

PART A

Fundamentals: Electrolytes in General

In this Part, we systematically summarize the fundamental knowledge about ideal electrolytes that consists of two major components: Ionics and Electrodictics. The former studies how ions and solvent molecules interact and move in the bulk electrolyte, and the latter deals with how the electrolyte interacts with an electrode. The electrolytes investigated here are assumed to be ideal, whereas non-ideal behaviors are discussed in Part C.

1 What Is an Electrolyte?

The word *electrolyte* was created by Faraday in his famous treatise of 1834,¹ when he was trying to explain why certain aqueous solutions can conduct electricity when placed between a pair of “electric poles” polarized by a *voltaic pile* (which was the very first battery, invented by Alessandro Volta in 1799). Since such conduction is accompanied in some cases by the generation of new species at the poles, such as oxygen, hydrogen, chlorine or metal deposition, many researchers before him, including Volta and Berzelius, had already inferred that some sort of decomposition occurred, in which the originally neutral solution is split by electric force into oppositely charged species. Faraday therefore coined a new word from ancient Greek etymology *ἠλεκτρολυτός*, where the prefix *ἠλεκτρο* (*ēlectro-*) indicates “electricity”, while *λυτός* (*lytos*) implies that it is “able to be taken apart”. In the same seminal article, he also introduced the terms *electrode* (the way for electricity), *cathode* (westward way) and *anode* (eastward way), based on an analog to the magnetism of the Earth that was induced by an imaginary current. Accordingly, the species that move towards the cathode and anode are a *cation* (westward going) and an *anion* (eastward going), respectively. The cation and anion share a generic name of *ion* (Greek “*ίόν*”, or “going”). Considering that at the time there was no molecular-level understanding about electrolytes, the electron was not discovered until some 60 years later (in 1897 by Thomson), and the structure of an atom was not proposed until nearly 80 years later (in 1911 by Rutherford), one is amazed at how prophetic the insight of Faraday was, because all of these terms are still in use

Electrolytes, Interfaces and Interphases: Fundamentals and Applications in Batteries

By Kang Xu

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today in electrochemistry and materials science after appropriate modifications!

Perhaps the most interesting and prescient statement that Faraday made was about the surface of the electrodes, which he considered as the “*most important place of action*”.¹ This incredible foresight precisely describes the importance of the electrode/electrolyte *interface* in enabling electrochemical reactions. In fact, it is such interfaces that differentiate electrochemistry from conventional chemistry. Such a two-dimensional interface becomes a three-dimensional *interphase* when the potential of the electrode goes beyond the stability limit of an electrolyte, which is usually the case in most of the advanced batteries such as lithium-ion batteries. Electrolytes and interphases are therefore two sides of the same coin.

However, Faraday was at least partially wrong in one aspect: he thought that ions generated from a neutral species were the result of an electrochemical decomposition. This belief is incorrect for most electrolyte solutes (salts, acids and bases).

A more accurate understanding of the chemical nature of liquid electrolytes came from breakthroughs made in studies on thermodynamics. When Pfeffer was investigating the osmotic pressure of aqueous solutions against neat water, he found that aqueous electrolytes (such as a solution of sodium chloride) induce a much higher pressure difference than non-electrolytes (such as an aqueous solution of sucrose).² Inspired by the rationale established by van't Hoff regarding how vapor pressure was generated, he correctly inferred that the pressure, like that in the gas phase, was also caused by the collision of tiny particles.³ In other words, a solution of sodium chloride has many more particles than a solution of sucrose at the same stoichiometric concentration. Given the fact the former conducts electricity and the latter does not, it became obvious that an electrolyte must have dissociated from the electrically neutral crystalline salt into a larger number of particles bearing opposite charges. These are the cations and anions that Faraday had predicted.

Arrhenius inherited such thinking, and conducted the first systematic study on electrolytes and proposed that ions are thus produced,⁴ but his bold hypothesis sounded too heretic at the time and was not warmly received by his doctoral advisers, which almost ruined his career. Fortunately, Ostwald and van't Hoff recognized the genius of Arrhenius's contribution. With their enthusiastic support, this generalized concept of an electrolyte *via* dissociation of neutral species was gradually accepted by the scientific community. In retrospect,

thanks to these pioneers (Ostwald, Pfeffer and Arrhenius), the quantities studied (osmotic pressure and conductivity) happened to be extremely sensitive to the addition of trace amounts of solutes (salt, acid or base), which allowed them to quantify these changes accurately in correlation with the solute concentration in the very dilute regime using 19th century techniques. Thus, the clever interpretations of the relation between a thermodynamic quantity (osmotic pressure) and an electrochemical quantity (conductivity) set the foundation of a new branch of science, the modern *Physical Chemistry*, and further on *Electrochemistry*.

From here on, we depart from the antiquity era of electrolytes, and enter the classical understanding of them.

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