Effect of the mass transport limitations on the stability window of electrolytes for metal-ion batteries

CrossMark

Anastasia Dushina *, Jelena Stojadinović, Fabio La Mantia *

Semiconductor & Energy Conversion–Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum, Universitätsstr. 150, 44780 Bochum, Germany

ABSTRACT

Stationary battery systems have been proposed as plausible alternative for the storage of renewable energy sources in power grid. For this application aqueous electrolytes are preferred, which offer several important advantages compared to organic electrolytes i.e. non-flammability, cost effectiveness, as well as higher ionic conductivity, solubility and thermal capacity. This work was undertaken to investigate the influence of pH on the electrochemical stability window of aqueous electrolytes for metal-ion batteries. The pH was deliberately controlled in the range from pH 2 to 11. Electrochemical chronopotentiometry method served for the electrochemical stability window measurements. It has been observed that the pH critically influenced the measured dynamic stability window, which shows a maximum and almost pH independent value for pH ranging from 5 to 9. The presence of buffering ions and gelling agents strongly affects the dynamic stability window of the electrolyte through the transport overpotential.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Nowadays, the large-scale stationary battery energy storage systems have been under development for applications where the battery energy is stored for use when needed. The stationary batteries are applied for electrical load leveling, standby emergency power, telecommunications equipment and uninterruptable power supplies (UPS), as well as for the storage of regenerative unstable energy sources, such as wind and solar energy.

Battery electrolytes are usually based on liquid solvents with added salts, as source of reactive ions, and can be subdivided into aqueous and organic electrolytes. One of the most important characteristics of the electrolyte is its stability window, which has to be compatible with the operational potential range of the active materials for the positive and negative electrodes. The electrochemical stability range of the electrolytes depends on the electrolyte composition.

The organic solvent based electrolytes, composed mostly of the mixture of organic carbonates, were commercialized by Sony in 1990 and are now widely used for long cycling capability and high energy density devices [1], due to their large stability window

equal to circa 3.2 V. However, the conductivity of organic electrolytes, ranging from 10^{-2} to 10^{-3} S cm^{-1} at ambient temperature, is significantly lower than aqueous electrolytes' conductivity. Other shortcomings of organic electrolytes are related to their flammability and high cost. All these drawbacks limit the application of organic electrolytes in large-scale batteries, which should be cost-effective, provide high safety and a long cycling life [2].

Aqueous electrolytes offer several important advantages compared to organic solvents. They easily reach conductivity in the order of 0.1 S cm^{-1}. The high conductivity of aqueous solvent-based electrolytes results from the high dielectric constant of water, which favors stable ionic species and the high solvating power [2]. Moreover, opposite to organic electrolytes, water is non-flammable, cost-effective and possesses higher thermal capacity. Even though, thermodynamically, the electrochemical stability window of aqueous electrolytes is equal to 1.23 V, Wessels et al. [3] and Stojadinović et al. [4] observed that kinetic effects may expand the stability limit to 1.65–1.90 V. In the preliminary study performed by Stojadinović et al. [4], it was demonstrated the possibility to enlarge the electrochemical stability window of aqueous electrolytes by gellifying 2 M Li$_2$SO$_4$ with carboxymethyl cellulose (CMC) and agar. It has been shown that the gain in electrochemical stability of 280 mV was accompanied with a decrease in the ionic conductivity of 45%.

While transport numbers for ions and conductivity of aqueous solutions containing lithium and sodium salts are largely available

* Corresponding authors. Tel.: +492343229432; fax.: +492343214420
E-mail addresses: anastasia.dushina@rub.de (A. Dushina),
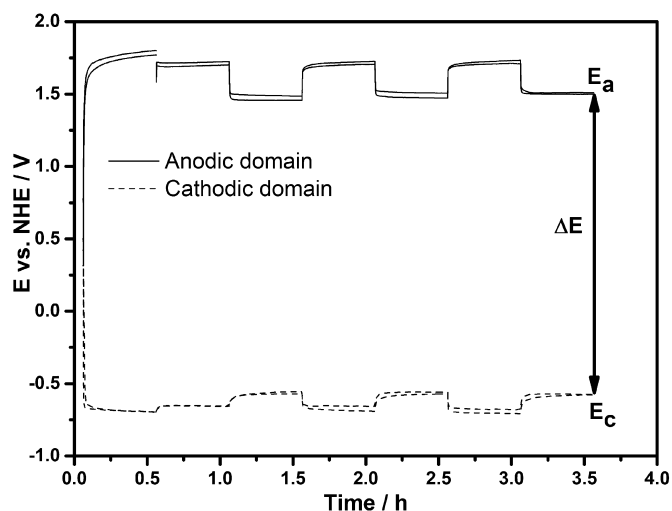fabio.lamantia@rub.de (F. La Mantia).

Fig. 1. Electrochemical stability window of 2 M Li$_2$SO$_4$ at pH = 7. The potentials are reported vs. NHE.

in literature, the value of the electrochemical stability window is not so frequently encountered. Therefore, in this work we investigated the complex relationship between the stability window of the electrolyte and its composition, with particular attention to the pH, nature of cations and anions, and presence of gelling agent (carboxymethyl cellulose), with the aim to identify the parameters that are relevant for the application of aqueous electrolytes in metal-ion batteries. In particular, aqueous electrolytes based on Li$_2$SO$_4$, Na$_2$SO$_4$, and phosphate buffer have been investigated.

