

Anodic stability of propylene carbonate on manganese dioxide electrodes

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Abstract

The overcharge stability of an electrolyte/solvent system is a relevant aspect concerning rechargeable lithium systems. We have analysed the volatile/gaseous products from the decomposition of LiClO_4/PC and LiAsF_6/PC on heat-treated manganese dioxide and acetylene black electrodes with on-line mass spectroscopy (DEMS).

Introduction

Manganese dioxide belongs to the positive electrode materials suitable for application in rechargeable lithium batteries. Its non toxicity, low cost and a relative high cell potential about 3.2 V versus Li are advantages often difficult to match with other cathode materials. This is particularly the case for applications requiring a battery system with high capacity and energy density (where, in addition, high charge retention is necessary). Manganese dioxide high-power primary systems with organic electrolytes fulfill these conditions and are since short available in the market [1].

The MnO_2 system with organic electrolytes is also a reasonable candidate for a reversible electrode. The development of secondary Li systems, requires longer development phases than primary systems. Main issues are: (i) the cycleability of Li; (ii) the searching of reversible MnO_2 phases with structures standing the intercalation of Li ions at high discharge rates; (iii) the finding of compatible electrolytes with a wide electrochemical stability window, and (iv) safety.

Results on the anodic stability of propylene carbonate (PC) electrolytes on platinum were already obtained using on-line mass spectroscopy (on-line MS) and were published [2–4].

In the present work on-line MS was applied to study the electrolyte electro-oxidation on a rechargeable electrode: polytetrafluoroethylene (PTFE)-bound MnO_2 .

Experimental

Materials

Propylene carbonate (PC) (Burdick Jackson) dried over molecular sieves for weeks and Li salts, LiClO_4 and LiAsF_6 (Fluka p.a.), dried at 170 °C were used. The water content of the electrolytes was controlled with a Metrohm 684 KF coulometer. The measured initial water concentration of the electrolyte in the cell was below 40 ppm.

Its increase after one day measurement was about 15 ppm H_2O . The measurements were performed on PTFE-bound heat-treated MnO_2 and acetylene black electrodes in disk form with a geometrical area of 0.64 cm^2 .

On-line mass spectroscopy

On-line MS (DEMS) is a combination of voltammetry and mass spectroscopy which enables the identification of volatile oxidation and/or reduction products of an electrochemical process. The mass spectrometric ion currents of products are recorded simultaneously with current as a function of potential in linear sweep voltammetry experiments or as a function of time in transient measurements. The principle of the method was published previously [5] and a review including applications in different fields of electrochemistry with a detailed description of the experimental setup was given in ref. 6.

Figure 1 shows the electrochemical cell. The porous working electrode (a 9 mm diameter disk) was gently pressed on a porous PTFE membrane at the bottom of the cell. A thin platinum wire pressed on the surface of the PTFE-bound heat-treated MnO_2 or acetylene black electrodes provided the electrical contact. A thin foil of Li metal placed in a glass capillary close to the working electrode was used as the reference and a second Li foil served as the counter electrode. To avoid water contamination, the cell was assembled and filled with electrolyte in a dry argon atmosphere. This was achieved by means of a glove box (Fig. 2) specially constructed for carrying out MS measurements: the outlet of the cell in the box is connected to the inlet of a differentially-pumped MS system (Balzers QMG 112 quadrupole mass spectrometer). The control of the MS and the data acquisition were performed with

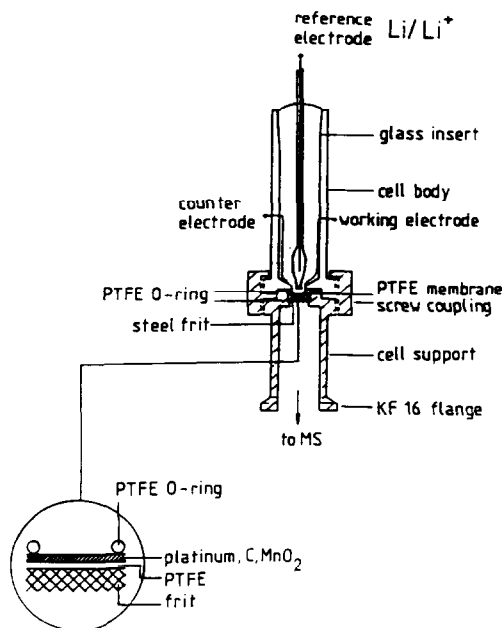


Fig. 1. Schematic diagram for the electrochemical cell (3 cm^3 electrolyte volume) used for on-line MS measurements on different porous electrodes (e.g., platinum, carbon and manganese dioxide).

