importance especially when developing new technologies⁴¹ in which no standard components exist. Indeed, the electrochemical response can be due to side reactions involving *a priori* inert components such as the electrolyte, the current collectors etc. and be easily misinterpreted, especially if the magnitude is relevant. Some examples would be corrosion or electrolyte decomposition in presence of high surface area materials. Last but not least, the length scale that can be probed with each technology e.g. surface for XPS, bulk for XRD, and atomic for TEM (transmission electron microscopy) needs to be properly taken into account to assess reactivity.

4. PERFORMANCE TESTING

Once redox activity assessed, validation of “practical” electrochemical performance is compulsory to ensure realistic application prospects. Often tests are carried out using electrodes prepared mimicking industrial fabrication protocols such as tape-casting. At this point, additional parameters come into play such as stability of the studied materials in the solvent used to prepare the slurry, the inertness of the current collector with respect to the electrolyte and conditions used, and the electrode formulation (active material loading, percentage and type of carbon black and binder additives, solvent used for the slurry, etc.). The latter has a tremendous influence on the electrochemical performance⁴² at the stage of benchmarking active materials and before disregarding any compound it must be ensured that results are not biased by a non-optimized formulation. Combined experiment design strategies can be useful to that respect.⁴³ Reproducibility and reliability of the results achieved should be ensured by replicate tests and assembly of twin cells with a setup closer to practical application as well. At small laboratory scale coin cells are generally used (e.g. 2032 type) with conventional setups (including casing, springs and *ad hoc* separators for either organic or aqueous electrolytes) and tape casted electrodes, with optimized formulation for each material. Yet, achievement of reliable and reproducible results can be tricky^{44,45} as it depends on electrode loading, positive/negative balancing and alignment, electrolyte volume and purity, etc. The effect of the amount of electrolyte is easily exemplified with the Li/S concept as tests made with electrodes containing low amounts of sulfur and electrolyte excess result in very high figures-of-merit per gram of sulfur.⁴⁶ Yet, such figures lack practical relevance if the weight of the electrolyte and other inert cell components is not considered.

At this point the type of separator is expected to have significant influence (composition, thickness, porosity) on the wettability by the electrolyte and the results achieved.⁴⁷ Polyolefins (PE, PP or laminates) and glass fiber are often used for organic and aqueous concepts, respectively.

Performance is usually tested with different charge/discharge protocols mimicking final practical operation conditions with respect to intensities (power demands) and cut off voltages. Again, it is worth to recall here that proper metrics should be given to enable comparison and benchmarking with commercial technologies and avoid misleading non-expert readers.⁴⁸ The results obtained at room temperature (ca. 25 °C) can be considered as baseline, and compared to results achieved upon testing the cells in controlled temperature chambers (cooling/heating e.g. to 5°C and 55 °C respectively). Standard deviation between identical tests should give an indication on the reliability of the methodology used. When testing cycle life, degradation can be quantified through analysis of either incremental capacity,⁴⁹ differential voltage⁵⁰ or coulombic efficiency.⁵¹

Finally, safety assessment on successful concepts is also advisable. Accelerated Rate Calorimetry⁵² tests under adiabatic conditions and at different states of charge (SOC): 0%, 50% and 100% can be complemented by Differential Scanning Calorimetry of harvested cell components (positive electrode, negative electrode and separator soaked in the electrolyte), to assess the individual contribution of each component to the observed behaviour.⁵³

5. THE LONG AND WINDING PATH TOWARDS MARKET

Results achieved following the above described protocols and research flow should enable benchmarking any new material/cell technology development against state-of-the-art and identification of explicit “success cases” for further “Proof-of-Concept” follow up. Unravelling

not only a brand new technology but also a mere new electrode material can be a complex task, as described above. Yet, the efforts needed in every stage of development can be very different.

