

Oxidative Electrolyte Solvent Degradation in Lithium-Ion Batteries

An In Situ Differential Electrochemical Mass Spectrometry Investigation

Roman Imhof and Petr Novák^z

Paul Scherrer Institute, Electrochemistry Section, CH-5232 Villigen PSI, Switzerland

Differential electrochemical mass spectrometry (DEMS) was used to study the electrochemical decomposition of organic carbonate electrolyte solutions at practical lithium metal oxide composite electrodes used in lithium-ion batteries. For propylene carbonate (PC), CO₂ evolution was detected at LiNiO₂, LiCoO₂, and LiMn₂O₄ composite electrodes. The starting point of gas evolution was 4.2 V vs. Li/Li⁺ at LiNiO₂, whereas at LiCoO₂ and LiMn₂O₄, CO₂ evolution was observed only above 4.8 V vs. Li/Li⁺. In addition, various other volatile electrolyte decomposition products of PC were detected when using LiCoO₂, LiMn₂O₄, and carbon black electrodes. In ethylene carbonate/dimethylcarbonate, CO₂ evolution was detected only at LiNiO₂ electrodes, again starting at about 4.2 V vs. Li/Li⁺.

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Safety aspects of lithium-ion batteries are widely discussed nowadays. However, the prediction and understanding of the behavior of lithium-ion batteries upon overcharge are still a major challenge because all commonly used lithium metal oxides become highly oxidizing when delithiated, and decomposition of the electrolyte salt and/or solvent can be initiated.

It is generally believed that one of the most important prerequisites for good cycling stability of Li-ion batteries is the formation of a complete and stable passivation film on the negative electrode during the initial charge/discharge cycles. The quality of this protective film strongly depends on the nature of the electrolyte solvents and also on the cycling conditions, and has been extensively investigated during the past few years.¹ In contrast, the existence of similar film formation processes at the positive electrode is still in question, although the oxidative electrochemical stability of a broad variety of organic electrolyte solvents has also been investigated in depth.² However, many of these studies were performed at model metal electrodes, and care has to be taken when applying such experimental results to real battery electrodes because the surfaces may exhibit different electrocatalytic activities.

Organic carbonate solvents are thought to release CO₂ upon oxidation.³ Such a behavior was observed for propylene carbonate (PC), which decomposes at platinum with the evolution of CO₂ at potentials as low as 2.1 V vs. Li/Li⁺. The decomposition potential and the amount of CO₂ evolved depend strongly on the cycle number and water content of the electrolyte solvent.^{4,5} An approach coming closer to real electrodes was recently chosen by Kanamura et al.⁶ They deposited thin layers of LiCoO₂ or LiMn₂O₄ onto current collectors and used subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) to detect potential-dependent changes at the electrode/electrolyte interface. However, due to experimental problems they could not determine whether or not CO₂ is evolved at these lithium metal oxide electrodes. Aurbach et al. detected Li₂CO₃ on the surfaces of LiNiO₂, LiCoO₂, and LiMn₂O₄, and attributed this finding to a reaction of the pristine oxides with CO₂ of the air.⁷ In addition, they suggested a mechanism based on the dissolution and migration of electrolyte decomposition products formed at the negative electrode, in order to account for the detection of lithium alkylcarbonates on the positive electrode after prolonged cycling.

We recently studied the reductive decomposition of PC and ethylene carbonate (EC)/dimethylcarbonate (DMC) based electrolytic solutions by differential electrochemical mass spectrometry (DEMS)^{8,9} in order to improve our understanding of the degradation paths of these solvents at real Li-ion battery electrodes. We demonstrated that this in situ technique gives valuable potential-dependent information about volatile decomposition products evolved during these complex electrode reactions. Here we report results of new

investigations concerning the oxidative decomposition of similar organic carbonate solvents at positive lithium metal oxide composite electrodes. For this study we used the three most common current positive electrode materials, namely, LiNiO₂, LiCoO₂, and LiMn₂O₄, all from commercial sources. Graphitized carbon black XC72 was added to improve the conductivity, while polyvinylidene fluoride (PVDF) was used as a binder because of its excellent chemical stability. These electrodes were investigated in two different electrolytic solutions, based on PC and a 1:1 mixture of EC/DMC.