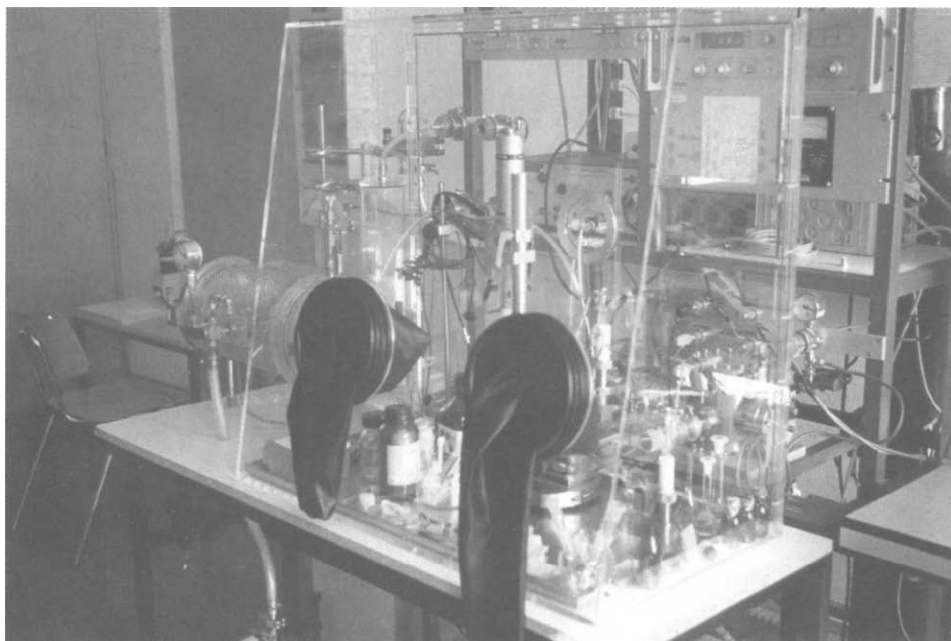


Fig. 2. Experimental setup: the cell is placed in a glove box.

a PC. The current and 10 different m/e mass signals were recorded as a function of time or potential in intervals of about 250 ms.

Results and discussion

Voltammetry of rechargeable electrodes

Linear sweep voltammograms (CVs) of rechargeable electrodes are useful for detecting oxidation/reduction processes as a function of applied potential. We have combined the usual CVs for Li_xMnO_2 with mass spectroscopic cyclic voltammograms (MSCVs) i.e., mass spectrometric ion currents of the ion fragments (m/e) of gaseous products are plotted against the applied potential. Some features of the MSCVs of MnO_2 electrodes are also observed on not rechargeable electrodes like porous platinum [2–4] or electrodes with very low capacity like acetylene black. During the discharge/charge of a rechargeable electrode, like heat-treated MnO_2 , new phases develop through Li intercalation/deintercalation. The structures of these reversible and irreversible reduced forms of MnO_2 (in general Li_xMnO_2) seem to depend on the (initial) MnO_2 phases and their identification is still a matter of controversy (see refs. 7 and 8).

