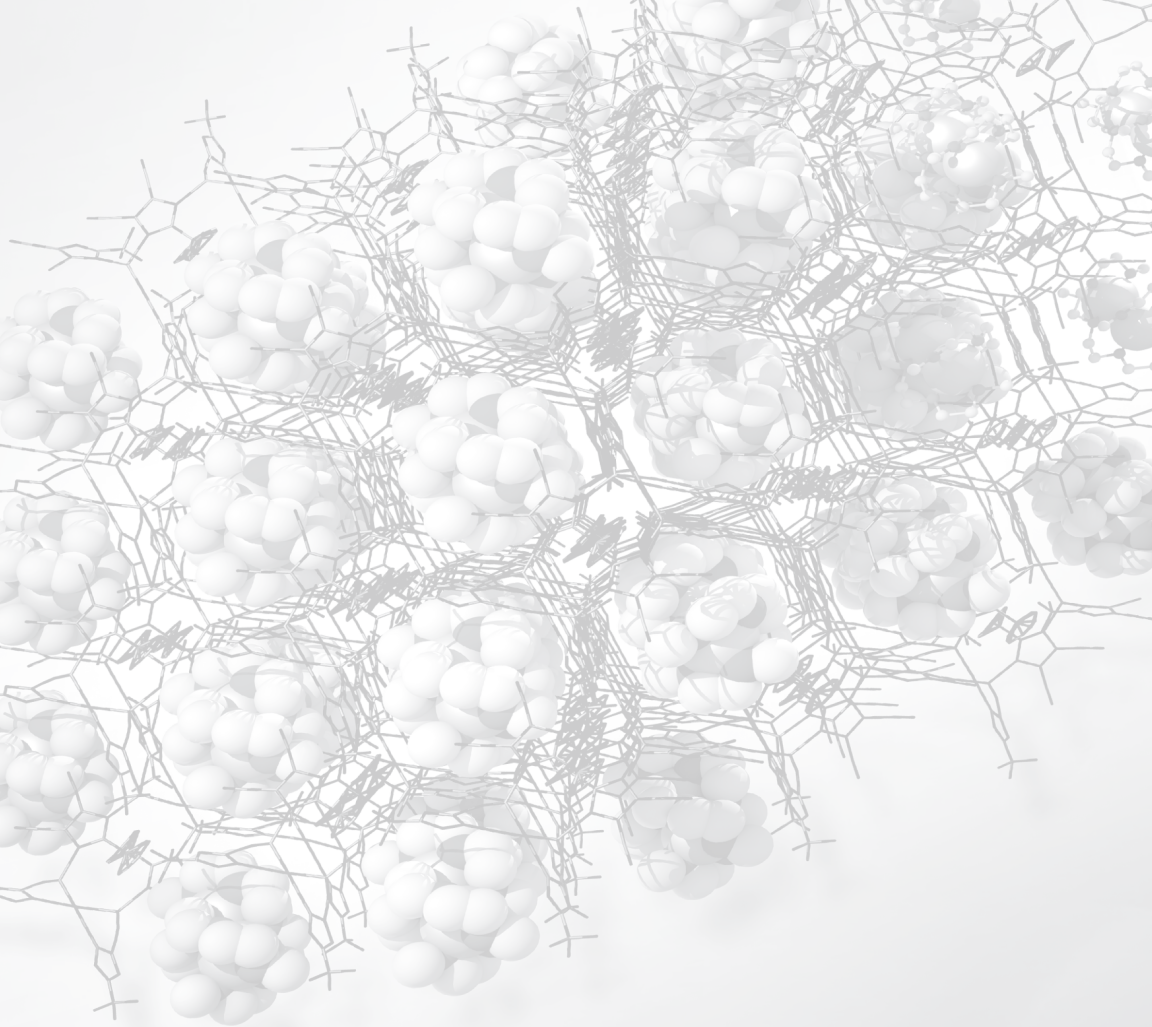


Designing Electrolytes for Lithium-Ion and Post-Lithium Batteries

edited by
Władysław Wieczorek | Janusz Płocharski





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Introduction: Challenges toward Designing Novel Electrolytes for Modern Lithium-Ion and Post-Lithium Batteries

