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Residual NMP and Its Impacts on Performance of Lithium-Ion Cells

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N-methyl-2-pyrrolidone (NMP) is the most common solvent used in coating positive electrode materials on aluminum foil during the manufacturing of lithium-ion batteries. NMP is a strongly polar aprotic solvent that effectively dissolves the polyvinylidene difluoride binder. While the majority of NMP typically evaporates during the electrode baking process, trace amounts may persist, particularly in positive electrodes containing nano-sized and highly-porous active materials. We noted residual NMP in the positive electrodes of Li-ion pouch cells containing $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ due to the extremely high surface area of the material and we wanted to determine the impact of this residual NMP. Therefore, a control electrolyte was purposely spiked with varying amounts of NMP and used in NMC532/graphite pouch cells to investigate the impact of residual NMP on lithium-ion battery performance. Experimental results indicate that NMP has the potential not only to neutralize the electrolyte additive ethylene sulfate but also to independently increase cathode impedance, leading to a higher rate of capacity loss during charge-discharge cycling. It is crucial to establish the appropriate procedure for baking electrodes containing NMP, both in laboratory and industrial settings, to mitigate these effects.

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In recent years, batteries have become a crucial element of our everyday life with the continued adoption in large-scale and long-term applications such as grid energy storage¹ and electric vehicles.² N-methyl-2-pyrrolidone (NMP) is used as a solvent in pharmaceutical production, chemical processing, and electronics, due to its excellent chemical and thermal stability. It has a high boiling point (202 °C) and low auto-ignition temperature (252 °C).^{3–6} NMP is also applied in the battery field world widely, due to its potential to dissolve the most frequently utilized binder, PVDF, in the cathode slurry formulation.⁷ Moreover, the low surface tension of NMP allows enhanced wetting of the cathode material slurries onto the current collector, consequently improving adhesion.^{8,9}

After coating slurries on the current collector, it is very important to select the right condition for the subsequent drying process in order to remove the NMP from the coatings. At the laboratory scale, baking electrodes format temperatures between 80 °C and 120 °C for about 12 h is commonly used no matter the particle size of the active material.^{6,10–12} Previously our lab introduced a method by measuring the weight of the small disks versus time to ensure most of the NMP is evaporated after the chosen drying condition.¹²

Electrodes made on industrial coaters are dried in lengthy drying ovens that follow the coating head. These ovens are heated to temperatures around 100 °C and utilize significant air flow to aid drying. Commercially prepared pouch cells and cylindrical cells can also be further vacuum dried after the electrode winding process to further reduce NMP and water content. However, the maximum drying temperature is limited by the separator melting point (~130 °C for polyethylene and ~155 °C for polypropylene).^{13–15} Trace amounts of NMP may persist within the cathode electrodes even after laboratory or industrial electrode drying procedures, especially if extremely high specific surface area electrode materials are being used. In such cases, one must wonder about the impact of residual NMP within the cell.

LMFP/graphite pouch cells obtained from a reputable manufacturer are first shown to contain residual NMP which was not totally removed during the electrode drying process. Then the impact of trace amounts of NMP on NMC532 pouch cells is studied by directly adding NMP to the electrolytes. Two types of electrolytes were selected: 1.5 M LiPF_6 EC:DMC (3:7) + 2 wt% vinylene

carbonate (VC) + 1 wt% ethylene sulfate (DTD) and 1.5 M LiPF_6 EC:DMC (3:7) + 2 wt% VC. Apart from comparing the cycling performance of cells with varying amounts of NMP, electrochemical impedance spectroscopy on symmetric cells was performed to elucidate which components were affected by the presence of NMP. This study provides insights into the consequences of residual NMP on the electrolyte and also its potential impact on cell performance.