Experimental

LiNiO₂ [Merck (two different batches) and Cyprus], LiCoO₂ (Cyprus), LiMn₂O₄ (BMTEC/BASF), carbon black XC72 (Cabot, graphitized at 2700°C for 2 h), EC (Merck, Selectipur), and DMC (Merck, Selectipur) were used as received. PC (Burdick and Jackson, distilled-in-glass grade) was dried over lithiated molecular sieves for several weeks before use. LiN(SO₂CF₃)₂ (from 3M) was dried under vacuum before use. Two different electrolytic solutions were used, based on PC and a 1:1 v/v mixture of EC/DMC, both with 1 M LiN(SO₂CF₃)₂ as the electrolytic salt. The electrolyte solutions were prepared and stored in an Ar-filled glove box. Their water content was determined by Karl-Fischer titration, and was always less than 20 ppm.

The DEMS setup and the preparation of the working electrodes were described in our recent papers.^{8,9} Working electrodes with two different carbon contents were prepared. The first contained 72% (wt %) of the lithium metal oxide, 18% of carbon black XC72, and 10% PVDF (Aldrich), the second contained 45% (wt %) of the oxide, 45% of carbon black XC72, and 10% PVDF. About 0.5 to 1 mg of these electrode material mixtures was deposited onto the electrode substrate [polytetrafluoroethylene (PTFE) membrane] having a geometrical area of about 1 cm². Metallic lithium was used as the counter and reference electrode. The measurements were carried out potentiodynamically by cycling the working electrode between the open-circuit potential (about 3 V vs. Li/Li⁺) and 5.5 V vs. Li/Li⁺ with scan rates of 0.1, 0.2, or 0.4 mV/s, respectively. The current and the mass signals were recorded as functions of potential and displayed as cyclic voltammograms (CV) and mass spectrometric cyclic voltammograms (MSCV), respectively.

The ohmic resistance of the electrochemical cell was evaluated from the impedance spectra measured with a Solartron 1250 frequency-response analyzer (Schlumberger). The specific surface area of the oxide electrode samples was measured by the Brunauer, Emmett, and Teller (BET) method with an ASAP 2000 (Micromeritics) instrument using nitrogen.

Results and Discussion

We applied DEMS to different lithium metal oxide electrode materials in order to obtain information about volatile electrolyte de-