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Every electrochemical source of electric current is composed of two electrodes and a layer of electrolyte in-between. Since the storage capacity—the crucial appropriable property of such a device—depends predominantly on the composition and design of the electrodes, most of the research and development efforts have been focused on them and many review publications have been dedicated to this subject [1]. Considerably less attention has been paid to the electrolyte, the third basic component of a battery. This review attempts to fill this gap and give more information on the role of electrolytes in modern batteries, limitations of lithium-ion batteries resulting from nonoptimal properties of commercial electrolytes, and the scientific and engineering challenges related to novel electrolytes for improved lithium-ion as well as future post-lithium batteries.

An effective electrolyte must fulfill a series of requirements. The most basic ones are as follows:

- **Sufficient chemical and electrochemical stability:** Electrolyte solutions must be stable at highly oxidative potentials at a battery cathode and at highly reductive potentials at a battery anode during charging. Generally speaking, stronger bonds connecting the atoms result in higher stability of

molecules present in an electrolyte. In the case of electrochemical stability, it can be quantified as the highest occupied molecular orbital and the lowest unoccupied molecular orbital levels, which can be calculated for a given structure and observed experimentally as oxidation and reduction potentials, respectively. In practical cases, however, electrolyte stability is of a kinetic character since there are simply no polar solvents of sufficient thermodynamic robustness. Predictions of possible reactions leading to electrolyte degradation should also consider the presence of highly reactive electrolyte additives improving the durability and transport properties of interphase layers. These considerations should involve a particular environment in which the electrolyte components are designed to operate and their interactions with electrode materials at very low and/or very high electrical potentials. Another factor is that the electrode materials often have catalytic properties—graphite, carbon black, compounds of cobalt, manganese, nickel, and iron are known catalysts for organic reactions. Effects of this catalytic activity are more clearly visible in systems working at elevated temperatures. On top of that, electrolytes must not react with other components of a battery, like current collectors and casing, or these reactions would be hindered due to passivation processes. It is also highly recommended that electrolytes not react with compounds typically present in the environment, like oxygen and water.

- **High ionic conductivity:** Electrolytes should efficiently support the transport of ions migrating between electrodes in consecutive cycles of charging and discharging. Therefore, a high ionic conductivity is required within the whole range of operating temperatures. This is particularly important for systems designed for high current applications and short charging times. Ionic conductivity of electrolyte solutions depends obviously on the molecular structures of solvents and salts. To find optimal compositions and concentrations, viscosity measurements could be helpful since viscosity is inversely related to molar conductivity in many systems. Both parameters—viscosity and conductivity—are influenced

by the size and shape of an anion (type of cation is fixed in a given battery system). In fact, only the transport of active ions—lithium cations in the case of lithium-ion batteries—contributes to electricity generating processes. The dissociation of an electrolyte salt into simple cations as well as unfavorable neutral ionic pairs and higher charged agglomerates depends predominantly on the dissociation energy of the salt and its concentration. It is then recommended to measure a cation's transference number and its dependence on the salt concentration and temperature. So, even slightly lower total conductivity can be accepted if the related transference number is closer to unity. To calculate the value of ionic conductivity that actually yields energy over the continued discharge of the cell, one needs to multiply the cation transference number by the total ionic conductivity ($\sigma_{\text{Li}^+} = \sigma T_{\text{Li}^+}$).

- Fulfilling the demands of the economy:** The commercial success of a particular battery design can be achieved only when the full cost of all components is economically justified. The typical material cost of the electrolyte in a battery does not exceed 10% of the total cost of all its active and inactive components [2]. In addition, the material costs of the necessary components are only a small part of all the expenses of a ready-to-use battery pack, which must also include investment and operation costs of a production plant, marketing, cost of capital, etc. This is a clear reason for the observable inertia of the industrial companies reluctant to introduce new components if they offer only slightly improved properties in comparison to the existing solutions. It is worth mentioning here, as we write about electrolytes, that notable costs are related to electrolyte handling, for example, a controlled/protective atmosphere for storage, desiccation processes, and cell assembly.
- Acceptable operational and environmental safety:** A battery must obviously be safe during its whole life and even in emergency situations. In particular, a battery should not catch fire, explode, or release toxic or corrosive gases even when it is damaged, unsealed, overheated, or improperly used. This is a

really tough requirement since a charged battery stores a lot of chemical energy and a typical electrolyte is made of flammable organic solvents containing compounds that generate toxic fumes. It is also critical to know what gaseous decomposition products can be released upon solid-electrolyte interphase (SEI) formation, thermal decomposition, and long-term exposure to high temperatures.