Schematic of the Overall Battery R&D Process from Conception to Production

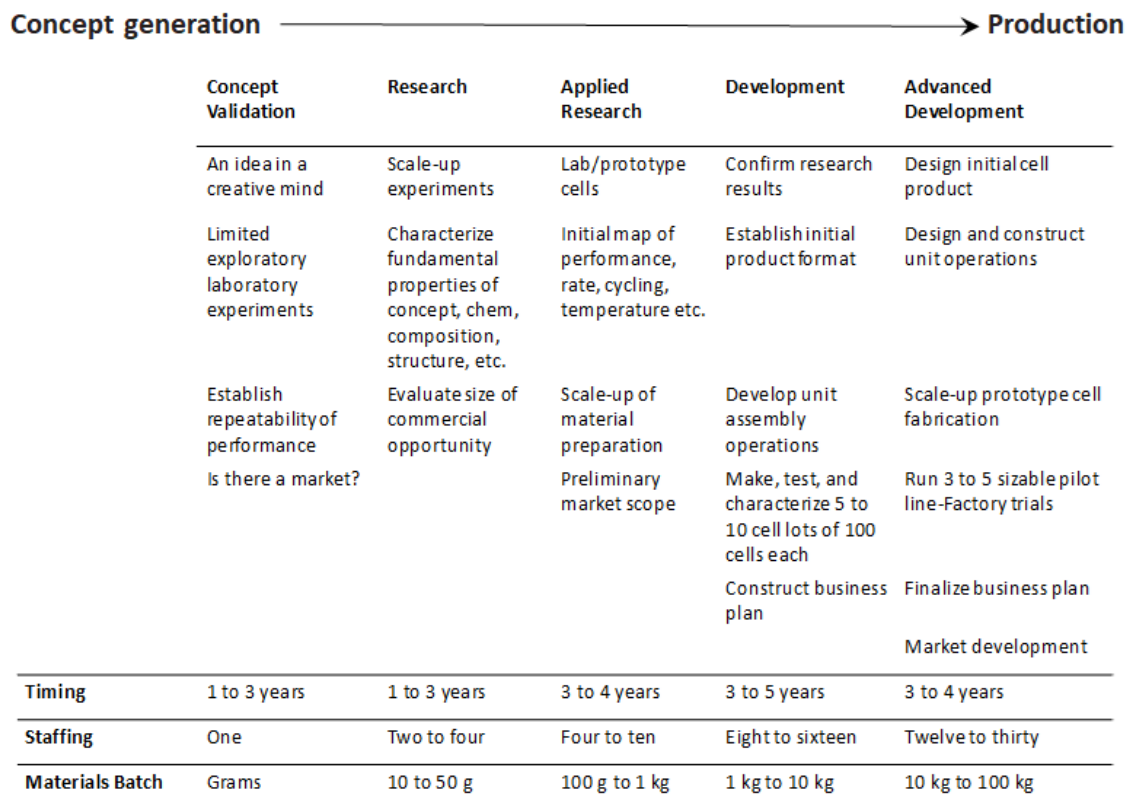


Figure 6. General overview of the overall battery R&D process from conception to production with indication of estimated timing, staff and materials amount required for each step according to ⁵⁴.

Figure 6 depicts a scheme depicting overall battery R&D from conception to production as defined by Ralph Brodd basing on the five stages in the generic product innovation process. ⁵⁴ Each concept may have different timings and costs in each step, but some generalities can be drawn, basing on historical development on different battery technologies. The golden rule throughout the process is to abandon concepts which fail to yield the initial expected performance and focus on others which are confirmed to accelerate progress.

Finally, it has to be taken into account that even in success cases for performance, the introduction of a new product in the market is far from being trivial, as pilot lines are expensive. The necessary investments will only be justified by the existence of applications for which the new technology will bring in benefits will draw the necessary investments. Moreover, the market being dynamic, volatile and continuously changing, such aspects may have a significant time dependence.

6. CONCLUSION

Developing novel battery materials (or even brand new technologies) is by no means an easy task. Besides technical requirements such redox activity, and suitable electronic and ionic conductivity, and sustainability aspects (cost, toxicity, abundance...) there is a myriad of practical parameters related to the stringent operation requirements of batteries as chemical energy storage devices which need to be considered at an early stage. Doing so will enable maximizing the impact and benefits of the performed research and hence a number of considerations should be taken into account when entering such research topics, not only related to materials design and characterization but also, and perhaps most important, to performance testing.

All these aspects will have a significant influence on the practical outcome of the research activities and largely determine the potential viability for entering the market. Yet, the market being dynamic and volatile, the opportunity may have a significant time dependence. Thus, at the level of oriented academic research in the first stages of development, scientific creativity is still the key.

AUTHOR INFORMATION

Corresponding Author

*M. Rosa Palacin: rosa.palacin@icmab.es

Institut de Ciència de Materials de Barcelona, ICMAB-CSIC, Campus UAB, 08193 Bellaterra,
Catalonia, Spain

orcid.org/0000-0001-7351-2005

SHORT BIO

M. Rosa Palacin is a research professor at the Institut de Ciència de Materials de Barcelona (ICMAB-CSIC, Spain). After her PhD in Chemistry (Universitat Autònoma de Barcelona), she entered battery research in 1996 through a post-doctoral stay with Prof. Jean-Marie Tarascon at LRCS (Amiens, France). Her research career has been fully focused in rechargeable battery materials initially either nickel or lithium based and more recently covering alternative chemistries such as sodium-ion, magnesium and calcium. Specific emphasis is set in tailoring structure and microstructure of electrode materials to maximise electrochemical performance for traditional technologies and in the development of new materials for emerging chemistries.