Experimental Methods

Pouch cell build, baking, normal electrolyte filling and formation.—The LMFP cells found with significant NMP residual were machine made 240 mAh Li-ion pouch cells (LiFUN Technology, Zhuzhou City, Hunan Province, China) containing high surface area (~26 m² g⁻¹ for BET) polycrystalline LMFP as positive active material and artificial graphite as negative active material. Cells were dried under vacuum at 120 °C or 150 °C for 14 h before being filled with 1.3 g (~1 ml) of electrolyte per cell and vacuum sealed under applied vacuum gauge pressure of -90 kPa. Electrolyte formulation, pouch cell filling and sealing were performed in an argon atmosphere. Cells were charged to 1.5 V and held at constant voltage for 24 h at 40 °C to facilitate wetting of the jellyroll with electrolyte while avoiding dissolution of the negative electrode current collector. Cells underwent a single formation cycle on a Maccor Series 4000 test system to the voltage between 2.5 and 4.2 V at a C/20 rate at 40 °C, after which they were opened in an argon atmosphere and re-sealed under vacuum to remove any gas produced during formation.

To investigate the impact of NMP on Li-ion pouch cells, similar machine made 240 mAh Li-ion pouch cells (LiFUN Technology, Zhuzhou City, Hunan Province, China) containing low surface area (<1 m² g⁻¹ for BET) single crystal NMC532 as positive active material and artificial graphite as negative active material were selected for part of this work. Cells were dried under vacuum at 120 °C for 14 h before being filled with 1.3 g (~1 ml) of electrolyte per cell and vacuum sealed under applied vacuum gauge pressure of -90 kPa. Electrolyte formulation, pouch cell filling and sealing were performed in an argon atmosphere. Cells were charged to 1.5 V and held at constant voltage for 24 h at 40 °C to facilitate wetting of the jellyroll with electrolyte while avoiding dissolution of the negative electrode current collector. Cells underwent a single formation cycle on a Maccor Series 4000 test system to voltage between 3.0 and

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4.3 V at a C/20 rate at 40 °C, after which they were opened in an argon atmosphere and re-sealed under vacuum to remove any gas produced during formation.

Cycling of the pouch cells.—LMFP/graphite cells were cycled on a Neware Battery Testing System (Shenzhen, China) using constant current-constant voltage charge (CCCV) and constant current discharge methods using C/3 rate, between 4.2 V and 2.5 V with a C/20 characterization cycle every 50 cycles, in temperature-controlled chambers at 40 °C ± 0.1 °C. Prior to cycling, electrochemical impedance spectra (EIS) were collected using a Biologic VMP3 Multichannel Potentiostat at 50% SOC. Cells were held at 10 °C in a Novonix Wide-Range Thermal Chamber while being supplied with a 10 mV stimulus that varied from 10 mHz to 100 kHz.

Similarly, NMC532 cells were cycled on a Neware Battery Testing System (Shenzhen, China) using constant current - constant voltage charge (CCCV) and constant current discharge methods using C/3 rate, between 4.3 V and 3.0 V with a C/20 characterization cycle every 50 cycles, in temperature-controlled chambers at 40 °C ± 0.1 °C. Prior to cycling, electrochemical impedance spectra (EIS) were collected using a Biologic VMP3 Multichannel Potentiostat at 3.8 V. Cells were held at 10 °C in a Novonix Wide-Range Thermal Chamber while being supplied with a 10 mV stimulus that varied from 10 mHz to 100 kHz.

Electrolyte types and extraction.—All electrolyte components were used as received and prepared in an Ar-filled glovebox. The solvent blend used in all the cells in this work was a mixture of EC and DMC in a ratio of 3:7 (w/w, <20 ppm water, Shenzhen Capchem). 1.5 M LiPF₆ (Capchem) salt was then mixed in EC:DMC (3:7). For LMFP cells, only one electrolyte was used with 2 wt% VC and 1 wt% DTD as additives which is the standard recipe of our lab. For NMC532 cells, two electrolytes were used to investigate the impact of NMP. One electrolyte used 2 wt% VC and 1 wt% DTD as additives. The second electrolyte used 2 wt% VC only as additives for comparison. Both electrolytes were intentionally spiked with different concentrations of NMP (Tokyo Chemical Company, >99%).