A battery should also be safe for the environment when discarded or recycled. The electrolytes in present use hardly fulfill this requirement. This kind of toxicity is mostly connected to fluorine, phosphorous, or arsenic content in electrolyte salts as well as in their thermal, chemical, or electrochemical decomposition products. Biological compatibility or ease of migration through the skin and/or cell membrane, as well as its carcinogenicity and/or mutagenicity, is also a potential risk factor if the salt or its decomposition products are toxic.

A short review of all the above requirements leads to the conclusion that there can be nothing like an ideal electrolyte. Instead we will rather search for a compromise to prepare “the least imperfect” electrolyte offering an acceptable combination of advantages and drawbacks.

- **Electrolytes in present use:** Today, almost all commercial lithium-ion batteries use the same electrolyte. This is 1.2 M solution of lithium hexafluorophosphate (LiFP_6) in a mixture of ethylene carbonate and ethyl methyl carbonate. Typically, some additives, like vinylene carbonate (VC), are used in order to improve the formation of stable and ionically conductive passive layers on negative electrodes (the so-called SEI). This electrolyte has a conductivity slightly exceeding 10 mS/cm at room temperature; electrochemical stability of >4.8 V versus that of the Li/Li^+ redox pair, which is sufficient for the presently used cathodes based on $\text{Li}_{1-x}\text{CoO}_2$; and does not create problems with other components of a battery system; detrimental corrosion of aluminum connectors is observed when some other electrolyte salts are used. On the other hand, the electrolyte undergoes decomposition above 70°C and is

very sensitive to traces of water—hydrolysis reactions take place, resulting in the emission of harmful hydrogen fluoride.

Challenges

A comparison of the above requirements with the properties of electrolytes in use clearly indicates the fields of necessary development. The expected improvements are often real challenges and should be preceded by extensive fundamental research. In fact, the battery industry waits now for an effective replacement of the LiPF_6 salt. The new one should offer a comparable level of ionic conductivity and support passivation of typical current collectors. On top of that, the new compound should be chemically and thermally stable, which means inhibition of hydrolysis reactions and resistance against temperatures far above 100°C . The molecular weight of such a salt should be relatively low because high molar concentrations are typically required. In addition, the planned introduction of the so-called high-voltage cathodes operating at about 5 V versus Li/Li^+ requires electrolytes of enhanced endurance against oxidation. Then, an obvious need of the market is the long operation time of energy storage systems, which means that batteries should withstand many thousands of cycles of charging and discharging during many years of service. This awaited high cyclability is strongly related to the stability and properties of the passive layers that form on electrodes (on anodes in most cases) during controlled reduction (or oxidation in a few cases) of electrolyte components. In this situation VC and other commonly used additives are not sufficient anymore and a systematic search for newer compounds is recommended.

More difficult goals appear when new battery systems are considered. This applies to all-solid-state-batteries, being a battery version of the Holy Grail, because the fulfillment of various conflicting needs, like high conductivity, good mechanical properties, and electrochemical stability, is extremely challenging. However, a vision of a storage battery with metallic lithium and a flexible thin film electrolyte is worth investing research efforts in.

Considering the problems of presently investigated multivalent batteries and batteries with conversion cathodes brings us to the

conclusion that electrolytes are crucial for these systems. The success of magnesium-, calcium-, or aluminum-based cells depends very much on the elaboration of electrochemically stable electrolytes supporting reversible deposition of these metals. Perhaps even a more demanding electrolyte is needed for the very promising lithium-sulfur cells since it should support the easy diffusion of lithium cations and block the migration of sulfur.