ACKNOWLEDGMENTS

The author is grateful to ALISTORE-ERI colleagues for helpful discussions and sustained interaction. The Spanish Research Agency is acknowledged for the Severo Ochoa Programme for Centres of Excellence in R&D (CEX2019-000917-S) and funding through grant MAT2017-86616-R.

REFERENCES

¹ *Scientific Background on the Nobel Prize in Chemistry 2019: Lithium-ion batteries* **2019**. Nobel Media AB <https://www.nobelprize.org/uploads/2019/10/advanced-chemistryprize2019.pdf>

² Schmuch, R.; Wagner, R.; Horpel, G.; Placke, T.; Winter, M. Performance and cost of materials for lithium-based rechargeable automotive batteries. *Nat. Energy*, **2018**, *3*, 267-278.

³ Croguennec, L.; Palacin, M.R. Recent Achievements on Inorganic Electrode Materials for Lithium-Ion Batteries. *J. Am. Chem. Soc.* **2015**, *137*, 3140-3156.

⁴ Meng, Y.S.; Introduction: Beyond Li-Ion Battery Chemistry. *Chem. Rev.* **2020**, *120*, 6327.

-
- ⁵ Famprakis, T., Canepa, P., Dawson, J.A. ; Islam, M.S. ; Masquelier, C. Fundamentals of inorganic solid-state electrolytes for batteries. *Nat. Mater.* **2019**, *18*, 1278–1291.
- ⁶ Ratner, M.A.; Johansson, P.; Shriver, D.F. Polymer Electrolytes: Ionic Transport Mechanisms and Relaxation Coupling. *MRS Bull.* **2000**, *25*, 31-37.
- ⁷ Janek, J., Zeier, W. A solid future for battery development. *Nat. Energy* **2016**, *1*, 16141.
- ⁸ *Electrochemistry in Non-Aqueous solutions*. Izutsu, K. Wiley WCH Weinheim **2002** ISBN 9783527323906.
- ⁹ Goodenough, J.B.; Park, K.S. The Li-ion rechargeable battery, a perspective *J. Am. Chem. Soc.* **2013**, *135*, 1167-1176.
- ¹⁰ Placke, T.; Kloepsch, R.; Dühner, S.; Winter, M. Lithium ion, lithium metal, and alternative rechargeable battery technologies: the odyssey for high energy density. *J. Solid State Electrochem.* **2017**, *21*, 1939-1964.
- ¹¹ Peljo, P.; Girault, H.H. Electrochemical potential window of battery electrolytes: the HOMO-LUMO misconception. *Energy Environ. Sci.* **2018**, *11*, 2306-2309.
- ¹² Xu, K.; von Cresce A. Interfacing electrolytes with electrodes in Li ion batteries. *J. Mater. Chem.* **2011**, *21*, 9849-9864.
- ¹³ de Guibert, A.; Palacin, M.R. Why do batteries fail? *Science* **2016**, *351*, 1253292.
- ¹⁴ *Intercalation Chemistry* Whittingham, M.S.; Jacobson, A.J: Eds. Academic Press, London **1982** ISBN 9780323140409.
- ¹⁵ Beck, F.; Ruetschi, P. Rechargeable batteries with aqueous electrolytes. *Electrochim. Acta*, **2000**, *45*, 2467-2482.
- ¹⁶ Blomgren, G.E. The development and future of Lithium ion batteries. *J. Electrochem. Soc.* **2017**, *164*, A5019-A5025.
- ¹⁷ Pillot, C. The rechargeable battery market and main trends 2018-2020. Avicenne Energy. Presentation at the *International Battery Seminar and Exhibit*, 25th March **2019**, Fort Lauderdale US.
- ¹⁸ Larcher, D.; Tarascon, J.M. Towards greener and more sustainable batteries for electrical energy storage. *Nat. Chem.* **2015**, *7*, 19-29.
- ¹⁹ *Chemistry of Materials and Energy. Examples and Future of a Millennial Science*. Inaugural Lecture delivered on 23rd January **2014** by Prof. Jean-Marie Tarascon. Paris, Collège de France, **2017**. ISBN : 9782722604612.
- ²⁰ Winter, M.; Xu, K. Before Li ion batteries *Chem. Rev.* **2018**, *118*, 11433-11456.
- ²¹ Melot, B.C.; Tarascon, J.M. Design and Preparation of Materials for Advanced Electrochemical Storage. *Acc. Chem. Res.* **2013**, *46*, 1226-1238.
- ²² Palacin, M.R. Understanding ageing in Li-ion batteries: a chemical issue, *Chem. Soc. Rev.* **2018**, *47*, 4924-4933.
- ²³ Tarascon, J.M.; Armand, M. Issues and challenges facing rechargeable lithium batteries *Nature*, **2001**, *414*, 359-367.

