Inhibition of solid electrolyte interface formation on cathode particles for lithium-ion batteries

Wentao Li, Brett L. Lucht *

Department of Chemistry, University of Rhode Island, Kingston, RI 02881, USA

Abstract

Thermal reactions between cathode particles ($LiNi_{0.8}Co_{0.2}O_2$, $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$) and ternary electrolyte (1.0 M $LiPF_6$ in 1:1:1 diethyl carbonate/dimethyl carbonate/ethylene carbonate) with or without the thermal stabilizing additive dimethyl acetamide (DMAc) have been investigated. Ternary electrolyte reacts with the surface of lithiated metal oxides ($LiNi_{0.8}Co_{0.2}O_2$, $LiCoO_2$ and $LiMn_2O_4$) upon storage to corrode the surface and generate a complex mixture of organic and inorganic surface species, but the bulk ternary electrolyte does not decompose. There is little evidence for reaction between the surface of carbon coated $LiFePO_4$ and ternary electrolyte upon storage at elevated temperature (>60 °C), but the bulk ternary electrolyte decomposes. Addition of DMAc to ternary electrolyte reduces the surface corrosion of the lithiated metal oxides and stabilizes the electrolyte in the presence of $LiFePO_4$.
© 2007 Published by Elsevier B.V.

Keywords: Li-ion batteries; Surface films; Cathodes; Additives

1. Introduction

The high energy density of lithium-ion batteries has resulted in wide application in portable electronic devices. While $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ and the corresponding mixed oxides are the most common cathode materials, $LiFePO_4$ and other metal phosphates have attracted significant recent attention due to the inherent safety and low cost [1,2]. The choice of cathode material is typically dependent upon the application, but capacity and power fade upon cell aging are observed for all types of cathodes. The loss of capacity and power are accelerated when the cells are exposed to elevated temperatures (>50 °C) [3–6]. One of the most important factors in performance fade is the growth of surface films on cathode materials [7–12].

We have reported that the formation of cathode surface films results from a combination of reactions between the electrolyte and cathode materials and deposition of electrolyte decomposition products [13]. The Li_2CO_3 surface films present on most commercial $LiCoO_2$ and $LiNi_{0.8}Co_{0.2}O_2$ help to stabilize the

electrolyte and inhibit further reactions to the underlying metal oxides. In cases where the surface concentration is low or reactions with electrolyte consume the Li_2CO_3, reactions of the electrolyte or electrolyte decomposition products will corrode the metal oxide. Modifications of metal oxide cathode materials via surface coating with MgO, ZrO_2, or Al_2O_3, have been reported to reduce the surface corrosion and improve battery performance [14–17].

The development of additives that thermally stabilize $LiPF_6$ based electrolytes has been ongoing [18–21]. Dimethyl Actamide (DMAc) is a polar aprotic solvent with a wide electrochemical stability window (0–4.5 V versus Li/Li^+) that has recently been investigated as a thermal stabilizing additive for $LiPF_6$ based electrolytes. Addition of 3% DMAc to 1.0 M $LiPF_6$ in 1:1:1 diethyl carbonate (DEC):dimethyl carbonate (DMC):ethylene carbonate (EC) (ternary electrolyte) can inhibit the thermal decomposition of the electrolyte at 85 °C for over 2 years [22]. In this report, electrolytes with or without DMAc were stored with $LiNi_{0.8}Co_{0.2}O_2$, $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$ cathode particles at elevated temperatures. The surface composition of the cathode particles were monitored by XPS and SEM with EDS and the liquid electrolyte composition was monitored by GC–MS and NMR spectroscopy.

* Corresponding author. Tel.: +1 401 874 5071; fax: +1 401 874 5070.
E-mail address: blucht@chm.uri.edu (B.L. Lucht).

It is shown that the additives reduce cathode surface corrosion, inhibit the deposition of electrolyte decomposition on the cathode particles and inhibit decomposition of the bulk liquid electrolyte.

2. Experimental

Samples for this study were prepared inside a nitrogen-filled glove box and flame sealed on a vacuum line. Unless specified otherwise, the samples with or without DMAc additive were prepared and analyzed in pairs under identical conditions. The spectra are compared directly without normalization. Glass vials were charged with 0.5 g of solid cathode materials ($LiNi_{0.8}Co_{0.2}O_2$, $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$) as loose powders as received from FMC, Merck, Aldrich or Phostech and 1.0 g of 1.0 M $LiPF_6$ in 1:1:1 EC/DEC/DMC with or without additive (ternary electrolyte, from EM Industries). Both the solid and liquid portions were analyzed. Glass NMR tubes were charged with between 30 and 60 mg of solid and 1.0 g of ternary electrolyte. Care was given to avoid contamination of the tube/vial walls near the sealing point. The sealed samples were then stored in an oil bath of set temperature. Samples were weighed before and after storage to confirm seal. Only samples with less than 5 mg variation were processed.