2. Experimental

A hermetically closed three-electrode electrochemical cell of 10 ml volume was used for all experiments. The cell contained a working electrode made of Pt wire (1 mm diameter) embedded in Teflon, a platinum mesh counter electrode of a large surface area (12 mm diameter, 12 mm length) and Ag/AgCl/KCl(3 M) reference electrode [5]. Prior to each measurement working electrode surface was polished using diamond suspensions of 1 and 0.1 μm (Struers).

BioLogic VSP-300 potentiostat was used for the electrochemical characterization of the electrolytes. Electrochemical impedance
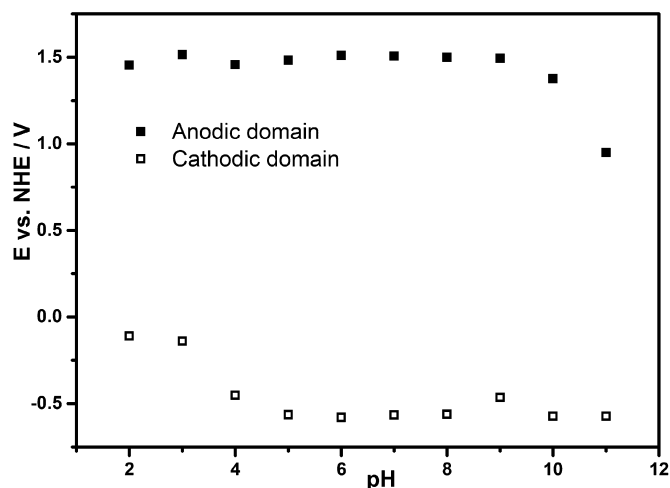

Fig. 2. The effect of the pH on the oxidation and reduction potential of 2 M Li$_2$SO$_4$. The potentials are reported vs. NHE.

spectra were recorded in a potentiostatic mode, at open circuit potential in order to determine the conductivity of the electrolytes. The frequency was swept logarithmically from 100 kHz to 100 mHz (10 points per decade) with a potential amplitude of 10 mV. For the investigation of the electrochemical stability window a chronopotentiometry method was used [3].The measurements in anodic domain started with applying the current density of +300 μA cm^{-2} for 30 min, followed by three cycles of current density alternations between +100 μA cm^{-2} and +10 μA cm^{-2}, each value applied for 30 min. The measurements in cathodic domain were performed in analogy with the anodic domain, but with applying negative current values. Cathodic and anodic domains were measured in separate experiments. The oxidation potential, E$_a$, and reduction potential, E$_c$, were defined as the ending potential values of the last cycle, obtained at +10 μA cm^{-2} and −10 μA cm^{-2}, respectively. The stability window ΔE was determined as a difference of E$_a$ and E$_c$ [3]. The following electrolytes were investigated in this study: 2 M Li$_2$SO$_4$ at pH 2–11 (Sigma Aldrich, purity >99%), 1.4 M Na$_2$SO$_4$ at pH 7 (Sigma Aldrich, purity >99%), 1.5 M KH$_2$PO$_4$ (Fisher Chemical, purity >99%)/1.5 M K$_2$HPO$_4$ (Fisher Chemical, purity >99%) at pH ≈ 7. In order to investigate the influence of pH in the range from 2 to 11, the pH of aqueous 2 M Li$_2$SO$_4$ was adjusted using either 0.5 M H$_2$SO$_4$ (J.T.Baker, 95–97%) or 0.5 M LiOH (Sigma Aldrich, purity >99%). Taking into account that the pH value of aqueous 1 M LiOH solution is equal to 11.8, it was not possible to adjust the pH of 2 M Li$_2$SO$_4$ beyond pH 11. Carboxymethyl cellulose (CMC, ASHLAND) at 10% by weight served as a gelling agent for gellification of 2 M Li$_2$SO$_4$ solutions at all pH values (pH 2–11), according to the gelling procedure described elsewhere [4].

Prior to each measurement, high purity argon gas was purged into the solution for 10 min in order to avoid interferences from the oxygen reduction reaction during the measurement of the cathodic potential limit. The argon supply was maintained above the surface of the electrolyte during the course of the experiments.

The value of the diffusion coefficients, Henry's constant, and dissociation constant of water were taken from reference [6].

3. Results and Discussion

Conductivities of investigated solutions, determined as explained in the previous work [1] show good reproducibility. For both liquid and gellified 2 M Li$_2$SO$_4$ the conductivity is independent of the pH and equals to 75 ± 3 mS cm^{-1} and 50 ± 2 mS cm^{-1}, respectively. The conductivity of the other solutions was equal to 85 ± 4 mS cm^{-1} for 1.4 M Na$_2$SO$_4$, 99 ± 4 mS cm^{-1} for 1.5 M KH$_2$PO$_4$/1.5 M K$_2$HPO$_4$.

The definition of the stability window for an electrolyte is somehow arbitrary, and depends on the technique used for its measurement (cyclic voltammetry, chronoamperometry, or chronopotentiometry), the material of the working electrode, and the oxidation and reduction potential data extrapolation method. The commonly used method is the cyclic voltammetry, performed with a relatively slow scan rate, typically 1 mV s^{-1}. Based on cyclic voltammograms, the oxidation and reduction potentials are obtained through a linear extrapolation of the i-V curve in the cathodic and anodic domain. Thus, the defined oxidation and reduction potentials cannot be related directly either to a kinetic or thermodynamic theory, due to the fact that the correlation between the linear extrapolation and the stability window is not clear. On the other side, the chronopotentiometric method facilitates the definition of cathodic, E$_c$, and anodic, E$_a$, potential limits as the value of the potential after a determined amount of time that a certain current density is applied to the working electrode. Of course, this is a dynamic definition of the stability window, which has to take into account the overvoltage of reaction. The choice of a proper current density corresponding to a