^z E-mail: Petr.Novak@psi.ch

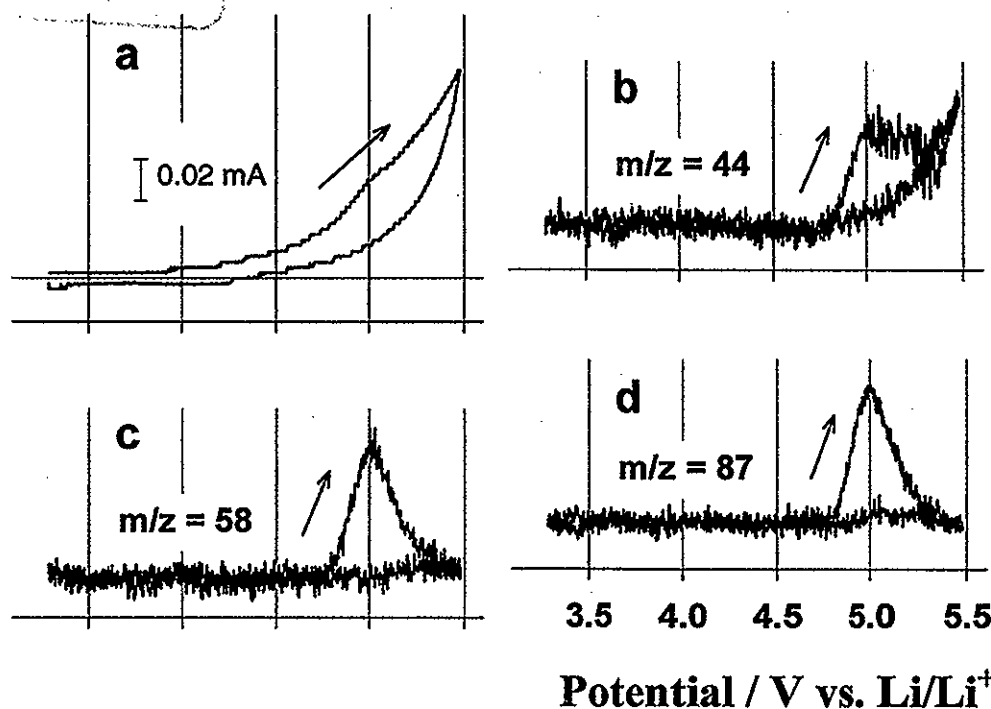


Figure 1. CV (a) and MSCVs of masses $m/z = 44$ (b), 58 (c), and 87 (d), respectively, representing decomposition products of PC generated at carbon black in PC/1 M $\text{LiN}(\text{SO}_2\text{CF}_3)_2$. Scan rate = 0.2 mV/s.

composition products upon overcharge to 5.5 V vs. Li/Li^+ during the first cycle. It is known that the BET specific surface area of the electrode materials is one of the key factors influencing the extent of the electrochemical oxidation of the electrolyte solvent.¹⁰ BET areas in the range of about 1 to 5 m^2/g were measured for all lithium metal oxides used in this study. In contrast, the BET area of the carbon black used is about 75 m^2/g . The surface of the composite electrode hence consists predominantly of carbon black. It is therefore necessary first to study the electrochemical behavior of this conductive filler. Figure 1 shows the cyclic voltammogram and MSCVs of a carbon black powder electrode with 10% PVDF in PC/1 M $\text{LiN}(\text{SO}_2\text{CF}_3)_2$.

In accordance with Arakawa and Yamaki, who studied the oxidative decomposition of PC at graphite,¹¹ we detect mass signals $m/z = 44$, 58, and 87, all starting at about 4.8 V vs. Li/Li^+ . Arakawa and Yamaki interpreted the three mass signals in terms of the formation of carbon dioxide, propanal, and 2-ethyl-4-methyl-dioxalane, respectively.

Figure 2 shows the results of three DEMS measurements made at LiNiO_2 (Merck) electrodes (containing 18% of carbon black) in the PC-based electrolyte at different scan rates. The cyclic voltammograms for each scan rate (a) and the corresponding mass signals $m/z = 44$ (b-d), representing carbon dioxide, are shown.

Obviously, CO_2 is evolved at LiNiO_2 electrodes. The starting point of CO_2 evolution (indicated by vertical arrows in Fig. 2) correlates well with the last current peak in the cyclic voltammograms.¹² It is well known that LiNiO_2 undergoes several phase transitions upon complete delithiation.¹³ We can therefore conclude that electrolytic decomposition processes are taking place simultaneously with these phase-transition processes in LiNiO_2 , which should therefore not be discussed separately. Similar results were found for LiNiO_2 composite electrodes prepared with LiNiO_2 powders of a different batch (Merck) and from a different supplier (Cyprus).

Furthermore, the starting point of CO_2 evolution shifts in parallel with the oxidative current peaks in the cyclic voltammograms when the scan rate is altered. This shift as well as the shape of the cyclic voltammograms suggest the presence of a substantial ohmic (IR) drop in our experimental setup. The reason for this IR drop resides in the fact that the working electrode is coated directly onto the non-conducting PTFE membrane, which implies a lateral current path along the electrode. The wetted, electrochemically active area of the

working electrode is limited by an O-ring (radius 5.8 mm), and the current is collected outside the O-ring with aluminum foil (Fig. 3). The distance from the center of the electrochemical cell to the edge of the aluminum foil is 8 mm. The aluminum foil is not in contact with the electrolytic solution.

The ohmic resistance of the electrochemical cell as measured by impedance spectroscopy has values in the range of about 1.5 $\text{k}\Omega$ for the PC-based electrolytic solution and electrodes containing 18% carbon black. Measuring the cell resistance as a function of distance between the counter and working electrode (and neglecting that the current density is not equally distributed over the electrode), one can obtain a rough estimate of the ohmic resistance of the electrolyte. In addition, extrapolating the resistance values to zero distance between the two electrodes yields values for the electrode resistance in the range of 350 to 450 Ω at room temperature (for a typical setup with 1 cm electrode distance). It is therefore possible to correct the cyclic voltammograms and the MSCVs mathematically for the IR drop contribution of the electrolytic solution (right side of Fig. 2) and to show that the starting point of CO_2 evolution is nearly independent of the scan rate. The poor resolution of the different oxidative current peaks in the cyclic voltammograms is due to the remaining lateral resistance distribution of the electrodes.