Nuclear magnetic resonance (NMR) spectroscopy and gas chromatography with mass selective detection (GC–MS) were used to analyze the liquid. NMR analyses were conducted on a JEOL 400 MHz NMR spectrometer. ^1H and ^{19}F spectra were collected using a single pulse method. ^{13}C and ^{31}P NMR spectra were acquired with broadband ^1H decoupling. Chemical shifts are referenced to EC at 4.51 ppm, EC at 64.6 ppm, $LiPF_6$ at 65.0 ppm and $LiPF_6$ at −145.0 ppm for ^1H, ^{13}C, ^{19}F and ^{31}P resonances, respectively. GC–MS analyses were conducted on an Agilent Technologies 6890 GC with a 5973 Mass Selective Detector and a HP-5MS Column. Helium was used as the carrier gas with a flow rate of 3.3 mL min^{-1}. Samples were ramped from 30 to 250 °C at 10 °C min^{-1}.

Solid samples were washed four times with DMC to remove $LiPF_6$ salt followed by vacuum drying overnight at room temperature. The samples were exposed to air briefly, less than 2 min, during the sample introduction process, which is not expected to change the surface composition. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) analyses were conducted on a JEOL-5900 SEM. X-ray photoelectron spectroscopy (XPS) was conducted with a PHI 5500 system using Al Kα radiation under ultra high vacuum. Depth dependent elemental composition was collected by Ar$^+$ ion sputtering with etching rate of approximately 1 nm min^{-1} for SiO_2. Lithium was not monitored due to its low inherent sensitivity and small change of binding energy. The universal carbon contamination peak at 284.8 eV or graphite at 284.0 in the case of $LiFePO_4$ was used to check the binding energy scale and charging effects. The spectra obtained were analyzed by Multipak 6.1A software. Line syntheses of elemental spectra were conducted using Gaussian–Lorentzian curve fit with Shirley background subtraction.

3. Result and discussion

3.1. DMAc as an additive in the electrolyte with $LiNi_{0.8}Co_{0.2}O_2$

A detailed investigation of the thermal reactions between $LiNi_{0.8}Co_{0.2}O_2$ and ternary electrolyte has recently been reported [13]. The study has been expanded with the investigation of the effect of added DMAc on the reactions between the electrolyte and the surface of the cathode particles. After storing the particles with the electrolytes for 14 days at 85 °C, the liquid and solid components were separated for analyses. NMR spectroscopy and GC–MS analysis of the liquid indicates that the electrolyte from both the sample containing ternary electrolyte and the sample containing ternary electrolyte with 3% DMAc have not changed upon storage. Analysis of $LiNi_{0.8}Co_{0.2}O_2$ by SEM–EDS provides no evidence for a change in the bulk material. However, surface analyses by XPS, which detects changes on the top few nanometers of the surface, reveals differences between the particles stored in ternary electrolyte with and without DMAc. Table 1 shows the surface element composition of $LiNi_{0.8}Co_{0.2}O_2$ stored with or without DMAc in the electrolyte, before and after 3 min of Ar$^+$ sputtering. More fluorine and less carbon were observed for the sample containing ternary electrolyte than for the sample with added DMAc. This trend is observed both before and after sputtering. As reported previously, the surface of $LiNi_{0.8}Co_{0.2}O_2$ is covered by a pristine Li_2CO_3 layer and has a high concentration of carbon and oxygen, and a low concentration of nickel and cobalt [13]. Higher concentrations of carbon or oxygen, in the form of Li_2CO_3, are consistent with less reaction of the electrolyte with the surface. Alternatively, the decomposition products of the electrolyte are rich in fluorine, so an increased concentration of fluorine suggests more reaction of the electrolyte with the surface. Thus, it appears that addition of DMAc inhibits the reactions of the electrolyte with the surface of the $LiNi_{0.8}Co_{0.2}O_2$.

Line shape analyses provide further insight into the role of DMAc in reducing the surface reaction. Fig. 1 contains C 1s, O 1s, F 1s, and Ni 2p3 spectra of $LiNi_{0.8}Co_{0.2}O_2$ particles stored in ternary electrolyte with or without added DMAc for 2 weeks at 85 °C. Small differences are observed in C 1s and O 1s spectra. The particles stored in electrolyte with added DMAc have stronger signals at 289 eV and 531 eV in C 1s and O 1s spectra, suggesting that more surface Li_2CO_3 is retained with added DMAc. The weaker intenstiy signals at 529 eV in O 1s spectra and 855 eV in Ni 2p3 spectra, which are

Table 1

Surface carbon, oxygen, fluorine, phosphorus, cobalt and nickel concentration of stored $LiNi_{0.8}Co_{0.2}O_2$, before and after sputtering 3 min by Ar$^+$