-
- ²⁴ Meng, Y. S.; Arroyo-de Dompablo, M.E. First principles computational materials design for energy storage materials in lithium ion batteries. *Energy Environ. Sci.* **2009**, *2*, 589-609.
- ²⁵ Jain, A.; Ping-Ong, S.; Hautier, G.; Chen, W.; Davidson-Richards, W.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K.A. The Materials Project: A materials genome approach to accelerating materials innovation *APL Mater.* **2013**, *1*, 011002.
- ²⁶ Padhi, A.K.; Nanjundaswamy, K.S.; Masquelier, C.; Okada, S.; Goodenough, J.B. Effect of structure on the Fe³⁺/Fe²⁺ redox couple in iron phosphates. *J. Electrochem. Soc.* **1997**, *144*, 1609-1613.
- ²⁷ Smith, K.S.; Huyck, H.L.O. An overview of the abundance, relative mobility, bioavailability and human toxicity of metals. *Reviews in Economic Geology* **1999**, *6*, 29-70.
- ²⁸ Placke, T.; Heckmann, A.; Schmich, R.; Meister, P.; Beltrop, K.; Winter, M. Perspective on performance, cost, and technical challenges for practical dual-ion batteries. *Joule*, **2018**, *2*, 2528-2550.
- ²⁹ Canepa, P.; Gautam, G. S.; Hannah, D. C.; Malik, R.; Liu, M.; Gallagher, K. G.; Persson, K. A.; Ceder, G. Odyssey of Multivalent Cathode Materials: Open Questions and Future Challenges. *Chem. Rev.* **2017**, *117*, 4287-4341.
- ³⁰ Poizot, P.; Gaubicher, J.; Renault, S.; Dubois, L.; Liang, Y.; Yao, Y. Opportunities and Challenges for Organic Electrodes in Electrochemical Energy Storage *Chem. Rev.* **2020**, *120*, 6940.
- ³¹ Casas-Cabanas, M.; Rodriguez-Carvajal, J.; Canales-Vazquez, J.; Palacin, M.R. New insights on the microstructural characterization of nickel hydroxides and correlation with electrochemical properties. *J. Mater. Chem.* **2006**, *16*, 2925-2939.
- ³² Dugas, R.; Forero-Saboya, J.D.; Ponrouch, A. Methods and protocols for reliable electrochemical testing in post-Li batteries (Na, K, Mg, Ca). *Chem. Mater.* **2019**, *31*, 8613-8628.
- ³³ Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*, National Association of Corrosion Engineers. Houston, USA, **1966**. ISBN: 9780915567980.
- ³⁴ Armand, M. Intercalation Electrodes. *Materials for Advanced Batteries*. NATO Conference Series (VI Materials Science) Murphy D.W., Broadhead J., Steele B.C.H. eds., Springer, Boston. **1980**, *2*, 145-161 ISBN: 9781468438536.
- ³⁵ Lu, L.; Han, X.; Liu, J.; Hua, J.; Ouyang, M. A review on the key issues for lithium-ion battery management in electric vehicles. *J. Power Sources* **2013**, *226*, 272-288.
- ³⁶ Harks, P.; Mulder, F.M.; Notten, P.H.L. In situ methods for Li-ion battery research: A review of recent Developments. *J. Power Sources* **2015**, *288*, 92-105.
- ³⁷ Lin, F.; Liu, Y.J.; Yu, X.Q.; Cheng, L.; Singer, A.; Shpyrko, O.G.; Xing, H.L.L.; Tamura, N.; Tian, C.X.; Weng, T.C.; Yang, X.Q.; Meng, Y.S.; Nordlund, D.; Yang, W.L.; Doeff, M.M. Synchrotron X-ray Analytical Techniques for Studying Materials Electrochemistry in Rechargeable Batteries, *Chem. Rev.* **2017**, *117*, 13123-13186.
- ³⁸ Sharma, N.; Pang, W.K.; Guo, Z.P.; Peterson, V.K. In Situ Powder Diffraction Studies of Electrode Materials in Rechargeable Batteries, *ChemSusChem*, **2015**, *8*, 2826-2853.