The starting potential of gas evolution is a crucial number when discussing decomposition reactions of electrolytic solutions; therefore, the IR drop should be minimized. Due to the relatively modest conductivity of lithium metal oxides, the measurements strongly depend on the amount of carbon black added to the electrodes. Increasing the amount of carbon black from 18 to 45% reduces the ohmic resistance of the electrochemical cell to about half of its value. Figure 4 shows an uncorrected comparison between two LiNiO_2 electrodes, one with 18% carbon black, the other with 45%, at a scan rate of 0.4 mV/s. It clearly shows the beneficial influence of the higher carbon black content on our measurements. The maxima of the oxidative current peaks in the cyclic voltammograms representing the extraction of lithium ions from the metal oxide shift several hundred millivolts to more negative potentials. In addition, the starting potential of CO_2 gas evolution is about 4.2 V vs. Li/Li^+ for the electrode with the higher carbon black content.

Be aware that, relative to the IR-drop-corrected measurements at LiNiO_2 (Fig. 2 right side) and also relative to the measurement of the

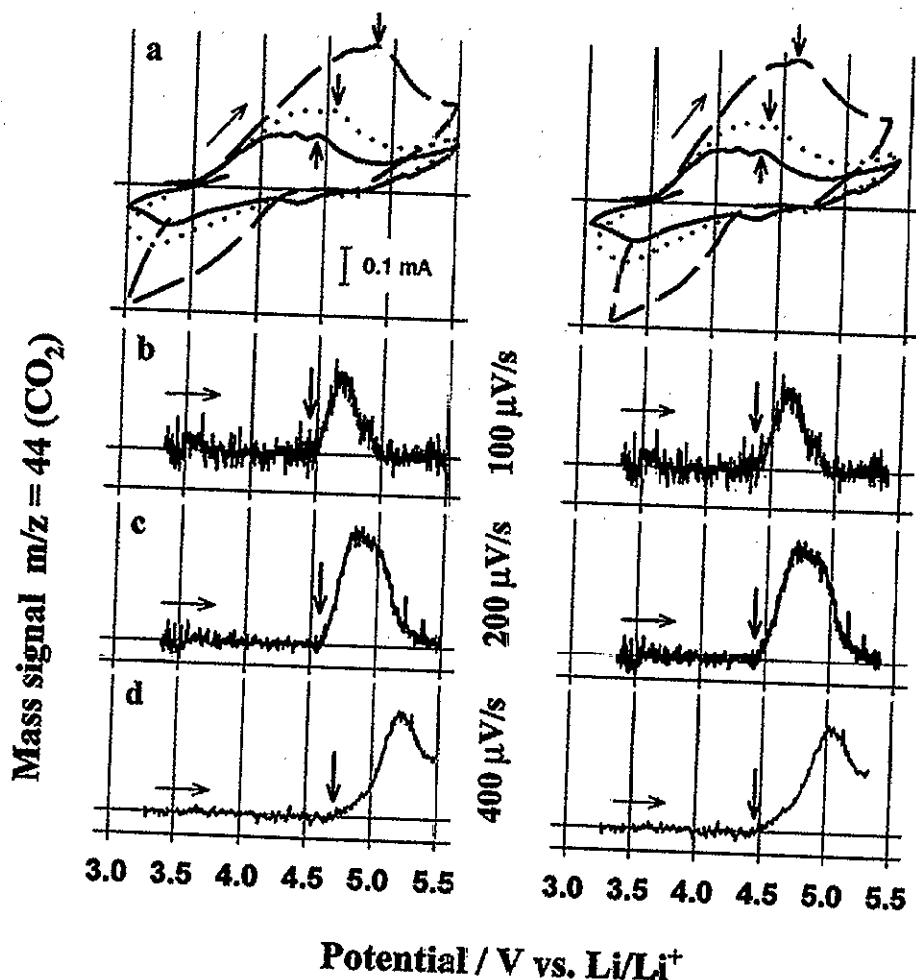


Figure 2. CVs (a) and MSCVs (b-d) of mass $m/z = 44$, representing CO_2 , recorded at LiNiO_2 electrodes in PC/1 M $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ at different scan rates: 0.1 mV/s (b, —), 0.2 mV/s (c, ···), and 0.4 mV/s (d, ---). To the left: before IR drop correction, to the right: after correcting for the IR drop contribution of the electrolyte. 18% carbon black content.