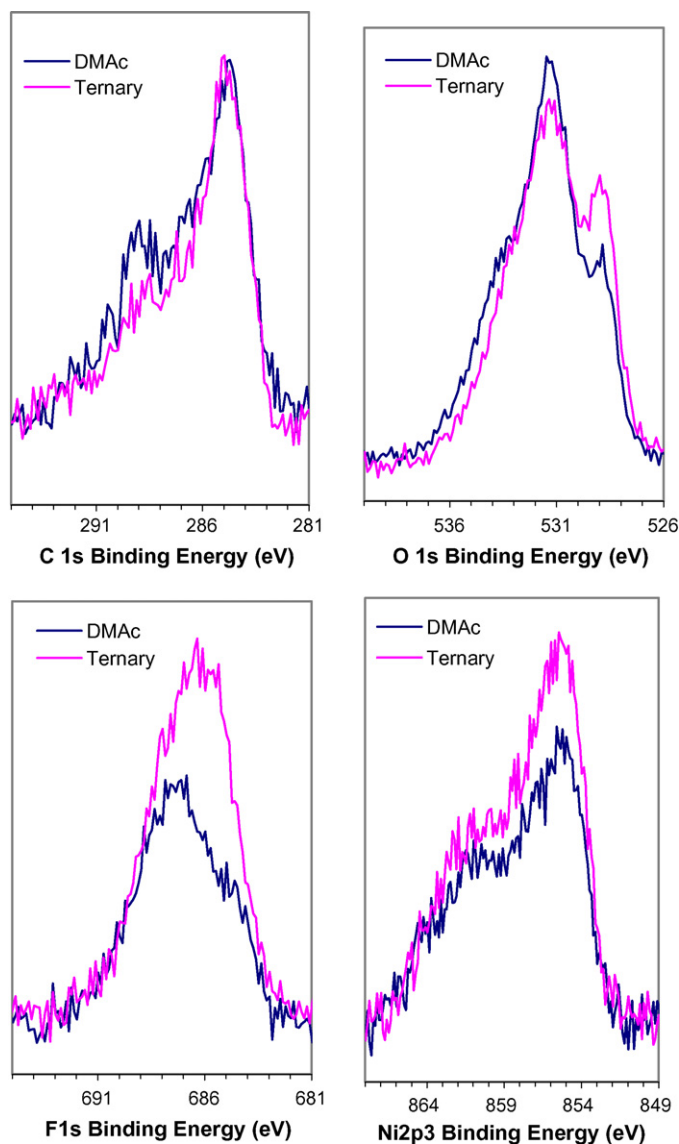|	C 1s	O 1s	F 1s	P 2p	Co 2p3	Ni 2p3
Fresh	30.9	59.0	0.0	0.5	2.6	7.1
Ternary	14.2	42.2	21.5	2.0	5.5	14.8
3% DMAc	18.3	45.1	16.4	5.0	2.3	12.9
Ternary, sputtered	6.4	41.2	19.0	0.0	11.1	22.3
3% DMAc, sputtered	9.8	46.0	9.4	0.0	13.8	21.0

Fig. 1. C 1s, O 1s, F 1s, and Ni 2p3 XPS spectra of the $LiNi_{0.8}Co_{0.2}O_2$ particles stored with standard ternary electrolyte and electrolyte containing 3% DMAc for 2 weeks at 85 °C.

Table 2
Surface carbon, oxygen, fluorine, phosphorus and cobalt concentration of stored $LiCoO_2$, 2 weeks at 85 °C or room temperature, with additive or without in the electrolyte

	C 1s	O 1s	F 1s	P 2p	Co 2p3
Fresh	18.9	58.0	0.0	0.0	23.1
Ternary 85 °C	14.8	44.0	17.0	3.6	20.6
3% DMAc 85 °C	16.9	43.8	12.0	2.6	24.7
Ternary RT	20.0	41.6	20.1	0.0	18.3
3% DMAc RT	18.4	55.7	4.7	0.8	20.4

DMAc on the reactions. Storage of $LiCoO_2$ in the presence of ternary electrolyte with or without DMAc at room temperature (RT) for 2 weeks reveals some differences between the two electrolytes. NMR spectroscopy and GC–MS analysis of the liquid electrolyte indicate that ternary electrolyte and ternary electrolyte with added DMAc are unchanged after storage for 2 weeks at RT. The bulk electrolyte does not decompose. Analysis of the solid $LiCoO_2$ particles by SEM–EDS reveals that there are no changes to the bulk particles, as observed for $LiNi_{0.8}Co_{0.2}O_2$ particles. Analysis of the surface of the $LiCoO_2$ particles by XPS reveals significant differences between samples containing ternary electrolyte with and without DMAc. The particles stored with DMAc have a higher concentration of oxygen and lower concentration of fluorine on the surface (Table 2, Fig. 2). Line shape analysis of Co 2p3 spectra reveals a single peak for cobalt oxide (780 eV) in samples containing DMAc. Samples of ternary electrolyte without DMAc contain peaks characteristic of both cobalt oxide at 780 eV and cobalt fluoride (685 eV in F 1s and 782 eV in Co 2p3 spectra). Fresh $LiCoO_2$ contains a thinner surface coating of Li_2CO_3 than $LiNi_{0.8}Co_{0.2}O_2$ [13]. Most of the Li_2CO_3 is removed from the surface of the $LiCoO_2$ after storage in ternary electrolyte. However, addition of DMAc results in the retention of some Li_2CO_3 (289 eV in C 1s, 531 in O 1s) on the surface suggesting less reaction with electrolyte. Upon loss of Li_2CO_3 the growth of organic polymer species (287 eV in C 1s and 533 eV in O 1s) result from the decomposition of the carbonate solvents.