An anodic linear sweep 2 ($\nu=5$ mV/min) of a PTFE-bound MnO_2 electrode (open-circuit voltage OCV = 3.58 V) in 1 M LiClO_4/PC is shown in Fig. 3. The electrode was previously: (i) potentiostatically discharged at 3.0 V, potentiodynamically recharged ($\nu=5$ mV/min) to 4.6 V, and (ii) potentiostatically discharged at 2.8 V and potentiodynamically recharged to 4.6 V again. The CV and the different MSCVs in Fig. 3 were recorded simultaneously with stepping the electrode from the OCV of the charged electrode, 3.78 V, down to 3.0 V. The current versus potential curve shows two small

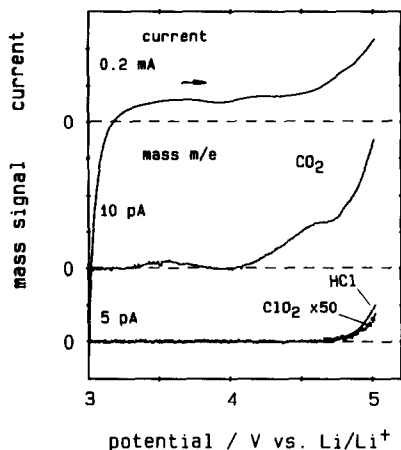


Fig. 3. MS positive scans (5 mV/min) for a 'charged' PTFE-bound MnO_2 electrode (0.64 cm^2) showing simultaneously measured current and ion current for $m/e=44$ (CO_2), 36 (HCl), and 67 (ClO_2), respectively as a function of potential.

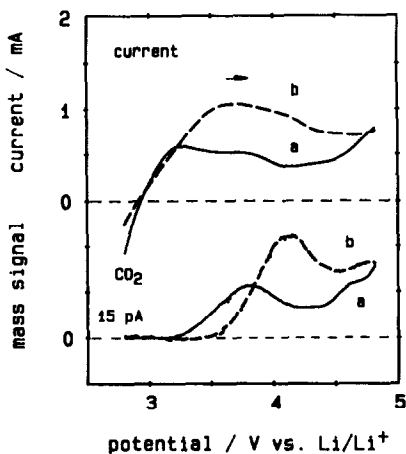


Fig. 4. MS positive scans (30 mV/min) for a PTFE-bound MnO_2 electrode (0.64 cm^2) showing a qualitative and quantitative different CO_2 formation for different states of charge; curve (a) less discharged, and curve (b) more discharged (see text). The current vs. potential curves are shown above and the corresponding ion currents for $m/e=44$ (CO_2) vs. potential are shown below.

maxima at 3.65 and 4.2 V, respectively. As a counterpart to CO_2 ($m/e=44$) ion current versus potential exhibits also two maxima (3.6 and 4.6 V). The steep increase of current and CO_2 mass signal starting at 4.0 V indicates a bulk oxidation of the electrolyte and the two weak current maxima are related to kinetic processes of the charging of the electrode.

Carbon dioxide formation at low potential

Curve (a) on the higher part of Fig. 4 shows the current as a function of potential for an anodic scan (30 mV/min) on a fresh MnO_2 electrode previously discharged potentiodynamically from the $\text{OCV}=3.57$ V. Curve (b) shows the anodic scan for the same electrode after two potentiodynamical charge and discharge cycles between 2.8 and 4.8 V. Before recording the curve (b) the electrode was potentiostatically discharged at 2.8 V for about 1 h. Curve (b) attained a higher value of current than curve (a) as being expected that a more discharged electrode would show higher capacity and the potentials for current maximum were shifted to higher potentials (about 400 mV).

Curves (a) and (b) on the lower part of Fig. 4 show the corresponding CO_2 ($m/e=44$) ion currents. The following features were observed: the CO_2 evolution started at 3.15 V in curve (a) and 3.4 V in curve (b). In both curves the maximum in current was attained at the value where CO_2 evolution started and the maxima for the CO_2 evolution correlated with a shoulder in the current.