-
- ³⁹ Pecher, O.; Carretero-Gonzalez, J.; Griffith, K.J.; Grey, C.P. Materials' methods: NMR in battery research. *Chem. Mater.* **2017**, *29*, 213-242.
- ⁴⁰ Wolf, M.; May, B.M.; Cabana, J. Visualization of electrochemical reactions in battery materials with X-ray microscopy and mapping. *Chem. Mater.* **2017**, *29*, 3347-3362.
- ⁴¹ Arroyo-de Dompablo, M.E.; Ponrouch, A.; Johansson, P.; Palacin, M.R. Achievements, Challenges, and Prospects of Calcium Batteries. *Chem. Rev.* **2020**, *120*, 6331-6357.
- ⁴² Ligneel, E.; Lestriez, B.; Guyomard, D. Relationships between processing, morphology and discharge capacity of the composite electrode. *J. Power Sources*, **2007**, *174*, 716-719.
- ⁴³ Rynne, O.; Dubarry, M.; Molson, C.; Lepage, D.; Prebe, A.; Ayme-Perrot, D.; Rochefort, D.; Dolle, M. Design of experiments for beginners – A quick start guide for application to electrode formulation. *Batteries* **2019**, *5*, 72.
- ⁴⁴ Long, B.R.; Rinaldo, S.G.; Gallagher, K.G.; Dees, D.W.; Trask, S.E.; Polzin, B.J.; Jansen, A.N.; Abraham, D.P.; Bloom, I.; Bareño, J.; Croy, J.R. Enabling high-energy, high-voltage lithium-ion cells: standardization of coin-cell assembly, electrochemical testing, and evaluation of full cells. *J. Electrochem. Soc.* **2016**, *163*, A2999-A3009.
- ⁴⁵ Murray, V.; Hall, D.S.; Dahn, J.R. A guide to full coin cell making for academic researchers. *J. Electrochem. Soc.* **2019**, *166*, A329-A333.
- ⁴⁶ Hagen, M.; Fanz, P.; Tubke, J. Cell energy density and electrolyte/sulfur ratio in Li-S cells. *J. Power Sources* **2014**, *264*, 30-34.
- ⁴⁷ Arora, P.; Zhang, Z. Battery Separators. *Chem. Rev.* **2004**, *104*, 4419-4462.
- ⁴⁸ Gogotsi, Y.; Simon, P. True performance metrics in electrochemical energy storage. *Science*, **2011**, *334*, 917-918.
- ⁴⁹ Dubarry, M.; Svoboda, V.; Hwu, R.; Liaw, B.Y. Incremental capacity analysis and close-to-equilibrium OCV measurements to quantify capacity fade in commercial rechargeable lithium batteries. *Electrochem. Solid State Lett.* **2006**, *10*, A454-A457.
- ⁵⁰ Dahn, H.M.; Smith, A.J.; Burns, J.C.; Stevens, D.A.; Dahn, J.R. User-friendly differential voltage analysis freeware for the analysis of degradation mechanisms in Li-ion batteries. *J. Electrochem. Soc.* **2012**, *159*, A1405-A1409.
- ⁵¹ Stevens, D.A.; Ying, R.Y.; Fathi, R.; Reimers, J.N.; Harlow, J.E.; Dahn, J.R. Using high precision coulometry measurements to compare the degradation mechanisms of NMC/LMO and NMC-only automotive scale pouch cells. *J. Electrochem. Soc.* **2014**, *161*, A1364-A1370.
- ⁵² Richard, M.N.; Dahn, J.R. Predicting electrical and thermal abuse behaviours of practical lithium-ion cells from accelerating rate calorimeter studies on small samples in electrolyte. *J. Power Sources*, **1999**, *79*, 135-142.
- ⁵³ Zheng, S.; Wang, Li.; Feng, X.; He, X. Probing the heat sources during thermal runaway process by thermal analysis of different battery chemistries. *J. Power Sources* **2018**, *378*, 527-536.
- ⁵⁴ Brodd, Ralph. 2005 "Factors affecting US production decisions: why are there no volume lithium-ion battery manufacturers in the United States?". ATP Working Paper Series, Working paper 05-01.

<https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.353.8677&rep=rep1&type=pdf>