The amount of ideal electrolyte filling for each cell is 1.3 g (~1 ml). If filled normally, not enough electrolyte could be easily

extracted for further NMR testing. As a result, two methods were used to increase the amount of the extracted solvent. The first method used “overfilling” by adding 2.6 g (~2 ml) of electrolyte into the pouch cells which made it easy to extract at least 0.5 ml directly with a syringe after cells had rested for one week to allow equilibration of the electrolyte concentration within and outside the electrode winding. The second method involved filling the post-cycled cells with an additional 0.85 g (~1.0 ml) of the inert solvent methyl acetate (MA) to increase the amount of extractable electrolyte at the expense of complicating procedure and NMR complexity. After the MA was added the cells were heat sealed closed again. The cells filled with MA also had to rest for 1 week to achieve equilibration of the electrolyte inside the pouch cell before extracting.

NMR measurement.—0.6 ml of the extracted solvent was injected into a borosilicate glass NMR tube which was sealed by Parafilm after the tube was capped. One-dimensional ¹H NMR spectra were recorded on a Bruker “AVANCE NEO 400 MHz” spectrometer using 1024 scans (NS) and a 4.0 s acquisition time (AQ) with a 1 s relaxation delay (D1). The center point of the spectrum (OIP) was set as 6.5 ppm and 20.5 was used as spectral width (SW). The sample temperature during the NMR measurement was 298 K. The subsequent spectrum was processed in Bruker TopSpin 4.2.0 and referenced to main solvent peak of DMC set at 4.0 ppm.

Symmetric coin cells.—To identify which electrode of the pouch cell was most severely affected by NMP, the method of symmetric coin cells was applied after the formation step. The pouch cells were opened in an argon-filled glove box to assemble graphite/graphite and NMC532/NMC532 symmetrical cells. One polypropylene blown microfiber separator (BMF—available from 3 M Co. 0.275 mm thickness, 3.2 mg cm⁻²) was used in the symmetric cells. 1 M LiPF₆ in EC/EMC (3:7 w/w) was used as electrolyte in the coin cells. The method of using symmetric cells to determine R_{ct} of the electrodes was detailed by Petibon et al.¹⁶ AC impedance spectra of the assembled symmetric cells were collected using a Biologic VMP-3 with ten points per decade from 100 kHz to 10 mHz and a 10 mV input signal amplitude at 10. ± 0.1 °C. This temperature was