The origin in this low potential CO_2 formation, observed when sweeping positively discharged MnO_2 electrodes, is not clear. It is not observed in similar experiments with the same setup on acetylene black electrodes (see Fig. 5). The fact that: (i) the observed CO_2 evolution depends of the state-of-charge of the electrodes (compare curve (b) with (a) in Fig. 4 and curves in Fig. 3), and (ii) no maxima of CO_2 ion

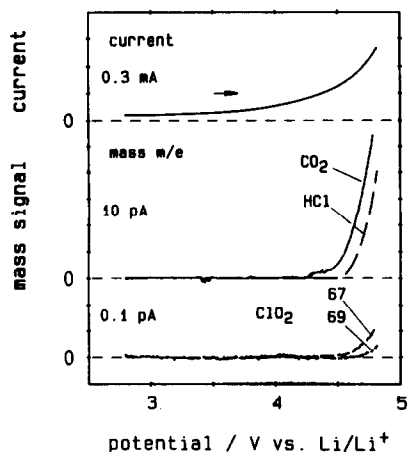


Fig. 5. MS positive scans (25 mV/min) for a PTFE-bound acetylene black electrode (0.64 cm²) showing the simultaneously measured current and ion current for $m/e = 44$ (CO₂), 36 (HCl), 67 and 69 (ClO₂), respectively as a function of potential.

current were observed in reverse scans (cathodic) in the investigated potential region, suggests the relation to the charging process (deintercalation of Li⁺ ions from the Li_xMnO₂ matrix).

A simple explanation for this effect would be a low potential oxidation of PC. This is known to occur at slow rate and open circuit in MnO₂ and systems like Li_xV₃O₈ (at 3.7 V, [9]), an effect being catalyzed by the presence of impurities (e.g., water) in the electrode or the electrolyte. The observed relationship between the amount of CO₂ evolution and the state-of-charge of the electrode (Fig. 4) could indicate a reaction of PC on some freshly-formed (either during the discharge or charge process) Li_xMnO₂ phase.

A different explanation could be the electro-oxidation of adsorbed reduced products of PC formed on MnO₂ during the discharge. This would account for the appearance of a shoulder on the curves (a) and (b) in Fig. 4. It is not known if different types of MnO₂ (different: Li_xMnO₂ phases; heat treatment; types of chemical or electrochemical MnO₂) would show this effect.

Anodic stability of ClO₄⁻ ions

The formation of chlorinated species on the decomposition of ClO₄⁻ ions was observed above 4.5 V. It was possible to identify: (i) ClO₂ with m/e fragments 67 (Fig. 3), 69 (from the ³⁷Cl isotope with 32% abundance) and 51 (³⁵ClO⁻ fragment), and (ii) HCl with m/e 36 (Fig. 3), 38 (³⁷Cl isotope), 35 and 37.

The formation of ClO₂ and HCl for 0.2 M LiClO₄/PC on platinum electrodes was reported in ref. 2. With some qualitative differences, this finding was corroborated by own measurements on platinum (unpublished data) and was also observed to occur above 4.5 V in 1 M LiClO₄/PC on acetylene black electrodes (Fig. 5). A comparison of relative mass signals shows that the ratio $m/e = 44$ (CO₂): $m/e = 36$ (HCl) for MnO₂ was about 5.2 times bigger than the corresponding ratio for acetylene black. Absolute quantitative values for gas formation on this kind of porous electrodes are unreliable and would require a calibration of the inlet and MS system.

The observed chlorinated species have their origin in the anodic decomposition of the ClO_4^- anions which concentrate at the surface of the electrodes at high anodic potentials as shown by *in situ* Fourier-transform infrared spectroscopy (FT-IR) measurements [4]. A possible reaction mechanism for the ClO_2 formation (cited in ref. 2) is:



In accordance with eqn. (1), oxygen evolution (not shown) similar to the ClO_2 curve was measured in the same experiment. Oxygen evolution was not observed in a similar experiment with 1 M LiAsF_6 ; concerning with this, a further investigation may be necessary as O_2 could have another origin. The instability of ClO_2 in existence of protons from the electro-oxidation of PC would produce HCl.

The decomposition of the ClO_4^- would occur only by accidental overcharging of the cell above 4.5 V: the upper limit for charging the electrode in PC should be set below 4.0 V, i.e., below the potential value where bulk electro-oxidation of PC sets on (Figs. 3 and 4).