Storage of the electrolyte at 85 °C for 2 weeks provided similar results to those observed at RT. NMR spectroscopy and GC–MS analysis of the liquid electrolyte suggest the electrolytes are unchanged. Analysis of the solid $LiCoO_2$ particles by SEM–EDS reveals that there are no changes to the bulk material, as observed for $LiNi_{0.8}Co_{0.2}O_2$ particles. Analysis of the surface of the $LiCoO_2$ particles by XPS reveals similar differences between samples containing ternary electrolyte with and without DMAc. The elemental concentrations are summarized in Table 2. Concentration of surface fluorine is lower while the concentrations of carbon and oxygen are higher upon addition of DMAc the electrolyte.

characteristics of the bulk metal oxide, further confirm that the surface Li_2CO_3 is retained and the bulk metal oxide is less exposed to the electrolyte. Identical line shapes are observed in P 2p spectra, indicating that the two surfaces have similar phosphorus containing groups, namely $Li_xPO_yF_z$ and residual Li_xPF_y at 134 eV and 136 eV, respectively. The most striking difference between the two samples is observed in the F 1s spectra, which show that the particles stored in presence of DMAc have much less resistive LiF on the surface (685 eV in F 1s). Similar effects were observed when the storage time was increased from 1 week to 4 weeks.

3.2. DMAc as an additive in the electrolyte with $LiCoO_2$

While a detailed investigation of the surface reactions of $LiCoO_2$ with ternary electrolyte has been previously reported, the investigation has been expanded to monitor the effect of

3.3. DMAc as an additive in the electrolyte with $LiMn_2O_4$

The surface of the fresh $LiMn_2O_4$ before contact with electrolyte was analyzed by XPS and SEM with EDS to provide a baseline for changes to the surface upon reaction with elec-
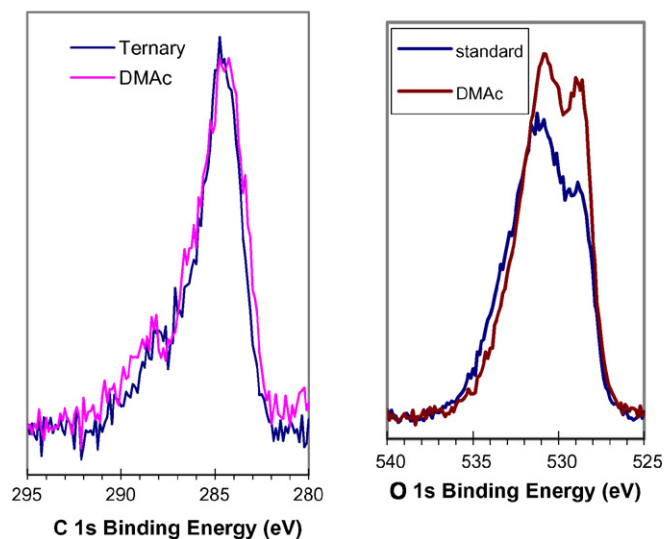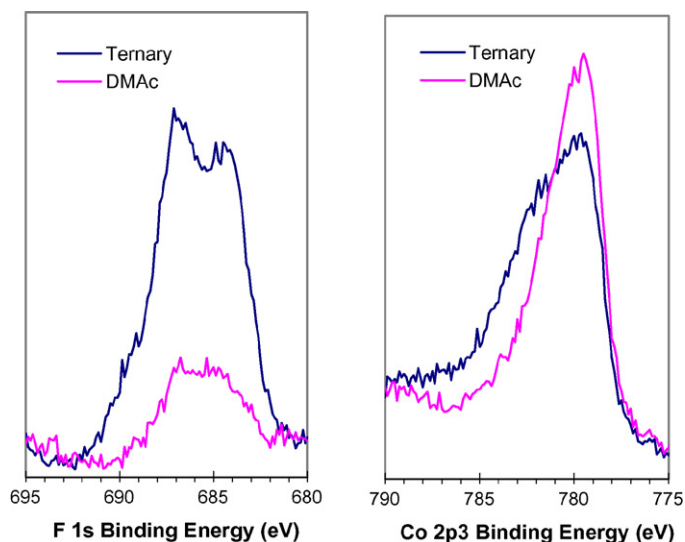
Fig. 2. C 1s, O 1s, F 1s and Co 2p3 spectra of the $LiCoO_2$ particles stored with standard ternary electrolyte and electrolyte containing 3% DMAc, 2 weeks at room temperature.
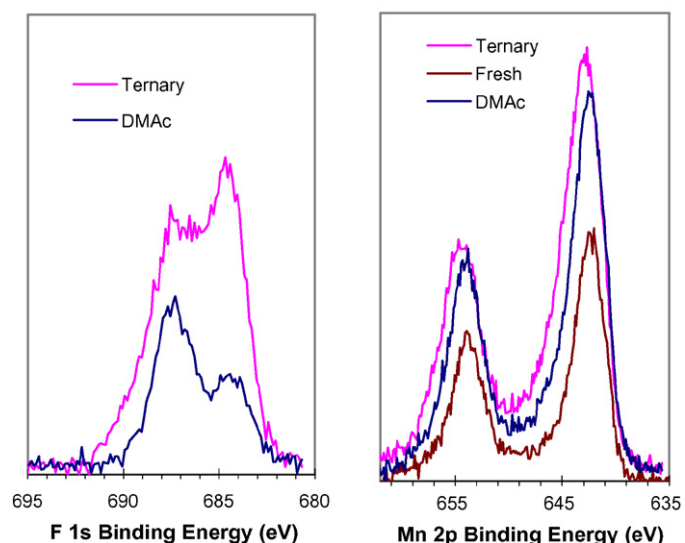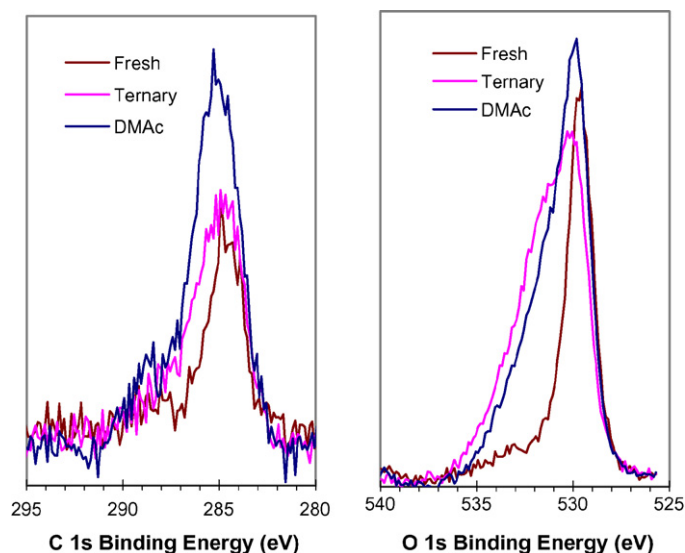

