

A Note on Conduction in Aqueous Electrolytes

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Abstract

Hittorf suggested the transference as fraction of current carried by each type of ion. In this note it appears that there is but one species that carries all the current through the electrolyte even when a membrane is used to separate the anode and cathode compartments. This carrier is produced at one electrode and consumed at the other. Such a finding explains why there is a disagreement between different methods to determine transference (transport) numbers.

Keywords: Energy; Kirchoffs Law; Electrodes; Conductors

Short Communication

The charge transfers at the solid/liquid interfaces represent either a source of energy or storage of energy. The two processes are antipolar and inseparable. The electrochemical systems, including the special cases of bioelectrochemical systems, are closed electrical circuits where energy is taken from the system or stored in the system and Kirchoffs Law applies to closed circuits, electrochemical as well as electrical. There is an anodic interface at which oxidation occurs where electrons cause a valence change followed by the electrons traveling through an electronic path and reaching the cathode where the interfacial process involves reduction. Finally, the species produced migrates through the solution (even when a membrane is present) to the cathode interface. Kirchoff requires the rate of oxidation/reduction be equal to the transport of charged ions through the solution and to the current in the external all be equal.

A membrane between electrodes does not have an effect upon the potential of the system, but can affect behavior of the system. As an example, the reserve type secondary silver oxide/zinc battery has a cellulosic membrane separating the electrodes. The activation by introduction of electrolyte enables the battery to be discharged immediately because the cellulosic membrane separator becomes conductive although the amounts of electrolyte in each compartment may not be optimized. Thus it is necessary to consider the transport of charge through the membrane as well as through the electrolyte.

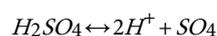
Ohms Law indisputably applies to electrochemical systems as well as to electrical systems, but it must be recognized that the cause and effect relationship between the potential and current in electrical systems, as well as the potential and ionic flux in electrochemical systems depends upon the nature of the conductors between the electrodes including the membranes.

While the above considerations appear obvious, there are important instances where they were not employed. One is the membrane potential as used by Goldman and as second instance is the transference number as defined by Hittorf. Goldman's assumption of a potential distribution in the electrolyte has been discussed previously.

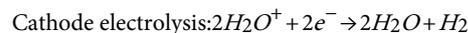
The concept of transference number is an object of this present discussion.

It is of interest to start the consideration of transference by investigation of the seminal work of Sir William Grove, the originator of what we now recognize as a hydrogen/oxygen fuel cell battery. His work started with the electrolysis of an aqueous H_2SO_4 solution at platinum metal electrodes. The H_2SO_4 increases the conductivity of the electrolyte so that electrolysis may proceed at reasonable rates in even though the SO_4 ion is not reducible under the conditions employed.

The ongoing processes in the electrolytic solution may be written as follows:



The mobile ionic current carrier is the hydrated proton which is capable of reaction at both electrodes, viz.:



Anode electrolysis: $3H_2O \rightarrow \frac{1}{2}O_2 + 2H_3O^+ + 2e^-$ When written this way only one species is involved at the electrodes, and it is the sole carrier of charge from one electrode to the other. Grove was able to series three of the electrolyzed cells to make a battery capable causing the electrolysis reaction shown above, thereby earning the title of "Father of the Fuel Cell" battery.

The finding of the flux of the hydrated hydrogen ion is consistent with the finding in other secondary battery systems such as [1] silver oxide/zinc, [2] nickel oxide/cadmium and [3] the common lead acid batteries. It appears that a general principle is that a single ionic species is responsible for the transport of charge in the solution phase of electrochemical systems. Hence the "Hittorf transference number" is unity. Thus, using methods to deduce a "transference number" measure something else, which probably explains the disagreements reported in the literature for transference numbers [4].

It is deduced that the process at the interfaces of solid/liquid cannot be ignored nor neglected electrochemical systems even those regarded as electro-kinetic process, i.e. electrophoresis or streaming potential or the others identified in the IUPAQC Technical Report. Thus, finding the ionic conduction in all electrochemical processes to be unity explains the difficulty in agreement between methods to determine the Hittorf transference number.

It is noted that the rate of reaction between hydrogen and oxygen can range from and explosion, when mixed together stoichiometrically and ignited as in a Parr Bomb, to a conflagration where a separator for bulk hydrogen is stripped away, as in the Hindenburg Zeppelin disaster (it took 36 seconds from first ignition to just burning of the cotton/linen covering at the tail) or to a controlled reaction as in a Grove type fuel cell. From the thermo chemical data with a Parr Bomb there is an expectation of 1.229 volts in an electrochemical cell, whereas a modern fuel cell using hydrogen and oxygen about 1.10 volts are measured. It might be speculated that the bomb has a reaction product of water and the fuel cell has a hydrated proton which is formed at one electrode and consumed at the other [5].

In an electrophoretic cell, the situation is complicated by adsorption of ions by micelles and the charge carried as required by Kirchoff's

Law, but the processes at the interface of solid/liquid are not considered. Yet it was reported that egg albumen behaves differently when pH of the medium is changed. Similar arguments arise in all bioelectrochemical systems including electrokinetic phenomenon. Identification of the charge transfer processes at the anode and cathode are necessary to interpretation of all parts including the ionic species flux as required by the conservative laws.

References

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