Galvanostatic experiments

The on-line MS technique permits to investigate the time dependence of the gas evolution for the electro-oxidation products on a porous electrode at constant charge/discharge currents. Ion currents for 1 M LiAsF_6/PC on MnO_2 were recorded as a function of time simultaneously with the usual potential versus time (capacity) curves shown in Fig. 6. Combining the CO_2 ($m/e=44$) and potential versus time (Fig. 6) pairs, we obtained the CO_2 mass spectrometric ion current versus MnO_2 potential curves shown in Fig. 7: charging for 1 h at 0.31 and at 0.78 mA/cm^2 . The curves obtained are similar to the MS voltammograms on Figs. 3 and 4. The monotonous increase of the CO_2 above 3.9 V indicates the bulk oxidation of PC and the flat

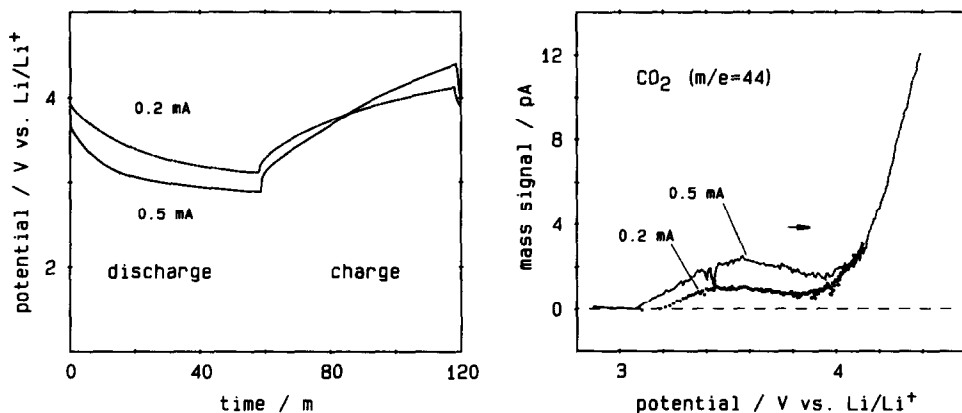


Fig. 6. Galvanostatic discharge/charge curves for a PTFE-bound MnO_2 electrode (0.64 cm^2): at 0.31 and 0.78 mA/cm^2 for 1 h, respectively.

Fig. 7. MS ion current for $m/e=44$ (CO_2) as a function of potential each obtained from the CO_2 ion current vs. time curves and their corresponding (simultaneously measured) potential vs. time curves shown in Fig. 6. The experiment shows an on-set potential of 3.9 V for the bulk electro-oxidation of PC, in agreement with the value from the potentiodynamic experiment shown in Fig. 3 for a different MnO_2 electrode.

maximum at about 3.5 V shows the low potential CO₂ formation mentioned on page 344. Galvanostatic measurements exhibit also a relationship between the CO₂ mass signal intensity and the charging current intensity in the low potential region (below 3.9 V).

It is worth mentioning that potential versus time curves (constant current curves like in Fig. 6) are not suitable for determining the anodic electrolyte stability for this system because they do not indicate the on-set of electrolyte decomposition as CVs do. The help of a mass spectrometer or a gas pressure sensor provides in this sense the complementary information about the processes occurring in the cell.

Summary

The anodic stability of electrolytes for Li batteries can be determined with the help of a cooperative analysis of linear sweep voltammetry and on-line mass spectroscopy (DEMS).

This method showed that PC with 1 M LiClO₄ and 1 M LiAsF₆ on PTFE-bound MnO₂ and acetylene black electrodes decomposes forming CO₂ above 4 V versus Li/Li⁺. Unexpectedly CO₂ evolution was also observed above 3.2 V on discharged MnO₂ electrodes with the amount of CO₂ depending on the state-of-charge of the electrode.

The anodic decomposition of ClO₄⁻ anions in 1 M LiClO₄/PC on MnO₂ and acetylene black electrodes starts above 4.4 V. Chlorinated ion mass fragments belonging to ClO₂ and HCl were detected.

Similar experiments on 1 M LiAsF₆ did not show the evolution of fluorinated species, i.e., no direct evidence for the anodic decomposition of AsF₆⁻ was found.

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