Fig. 3. C 1s, O 1s, F 1s, and Mn 2p spectra of the $LiMn_2O_4$ particles stored with ternary electrolyte and with electrolyte containing 3% DMAc, compared to the spectra of the fresh $LiMn_2O_4$. Storage conditions: 1 week at room temperature.

trolyte. As shown in Fig. 3, sharp signals for Mn 2p (642.3 eV) and O 1s (529.7 eV) characteristic of manganese in an oxygen matrix were observed. Unlike the surface of the layered metal oxide particles, $LiCoO_2$ and $LiNi_{0.8}Co_{0.2}O_2$, there are few surface species on fresh $LiMn_2O_4$. Instead, the bulk spinel is exposed to the surface. Only weak intensity peaks characteristic of impurities are observed at 533 eV in O 1s and 289 eV in C 1s spectra. The lack of surface species is further verified by the surface ratio of Mn to O, which is very close to the ideal 1:2 as expected for bulk spinel.

Storage of $LiMn_2O_4$ in the presence of ternary electrolyte with or without DMAc for 1 week at RT or 60 °C does not result in any changes to the composition of the electrolyte by GC–MS or NMR spectroscopy. Analysis of the $LiMn_2O_4$ by SEM–EDS suggests that 1 week of exposure to the electrolyte does not significantly change the bulk material. However, significant changes are observed on the surface by XPS (Figs. 3 and 4). The surface compositions of the $LiMn_2O_4$ before and after stor-

age are summarized in Table 3. The fluorine concentration is lower for samples stored with DMAc suggesting a reduction in the reaction between the surface and electrolyte. Comparisons of C 1s, O 1s, Mn 2p, and F 1s XPS spectra of $LiMn_2O_4$ before and after storage with electrolyte provide further support for inhibition of surface reactions by DMAc.

Table 3
Surface carbon, oxygen, fluorine, phosphorus and cobalt concentration of stored $LiMn_2O_4$, 1 weeks at 60 °C or room temperature, with additive or without in the electrolyte

	C 1s	O 1s	F 1s	P 2p	Mn 2p3
Fresh	21.8	51.1	3.5	0.0	23.6
Ternary RT	10.7	38.5	28.3	3.2	19.4
3% DMAc RT	22.6	41.9	14.4	3.3	17.9
Ternary 60 °C	27.9	28.2	30.9	3.6	9.5
3% DMAc 60 °C	10.7	38.3	28.0	2.9	20.0

