Volatile products of electrode reactions in inorganic electrolyte

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Abstract

The investigation technique differential electrochemical mass spectrometry (DEMS) combines cyclic voltammetry with mass spectrometry. DEMS measurements enables to detect on-line gaseous products formed by electrochemical reactions. A new, simplified experimental set-up is presented, which allows to expand this method to high concentrated electrolyte solutions. For inorganic electrolyte, elaborated for a rechargeable $Li/LiCoO_2$ battery system, the usually DEMS cell is improved as compact thin-layer flow cell. Chlorine evolution — substantial for overcharge protection in this battery system — is examined at Ni and Au electrodes.

Introduction

Differential electrochemical mass spectrometry (DEMS) is an on line technique using a hydrophobic, porous ETFE (copolymerisat of ethylene and polytetrafluoroethylene (PTFE)) membrane as substrate for porous metal layer [1]. The nonwetting membrane serves as a barrier between the liquid phase and the vacuum system of the mass spectrometer. This method has been applied successfully to aqueous solutions and widely-used organic solvents like propylene carbonate (PC) [2]. In this work, DEMS measurements has been started on the investigation of inorganic electrolyte, consisting essentially of $LiAlCl_4$ and SO_2, to support the development of a rechargeable $Li/LiCoO_2$ battery system [3, 4].

Experimental

The DEMS apparatus consists of a electrochemical cell and the mass spectrometer unit. A scheme of the simplified, compact vacuum system with only one turbomolecular and two membrane pumps is presented in Fig. 1, — details are explained in ref. 5.

The gaseous species passing the membrane flows into a fine vacuum (2×10^2 Pa from a membrane pump); a small amount streams via pressure transformer with tunable blend into the high vacuum (10^{-3} Pa operation pressure), generated by a turbomolecular pump. The simplified, modular vacuum equipment, constructed with commercially available components, is distinguished by a high function security; leakage in the membrane leads only to a small pressure increase in the high vacuum of the mass spectrometer.

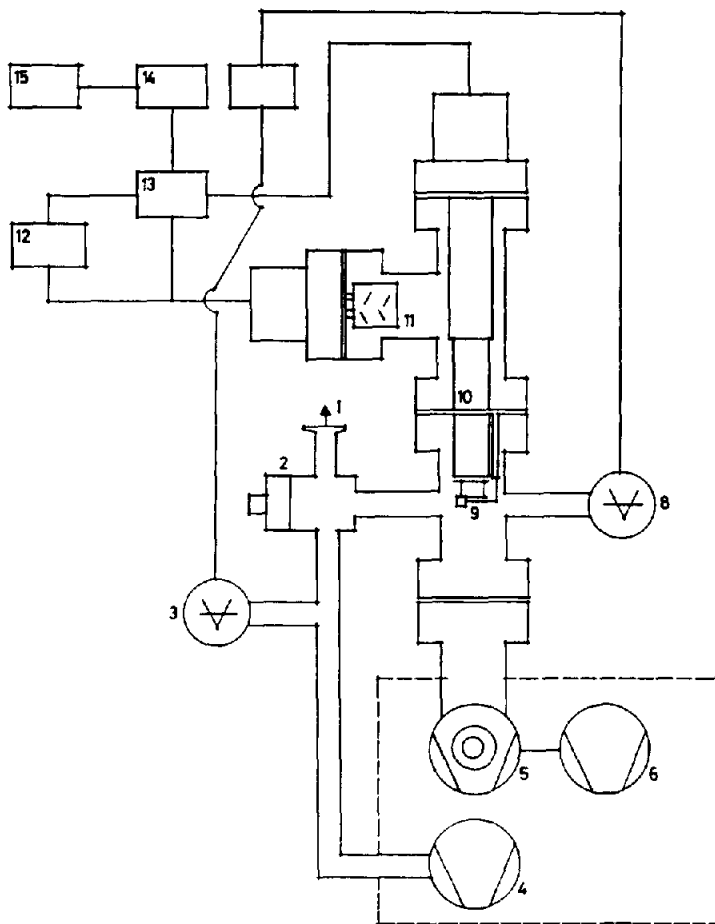
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Fig. 1. Experimental setup of the DEMS apparatus; the electrochemical part is not exhibited; 1: junction to cell; 2: pressure transformer; 3: Pirani-tube; 4: membrane pump; 5: turbomolecular pump; 6: membrane pump; 7: pump unit; 8: Penning-tube; 9: ion source; 10: quadrupole mass filter; 11: sem; 12: electrometer amplifier; 13: quadrupole/sem control; 14: ms-controller, and 15: recorder.

As gas-inlet system serves a porous, nonwetting ETFE (Tefzel®) membrane. Most of the plating experiments were done with a microporous Scimat® membrane (200/60), often used as separator in Li cells. The membrane was deposited with a gold layer (~300 Å) with high electronic conductivity, resistance about 1.7 Ω/cm; usual DEMS electrode with PTFE membrane have values of 50 Ω/cm [2].