LiNiO_2 electrode with the increased carbon black content (Fig. 4), the starting point of gas evolution at carbon black is found at a considerably more positive potential (Fig. 1) independently of the scan

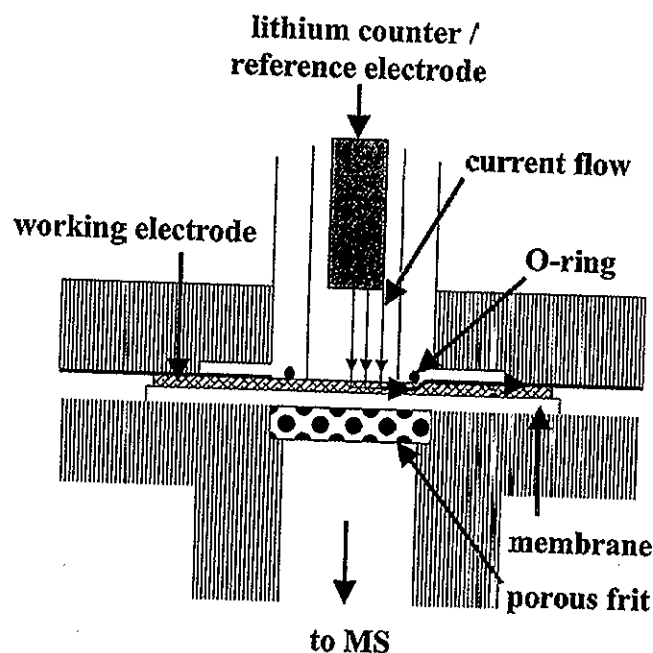


Figure 3. Current path in the electrochemical cell for DEMS measurements.

rate. Thus, the origin of the CO_2 evolved at LiNiO_2 is certainly not associated with the carbon black present in these electrodes. In addition, at LiNiO_2 the mass signals $m/z = 58$ and 87 were not detected despite the fact that the electrode surface consists mainly of carbon black. We believe that the electrolyte and/or electrode decomposition products cover the electrode surface and possibly change the reaction mechanism. This could explain also the vanishing CO_2 evolution at higher potentials.

Figure 5 compares the DEMS measurements at LiNiO_2 in the PC-based electrolytic solution with the results obtained at LiMn_2O_4 , LiCoO_2 , and carbon black composite electrodes in the same electrolyte solution. The oxide electrodes contained 45% of carbon black, the scan rate was 0.4 mV/s, and the data are not corrected for the IR drop.

Obviously, all lithium metal oxide composite electrodes evolve CO_2 upon oxidation in the PC-based electrolyte. However, the electrochemical behavior of the LiCoO_2 and LiMn_2O_4 electrodes resembles the results found on the carbon black electrode (Fig. 1). CO_2 evolution does not start before 4.8 V vs. Li/Li^+ , and intensity changes in the mass signals $m/z = 58$ and 87 were detected too. However, it is not possible to decide whether the observed generation of volatile decomposition products occurs at the LiCoO_2 and LiMn_2O_4 or at the carbon black component of the composite electrodes.

The results of the DEMS measurements in the EC/DMC-based electrolyte are summarized in Fig. 6. Again, LiNiO_2 (with 45% of carbon black) shows CO_2 evolution starting at about 4.2 V vs. Li/Li^+ . In contrast, volatile oxidation products were detected neither at the other two lithium metal oxide materials nor at carbon black in this electrolytic solution.