The sample stored with standard electrolyte at RT has additional small shoulders between 286 and 289 eV in the C 1s spectra and large shoulders between 531 and 535 eV in O 1s spectra. The new peaks are consistent with the appearance of polymeric carbonate species on the surface. New signals characteristic of phosphorus and fluorine are present after the storage. In addition to the appearance of new peaks, the binding energies for the $LiMn_2O_4$ are shifted to higher energy. The O 1s peak is shifted from 529.7 to 530.2 eV while the Mn 2p3 peak is shifted from 642.3 to 642.8 eV. This shift suggests that storage with the electrolyte increases the oxidation state of the manganese on the surface, probably through a disproportionation reactions followed by partial Mn^{2+} dissolution, leaving Mn^{4+} on the surface [24,25]. However, the peaks characteristic of $LiMn_2O_4$ do not shift upon storage in electrolyte with added DMAc. Finally, LiF (684.5 eV, F 1s) concentration is much lower for samples stored with electrolyte containing DMAc.
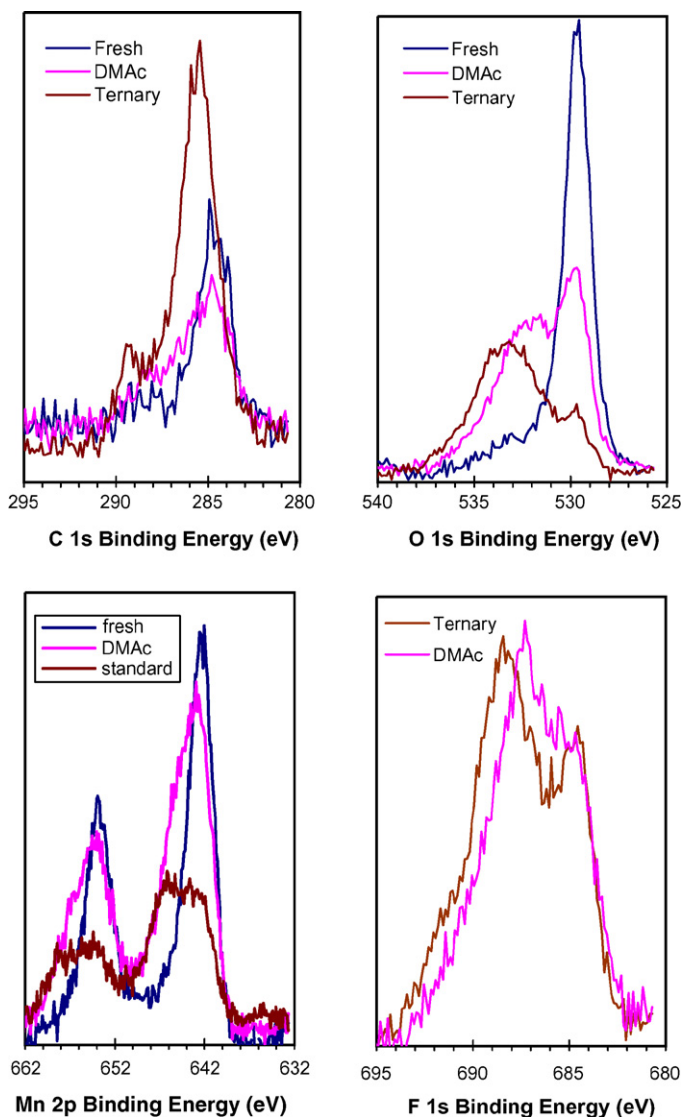
When the storage temperature is increased to 60 °C, thicker surface films are observed (Fig. 4). Samples stored in ternary electrolyte have dominant O 1s signals characteristic of organic species (531–536 eV) and a small signal associated with $LiMn_2O_4$ (529.5 eV), suggesting that the surface film is almost thick enough to prevent the penetration of photoelectron from bulk spinel. At the same time, Mn 2p spectra decrease in intensity and show an additional peak around 646 eV, characteristic of manganese in a higher oxidation state or in a fluorine environment. Samples stored in electrolyte with added DMAc retain the $LiMn_2O_4$ signal as the dominant peak in both O 1s and Mn 2p spectra. The addition of DMAc to the electrolyte inhibits the corrosion and formation of surface films on $LiMn_2O_4$.

3.4. DMAc as an additive in the electrolyte with LiFePO₄

Analysis of the surface of $LiFePO_4$ by SEM with EDS and XPS before contact with electrolyte confirms the expected composition. The presence of a thin layer of graphite on the surface of the particles is identified by XPS (284.0 eV in C 1s, Fig. 5). The $LiFePO_4$ particles are coated with graphite to increase the conductivity [26]. The bulk $LiFePO_4$ particles have signals at 531.0, 132.9 and 711 eV in O 1s, P 2p and Fe 2p3 spectra, respectively (Fig. 5).

After storage of $LiFePO_4$ with ternary electrolyte for 1 week at room temperature, there is no evidence for electrolyte decomposition by NMR or GC–MS. There is no evidence for a change in the bulk $LiFePO_4$ by SEM with EDS. However, XPS analysis supports a modification of the surface of $LiFePO_4$ (Table 4). There is a small reduction in the concentration of carbon along with a significant increase in the concentration of fluorine. The F 1s signal is broad and appears to be a combination of $Li_xPO_yF_z$ (686.7 eV) and LiF (684.5 eV). The presence of $Li_xPO_yF_z$ is further supported by the appearance of a shoulder in the P 2p region (134.5 eV). The lack of new C 1s signal further supports the surface species being inorganic salts. Similar phenomena have been reported for cycled carbon coated $LiFePO_4$ electrodes [11].

When the storage temperature is increased from room temperature to 60 or 85 °C, only minor changes in the surface composition are observed by XPS or SEM with EDS, with or without added DMAc. The concentrations of carbon and oxygen are decreased while the concentration of fluorine is increased, indicating that more $Li_xPO_yF_z$ and LiF are deposited on the surface. The minor changes to the surface of $LiFePO_4$ compared to the metal oxides ($LiCoO_2$, $LiNi_{0.8}Co_{0.2}O_2$, and $LiMn_2O_4$)

Fig. 4. C 1s, O 1s, F 1s and Mn 2p spectra of the $LiMn_2O_4$ particles stored with standard ternary electrolyte and with electrolyte containing 3% DMAc, compared to the spectra of the fresh $LiMn_2O_4$. Storage conditions: 1 week at 60 °C.