About the Book

As mentioned above, the challenges in front of researchers have different characters and, in particular, different time perspectives. Therefore, in order to organize the contents of this book in a logical way, it has been divided into two parts. Part I, “Novel Electrolytes for Lithium Batteries,” describes ideas that can be introduced into the industrial practice in the relatively near future since they do not require a very different technology—they can be treated as useful modifications of the existing lithium-ion batteries that result in a higher capacity or lifetime of not more than a few dozen percent. Part II, “Electrolytes for Post-Lithium-Ion Systems,” is addressed to riskier projects whose commercial implementation is still doubtful for many researchers but if successful could create a real breakthrough in the field of the electrochemical storage of electricity.

Thus, Chapter 1 describes strategies for designing electrolytes with new compositions capable of replacing the commonly used LiPF_6 keeping its high conductivity and good electrochemical stability but less prone to reactions with moisture and less harmful to the environment. It seems now that the developed electrolytes based on the newly designed and synthesized salts are close to commercial implementation. In addition, some concepts of electrolytes fulfilling their role at very high and very low temperatures are shown. These new ideas are complemented with a new approach presented in Chapter 2. It shows that crystallographic studies allow for a better understanding of the electrochemical properties of the proposed lithium salts comprising heterocyclic anions with electron-withdrawing groups. It turns out that crystalline structures

of these salts form a perfect basis to reveal real aggregation modes in concentrated liquid electrolytes. There is no doubt that solid-state structural studies have now become a powerful tool supporting the search for better electrolytes.

Since the very beginning of the search for better batteries the concept of replacing liquid electrolytes with solid ones was present. This is because it offers a more compact design, easier assembly, higher safety, and, which is perhaps the most important, partial suppression of lithium dendrite growth, opening the possibility of the application of lithium metal anodes. The “only” problem seems to be the too-low conductivity of solid electrolytes. However, due to the recent progress in reaching conductivities of 1 mS/cm, all-solid-state cells are not an illusion any more. Various aspects of solid electrolytes for lithium batteries are discussed in Chapter 3, including newly introduced classes of solid electrolytes. In addition, some properties of composite polymer electrolytes with inorganic fillers are discussed. The chapter also contains a concise description of mechanisms of ionic transport in solid and polymer electrolytes. This is justified by the fact that the related transport phenomena in solid phase are considerably different from ionic conduction mechanisms in liquid electrolytes and as such they are less familiar to the battery research community.

Part II of the book, as already mentioned, focuses on concepts for the more or less remote future. It starts with Chapter 4 reporting the recent progress in the research on electrolytes for sodium and sodium-ion batteries. A great demand for all kinds of lithium batteries finding applications both in stationary and mobile systems can result in a lithium shortage and an increase in its price. A natural candidate to replace lithium is sodium, which offers lower energy density but which due to its unlimited and scattered resources can be successful in less demanding products. In particular, sodium batteries can be applied as stationary storage facilities necessary for renewable energy sources and prosumer systems. As already proved by many research groups, sodium batteries cannot be manufactured by simply copying the known concepts taken from lithium systems; new chemistry, including new electrolytes, is required.

Chapters 5 and 6 cover the problem of electrolytes for the current multivalent cation batteries. The concept of such cells

is attractive due to their potentially higher volumetric capacity in comparison to lithium; a reported reduced tendency toward dendrite growth, allowing the application of metallic anodes; and abundance of resources. Unfortunately, reversible electrodeposition of magnesium, aluminum, or calcium with low overpotential is a problem that up to now has not been solved in full. The existing concepts as well as suggestions for future research will be discussed.

Batteries that potentially offer the highest energy densities and could be a real turning point in the energy supply for electric vehicles are reversible metal-air cells. Chapter 7 reviews recent achievements in and future strategies for the prospective but research-demanding metal-air systems, with particular attention paid to electrolytes for them.

Another idea to build a high-capacity battery relies on replacing graphite anodes and oxide intercalation cathodes by metallic lithium and elemental sulfur. The problems related to lithium-sulfur batteries are described in Chapter 8, the last chapter. At the moment, the biggest challenges for researchers in this field are to improve the cyclability and available current densities of cells as well as to counteract the rapid decrease in the cell capacity. The main reason for the unsatisfactory performance of the existing systems results from the uncontrolled migration of sulfur within the applied electrolyte. Select concepts to solve this problem are included in the chapter.

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