These observations are in good agreement with a SNIPTIRS investigation on model nickel metal electrodes performed in our laboratory, where PC was also found to be more readily oxidized than

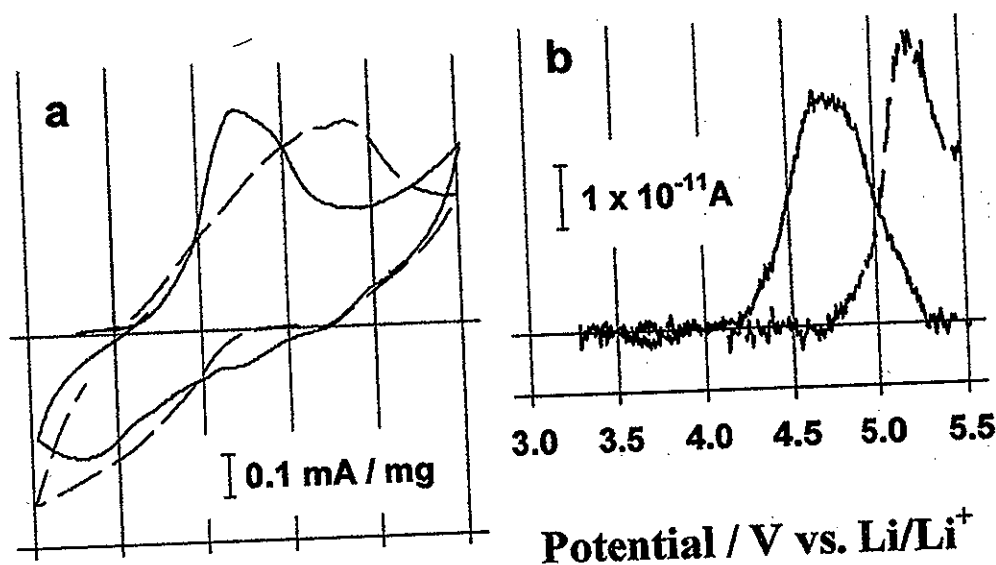


Figure 4. CVs (a) and MSCVs (b) of mass $m/z = 44$, representing CO₂, recorded at LiNiO₂ electrodes containing 18% (- -) and 45% (—) carbon black in PC/1 M LiN(SO₂CF₃)₂. Scan rate = 0.4 mV/s.

EC/DMC.¹⁴ However, the unique behavior of LiNiO₂ concerning the gas evolution in both electrolytic solutions shows that each electrode material has to be studied by itself. Different electrocatalytic activities of the electrode materials can substantially influence the course of the electrolytic decomposition reactions. The presumed protective film forming on different materials is probably quite the same; how-

ever, the way in which it is formed may be rather different. The fact that at LiNiO₂, the CO₂ evolution starts in a potential region where the electrode material is not yet completely delithiated shows that discussions about irreversible charge losses during the first charging cycle should include also solvent decomposition reactions and not merely focus on irreversible phase transitions.