Table 4
Surface carbon, oxygen, fluorine, phosphorus and iron concentration of $LiFePO_4$ before and after 1 week storage at the indicated temperature

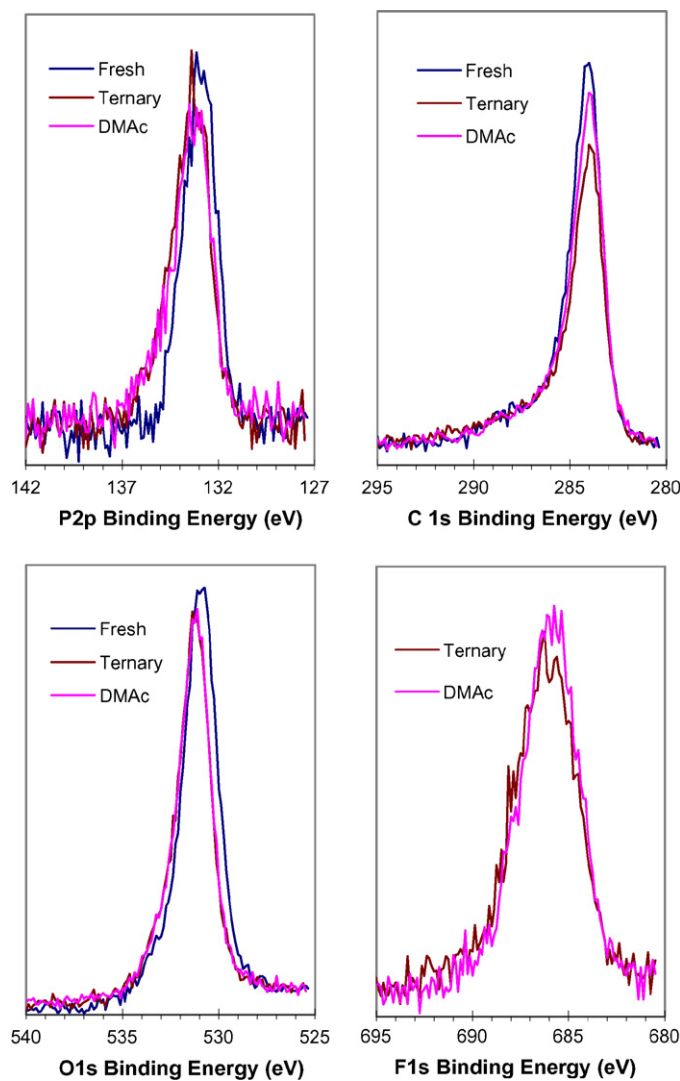|	C 1s	O 1s	F 1s	P 2p	Fe 2p3
Fresh	57.8	32.5	0.0	5.5	4.3
Ternary RT	53.5	29.6	7.8	4.8	4.3
3% DMAc RT	58.4	27.6	6.0	4.5	3.5
Ternary 60 °C	49.3	27.3	11.5	7.4	4.5
3% DMAc 60 °C	52.3	25.7	10.1	6.9	5.0
Ternary 85 °C	50.5	26.2	11.7	5.9	5.7
3% DMAc 85 °C	51.4	25.6	11.2	6.3	5.5

Fig. 5. C 1s, O 1s, F 1s and P 2p spectra of LiFePO$_4$ particles stored with ternary electrolyte with or without 3% DMAc for 1 week at 60 °C, compared to the spectra of the fresh LiFePO$_4$.

upon storage with the electrolyte, suggest that LiFePO$_4$ does not react with the electrolyte or electrolyte decomposition products. This is in agreement with previous investigations which suggest that LiFePO$_4$ has superior thermal stability in the presence of electrolyte [27]. However, while the surface of the LiFePO$_4$ is only slightly modified after storage in the presence of ternary electrolyte without added DMAc at elevated temperatures, the electrolyte undergoes significant decomposition. Complex decomposition products are observed by GC–MS and NMR spectroscopy of the electrolyte stored at 85 °C, indicating that LiFePO$_4$ is unable to stabilize the electrolyte at elevated temperature [19,23].

Due to the lack of reactions between LiFePO$_4$ and the electrolyte, addition of 3% DMAc to ternary electrolyte has smaller effect on the surface of LiFePO$_4$ at all temperatures (Table 4 and Fig. 5). XPS spectra indicate that the DMAc containing samples have slightly less fluorine than the sample with standard ternary electrolyte at all temperatures (Table 4). Other differences in the XPS spectra with and without DMAc are subtle (Fig. 5).

However, significant differences are observed for the electrolyte stored with LiFePO$_4$ at elevated temperatures. When DMAc is incorporated into the electrolytes, no electrolyte decomposition products are observed by GC–MS or NMR spectroscopy. The observations indicate that addition of DMAc stabilizes the electrolyte and reduces the deposition of inorganic salts on the surface of LiFePO$_4$. Similar results were reported for electrolyte stored in the presence of meso-carbon micro-beads (MCMB) [22].