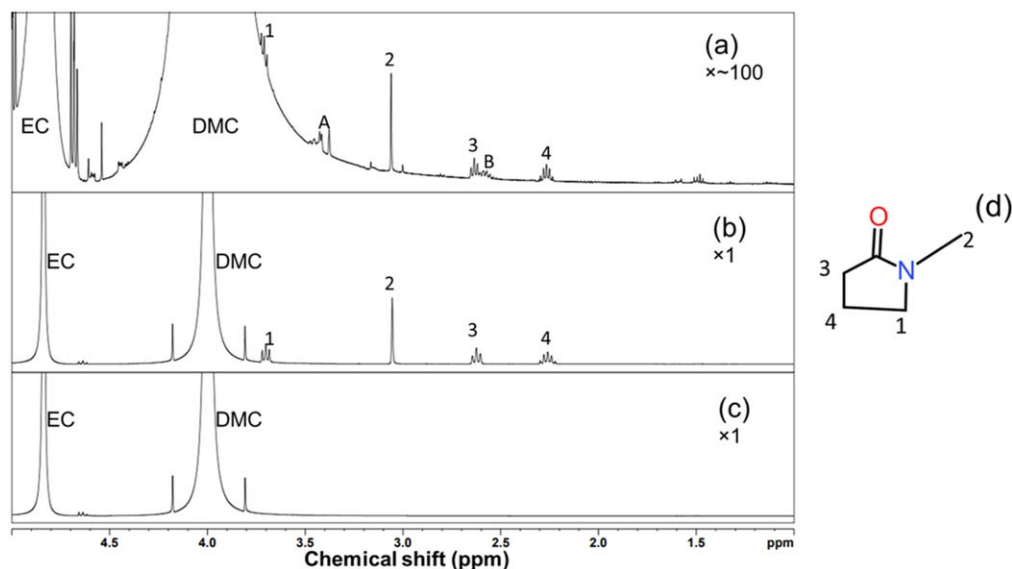


Figure 1. ¹H NMR spectrum of (a) electrolyte extracted from LMFP cells after formation. The cells were vacuum dried at 120 °C for 14 h before electrolyte filling and formation, (b) ¹H NMR spectrum of the original electrolyte of 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC + 1 wt% DTD intentionally spiked with 2 wt% NMP and (c) ¹H NMR spectrum of the pure original electrolyte of 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC + 1 wt% DTD. (d) Molecular structure of NMP and the corresponding position of the protons for the peaks labeled as 1, 2, 3 and 4 in the spectra. A and B are peaks from the reaction product between DTD and NMP.

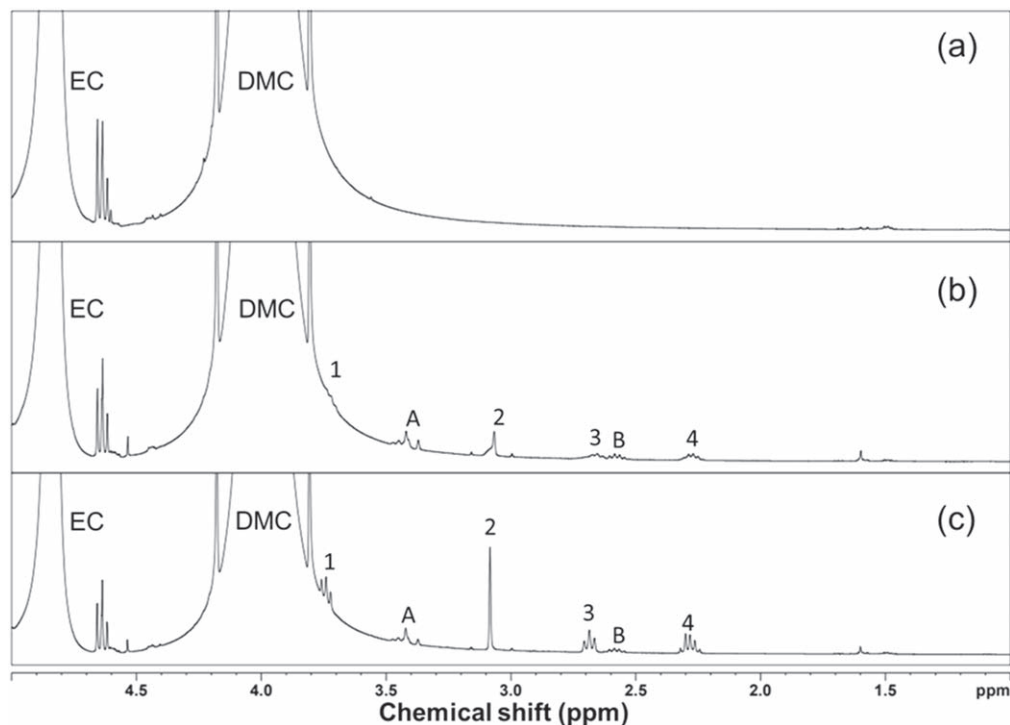


Figure 2. ^1H NMR spectrum of extracted electrolyte from (a) NMC532/graphite cell vacuum dried at 120 °C after “overfilling” (without formation), (b) LMFP/graphite cell vacuum dried at 150 °C after “overfilling” (without formation) and (c) LMFP/graphite cell vacuum dried at 120 °C after “overfilling” (without formation).

chosen to amplify the differences between the electrodes taken from different cells.