Various special three-electrode cells were used. The working electrode consists either of a nickel sheet or the described gold-layered membrane. Reference and counter electrodes consist of lithium on nickel net as substrate. First investigations were done with a three-electrode DEMS cell, simular to usual cells [2], but hermetically closed. The gastightness of the cell ensures that no other gases (e.g., from atmosphere like N_2, O_2, H_2O) penetrate into the electrolyte. In this setup the membrane pores were sealed after a short time by crystallized electrolyte.

This problem could be detached with a thin-layer flow cell with permanent flowing solution [6]. The compartments for working and counter electrode are separated by a glass frit. The electrolyte is pumped continuously along the electrode by a PTFE piston pump. The solution containing the electrochemically-generated species flows to a secondary connected cell providing the membrane gas-inlet system. The time constant for detection depends in the main on the volume of the connecting parts respectively thin-layer cells and on the flow rate.

Better performance is achieved by the combination of the two parts in one compact thin-layer DEMS cell (Fig. 2). Consequently, the time constant for the detection of electrochemically-generated products, essentially dued to the diffusion in the solution from the electrode to the phase boundary, is typically smaller than 0.5 s. The corresponding rise time of the mass intensity is short enough to allow a correlation to the faradaic current at various electrode potential, the feature of the method DEMS.

Results and discussion

As described above first investigations of continuously-flowing electrolyte were done with the two-cell arrangement. The separate electrochemical flow cell allows to use any metal sheet as working electrode.

To determine all gaseous and volatile species in the electrolyte, mass spectra up to $m/z = 200$ were recorded. The spectrum in Fig. 3 verifies the gas permeation through the membrane, no more sealing by crystallized electrolyte occurred. Potential jump experiments with nickel working electrode were carried out. Figure 4 shows the chlorine evolution ($m/z = 35$) at a potential of 5 V versus Li. Meanwhile no formation of SO_2Cl_2 could be detected.

At present the increased time constant (about 50 s) depending mainly on the liquid volume between electrode and gas inlet enables not yet correlated mass detection to electrochemical conversion. Therefore, first mass spectrometric cycling voltammograms (MSCV) were recorded with the compact thin-layer flow cell. Figure 5 shows anodic chlorine evolution as a function of the potential. At 4 V versus Li the signal $m/z = 35$ increases simultaneously to the electrochemical current. The difference of chlorine evolution and electrochemical current between positive and negative sweep direction
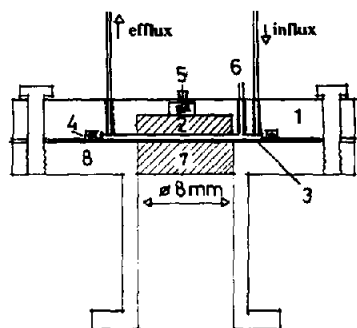

Fig. 2. Electrochemical thin-layer flow cell with membrane gas-inlet system; 1: Kel-F cell; 2: glass frit; 3: working electrode; 4: Viton-ring; 5: counter electrode; 6: reference electrode; 7: steel frit, and 8: KF-junction.
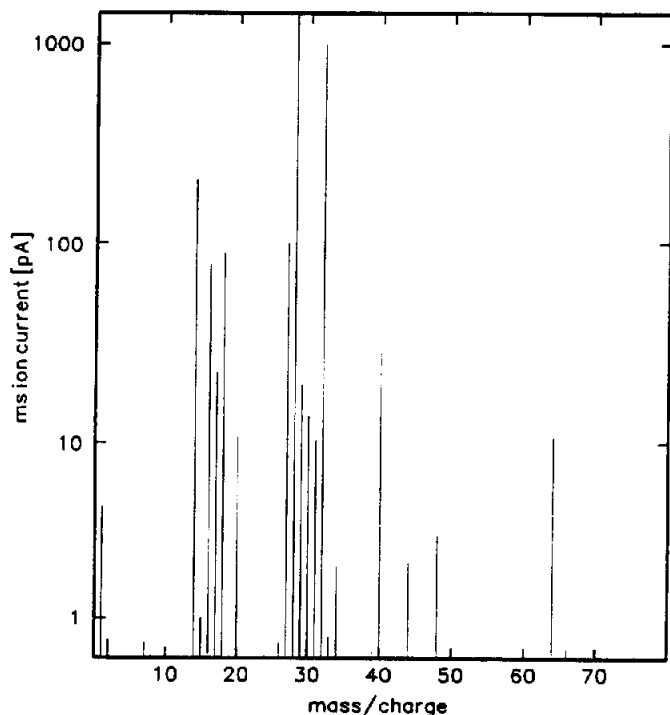
Fig. 3. Mass spectrum of LiAlCl₄ and SO₂, pumped through a membrane thin-layer flow cell.
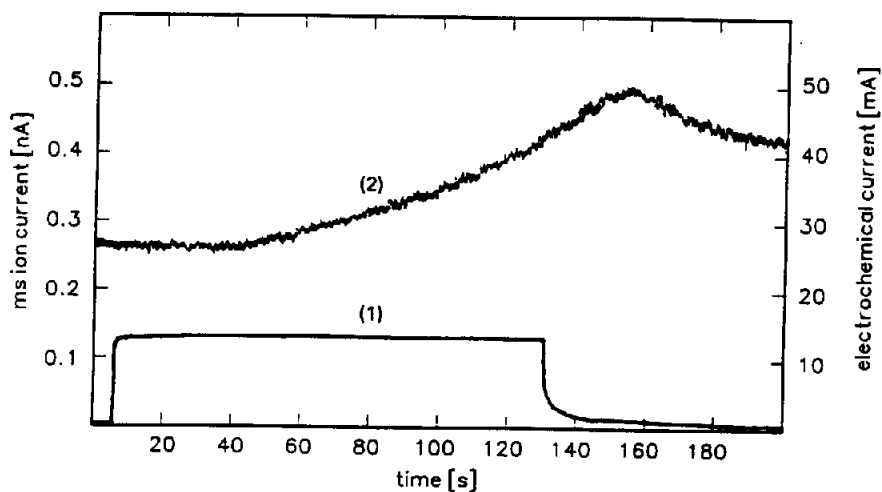

