

Advanced electrochemical mass spectrometry

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Introduction

Electrochemical Mass Spectrometry (EMS) is known to be a useful tool for the *in situ* measurement of volatile species that are evolved at an electrode of an electrochemical cell [1], [2], [3]. Gases that evolve at the working electrode are drawn from the electrochemical cell into the mass spectrometer. The aim is to measure only gases evolved at the working electrode according to the applied potential without limitation by the used electrodes or electrolyte.

Experimental

Quadrupole mass spectrometer usually provides two measurement methods – an analog scan across a predefined atomic mass unit (amu) range and the multiple ion detection, where the intensity of previously selected masses can be measured.

Two different cell systems have been proposed in the literature for investigating gas evolution in Li-ion cells. The so called membrane cell [4] and the headspace cell type [5]. The membrane cell is based on a porous hydrophobic (“solvent-phobic”) membrane that works as a solvent barrier between the electrochemical cell and the vacuum system of the mass spectrometer. The active mass must be coated directly on a metalized membrane or coated on stainless steel grid and placed directly on the membrane. The disadvantage of this cell is that the membrane must not be wetted by the electrolyte. Unfortunately, many low-viscosity electrolytes and, in particular, complex electrolyte systems containing wetting agents and related additives cannot be investigated. The advantage of this cell type is the exclusive detection of gases which evolve at the working electrode.

The headspace cell type has no limitations according to the used electrolyte but has the disadvantage of not being able to distinguish between gases evolved at the anode or cathode. A solution could be to determine the gases evolving at the counter electrode separately and to blind out the resulting masses in the mass spectrum. The second possibility is the usage of a counter electrode (e.g. $\text{Li}_4\text{Ti}_5\text{O}_{12}$) which works in a more moderate potential range than lithium or LiCoO_2 and can be expected not to decompose the electrolyte. Another approach is to separate the gas compartments above the electrodes and pump off the gases evolved on working and counter electrodes separately. Our contribution will present 6 different (examples given Fig. 1, 2, 3) cells for online EMS, their characterization and application in electrolyte decomposition reactions in Li-ion cells.

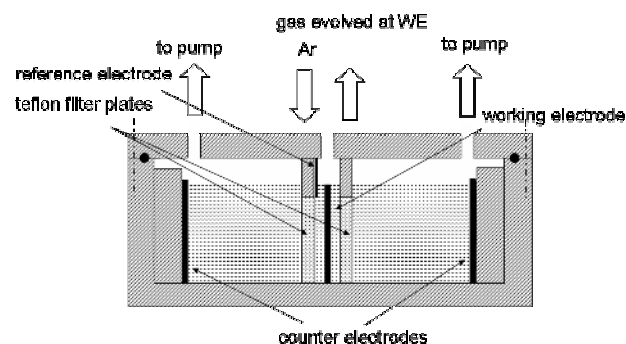


Fig. 1: Headspace EMS cell with separated gas rooms

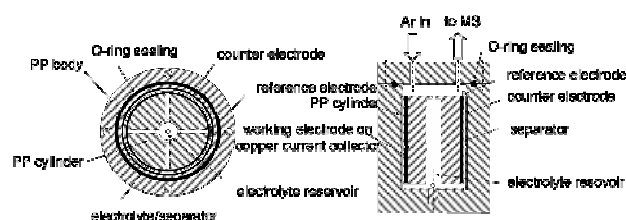


Fig. 2: Cylindric headspace EMS cell with optimized for high electrode surface

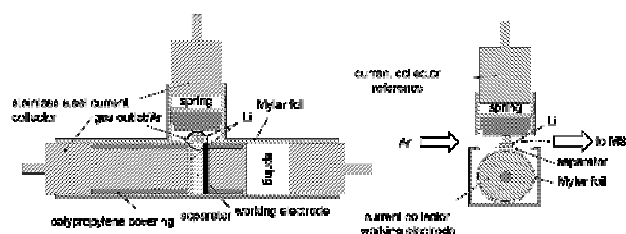


Fig. 3: Swagelok headspace EMS cell

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Support by the Austrian Science Funds through the special research program "Electroactive Materials" and by the "Herbert Quandt - Foundation" is gratefully acknowledged.