Results and Discussion

NMP detection.—This section introduces how NMP was found in the LMFP pouch cells and the method for identifying the presence of NMP in pouch cells.

The story starts from the regular electrolyte check for the previous mentioned LMFP/graphite pouch cells just after formation using 120 °C as baking temperature before filling with electrolyte (1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC + 1 wt% DTD). Since long term cycling was not needed, the overfilling method to extract electrolyte was used to identify the potential existence of some degradation products from the cell. Figure 1a shows the ^1H spectrum of the extracted electrolyte from LMFP/graphite pouch cells after formation where some unexpected peaks from 4.0 ppm to 2.0 ppm were found. Figure 1b shows the NMR ^1H NMR spectrum of the electrolyte intentionally spiked with 2% NMP while Fig. 1c shows the corresponding data for the pure electrolyte. Peaks in Fig. 1b labelled 1, 2, 3 and 4 arise from NMP and Fig. 1d clearly demonstrates the corresponding position of H responsible for each peak from NMP. A comparison of Figs. 1a and 1b clearly shows that electrolyte extracted from the LMFP/graphite cell after formation contains NMP at a level approximately equal to 0.02% (note the difference in Y-axis scales between Figs. 1a and 1b). The possibility of NMP originating from reaction products between the electrolyte and the charged electrode materials during formation is impossible, as none of the solvents or salts in the electrolytes nor the electrode materials contain nitrogen. The only plausible source of NMP is residual NMP from incomplete cathode drying. (Additionally, peaks labelled A and B in Fig. 1a were found to arise from the reaction product between DTD and NMP, a discussion of which will follow.)

To prove the previous hypothesis of incomplete drying resulting in residual NMP and to determine the amount of NMP dissolved in the electrolyte after the baking of the LMFP/graphite pouch cells, the overfilling method was employed to extract the electrolyte for

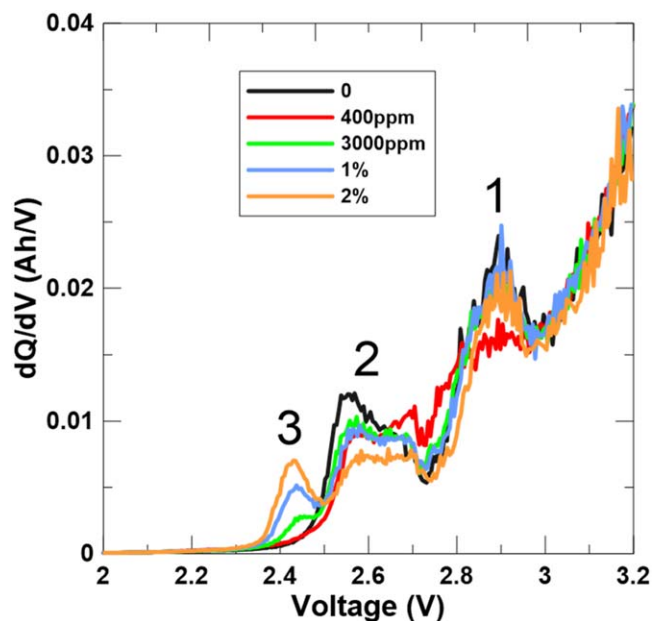


Figure 3. Differential capacity versus voltage during the initial stages of formation of NMC532/graphite cells using electrolyte of 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC + 1 wt% DTD with different concentrations of intentionally spiked NMP. The formation was done at 40 °C using current of C/20.

subsequent NMR tests. Figure 2 and Table I show the spectra and concentrations of NMP, respectively, in pouch cells treated in different ways. As mentioned earlier, the maximum temperatures for vacuum drying pouch cells are 120 °C for cells with PE separators and 150 °C for cells with PP separators. Even after vacuum drying at 150 °C for 14 h, 401 ppm of NMP still remained in the electrolyte extracted from an LMFP/graphite cell (no formation).