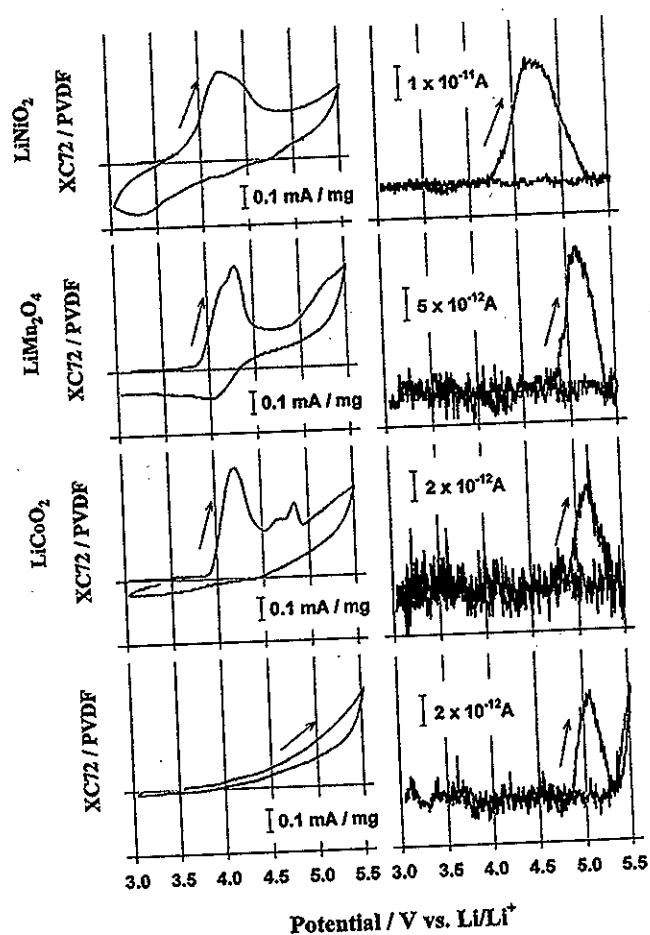


Figure 5. CVs and MSCVs of mass $m/z = 44$, representing CO₂, recorded at the three lithium metal oxide electrodes and a carbon black electrode in PC-based electrolytic solution. Scan rate = 0.4 mV/s, 45% carbon black in the lithium metal oxide electrodes.

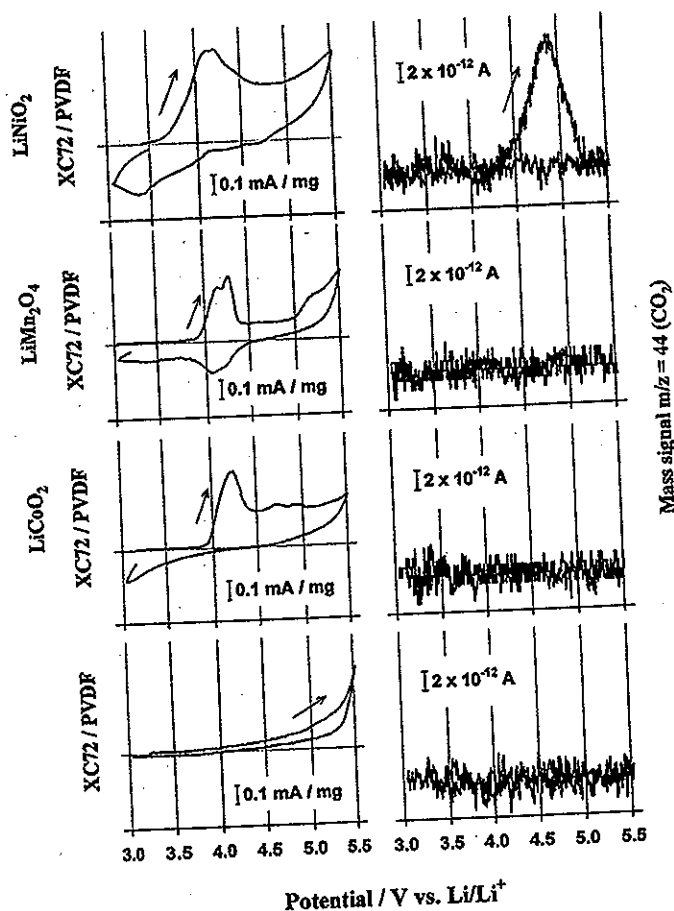


Figure 6. CVs and MSCVs of mass $m/z = 44$, representing CO₂, recorded at the three lithium metal oxide electrodes and a carbon black electrode in EC/DMC-based electrolytic solution. Scan rate = 0.4 mV/s, 45% carbon black in the lithium metal oxide electrodes.

Conclusions

The electrochemical behavior of organic carbonates as Li-ion battery electrolyte solvents was studied by DEMS at LiNiO_2 , LiCoO_2 , and LiMn_2O_4 upon overcharge to 5.5 V vs. Li/Li^+ during the first cycle. No gas evolution was detected at any of these electrode materials in the range where reversible cycling is usually performed. However, at LiNiO_2 composite electrodes, CO_2 was detected at potentials as low as 4.2 V vs. Li/Li^+ . The starting point of the intensity changes in the mass signal $m/z = 44$ correlate well with the last current peak in the cyclic voltammogram of LiNiO_2 . This indicates that at LiNiO_2 , solvent decomposition reactions are taking place simultaneously with the final phase transition processes upon delithiation, which should therefore not be discussed separately. Compared to LiNiO_2 , both LiCoO_2 and LiMn_2O_4 reveal a different electrochemical behavior concerning gas evolution. Therefore, it is important to emphasize that each electrode material should be investigated as close to its practical environment as possible, and care has to be taken when interpreting experimental results from model electrodes.

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