Fig. 4. Chlorine evolution during a potential jump experiment: the potential alternates between open circuit (3.5 V) and 5 V vs. lithium. Curve (1) shows the electrochemical current; curve (2) corresponds to the ms ion current of chlorine ($m/z = 35$).
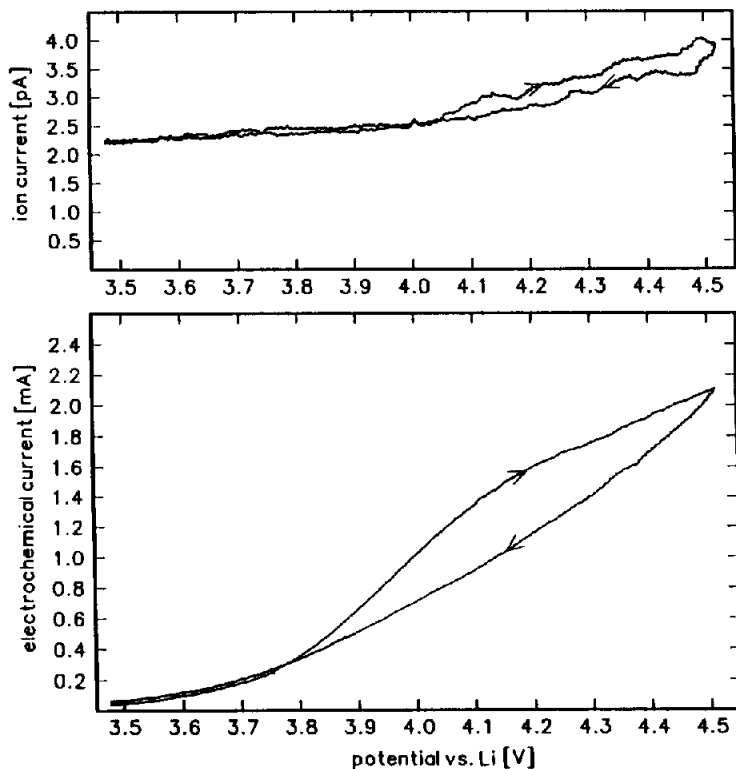
Fig. 5. Mass spectrometric cycling voltammogram of inorganic electrolyte: chlorine evolution.

seem to depend on impurities of the electrolyte solution. In further measurements we still have to investigate these effects.

The chlorine evolution corresponds to the overcharge mechanism of the rechargeable Li/LiCoO$_2$ battery system with LiAlCl$_4$ and SO$_2$ [7]. On overcharge, an AlCl$_4^-$ anion will be oxidized at the anode and forms AlCl$_3$ and Cl$_2$. Simultaneously Li is deposited at the counter electrode. The high solubility of AlCl$_3$ and Cl$_2$ in the electrolyte leads to the recombination of electrolyte salt at the negative electrode:

$$Cl_2 + 2AlCl_3 + 2Li \longrightarrow 2LiAlCl_4 \tag{1}$$

Conclusion

The application of DEMS is expanded on the investigation of solutions with high salt freight, here inorganic electrolyte LiAlCl$_4$ and SO$_2$.

The simplified, corrosion-resistant vacuum system needs only one turbomolecular and two membrane pumps and is constructed with commercially-available components. Thin-layer flow DEMS cells with firstly tested Li-resistant ETFE membrane allow to examine electrochemical processes with different working electrodes. The Cl$_2$ evolution could be demonstrated at nickel as well as at gold electrodes.

Further work is concentrated to improve the cells concerning shorter time constants and higher sensitivity. Our aim is to identify the formation of gaseous species at the positive and negative electrode of the $Li/LiCoO_2$ battery system, which decreases the cycling efficiency.

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