3.5. Mechanism of corrosion inhibition

Incorporation of DMAc into LiPF$_6$ containing electrolytes suppresses the corrosion of cathode particles by inhibiting thermal decomposition reactions of the electrolyte. The thermal dissociation of LiPF$_6$ to generate LiF and PF$_5$ initiates the thermal decomposition of LiPF$_6$ based electrolytes [19,23]. DMAc and related Lewis bases complex and stabilize PF$_5$ preventing reaction with the carbonate solvents and the subsequent generation of HF and fluorophosphates (OP(OR)F$_2$) [18,28]. Addition of DMAc impedes the formation of acid species in the electrolyte which decreases the surface corrosion of cathode particles.

4. Conclusions

Storage of metal oxide cathode particles (LiCoO$_2$, LiNi$_{0.8}$Co$_{0.2}$O$_2$, and LiMn$_2$O$_4$) in the presence of ternary electrolyte leads to surface corrosion and deposition of electrolyte decomposition products, but no decomposition of the bulk electrolyte. Storage of carbon coated metal phosphate cathode particles (LiFePO$_4$) in the presence of ternary electrolyte results in deposition of electrolyte decomposition products and bulk electrolyte decomposition, but no surface corrosion. Addition of DMAc to ternary electrolyte increases the thermal stability of the electrolyte and reduces both surface corrosion and deposition of electrolyte decomposition products on cathode particles.

References

[1] J.O. Besenhard (Ed.), Handbook of Battery Materials, Wiley-VCH, New York, 1999.
[2] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. 44 (1997) 1188.
[3] Y. Itou, Y. Ukyo, J. Power Sources 146 (2005) 39.
[4] I. Bloom, B.W. Cole, J.J. Sohn, S.A. Jones, E.G. Polzin, V.S. Battaglia, G.L. Henriksen, C. Motloch, R. Richardson, T. Unkelhaeuser, D. Ingersol, H.L. Case, J. Power Sources 101 (2001) 238.
[5] Z. Chen, K. Amine, J. Electrochem. Soc. 153 (2006) A316.

[6] K. Amine, J. Liu, I. Belharouak, Electrochem. Commun. 7 (2005) 669.

[7] A.M. Andersson, D.P. Abraham, R. Hasch, S. MacLaren, J. Liu, K. Amine, J. Electrochem. Soc. 149 (2002) A1358.

[8] T. Eriksson, M.M. Andersson, A.G. Bishop, C. Gejke, T. Gustafsson, J.O. Thomas, J. Electrochem. Soc. 149 (2002) A69.

[9] M. Kerlau, J.A. Reimer, E.J. Cairns, J. Electrochem. Soc. 152 (2005) A1629.

[10] D. Aurbach, K. Gamolsky, B. Markovsky, G. Salitra, Y. Gofer, U. Heider, R. Oesten, M. Schmidt, J. Electrochem. Soc. 147 (2000) 1322.

[11] K. Edstrom, T. Gustafsson, J.O. Thomas, Electrochim. Acta 50 (2004) 397.

[12] M. Wu, P.J. Chiang, J. Lin, J. Electrochem. Soc. 152 (2005) A1041.

[13] W. Li, B.L. Lucht, J. Electrochem. Soc. 153 (2006) A1617.

[14] Z. Wang, C. Wu, L. Liu, F. Wu, L. Chen, X. Huang, J. Electrochem. Soc. 149 (2002) A466.

[15] Y. Kim, J. Cho, T. Kim, B. Park, J. Electrochem. Soc. 150 (2003) A1723.

[16] Y. Kim, T. Kim, J. Shin, B. Park, J. Cho, J. Electrochem. Soc. 149 (2002) A1337.

[17] R. Vidu, P. Stroeve, Ind. Eng. Chem. Res. 43 (2004) 3314.

[18] W. Li, C.L. Campion, B.L. Lucht, B. Ravdel, J. DiCarlo, K.M. Abraham, J. Electrochem. Soc. 152 (2005) A1361.

[19] C.L. Campion, W. Li, W.B. Euler, B.L. Lucht, B. Ravdel, J. DiCarlo, R. Gitzendanner, K.M. Abraham, Electrochem. Solid-State Lett. 7 (2004) A194.

[20] K. Xu, Chem. Rev. 104 (2004) 4303.

[21] S.S. Zhang, K. Xu, T.R. Jow, Electrochem. Solid-State Lett. 5 (2002) A206.

[22] A. Xiao, W. Li, B.L. Lucht, J. Power Sources 162 (2006) 1282.

[23] C.L. Campion, W. Li, B.L. Lucht, J. Electrochem. Soc. 152 (2005) A2327.

[24] R.J. Gummow, A. de Kock, M.M. Thackeray, Solid State Ionics 69 (1994) 59.

[25] A. Du Pasquier, A. Blyr, P. Courjal, D. Larcher, G. Amatucci, B. Gérand, J.-M. Tarascon, J. Electrochem. Soc. 146 (1999) 428.

[26] Z. Chen, J.R. Dahn, J. Electrochem. Soc. 149 (2002) A1184.

[27] A. Yamada, S.C. Chung, K. Hinokuma, J. Electrochem. Soc. 148 (2001) A224.

[28] S. Zhang, J. Power Sources 162 (2006) 1379.