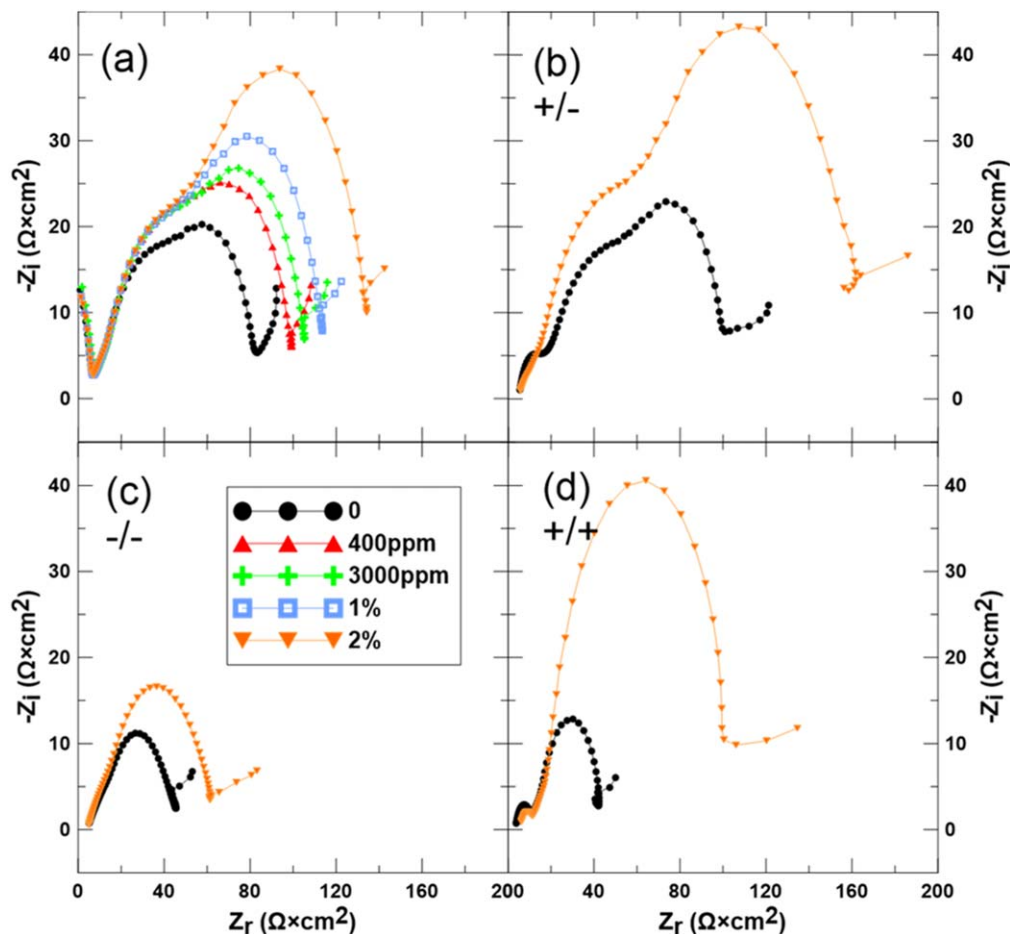


Figure 4. Nyquist plots of the (a) pouch cell, (b) corresponding full coin cell, (c) anode symmetric cell divided by 2 and (d) cathode symmetric cell divided by 2. Electrolyte used in the pouch cells was 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC + 1 wt% DTD spiked with different concentrations of NMP. The spectra were measured at 10 °C.

This is attributed to the high specific surface area of the LMFP cathode material ($\sim 26 \text{ m}^2 \text{ g}^{-1}$) and a drying protocol used in cathode production which was suitable for lower surface area materials like NMC. Furthermore, the NMP concentration decreased from 1498 to 201 ppm during formation, suggesting the instability of NMP in the battery system. Therefore, the impact of NMP on pouch cell performance needs to be addressed. Figure 2a and Table I show that the NMC532/graphite pouch cells were free of NMP and, consequently, were chosen for the subsequent experiments.

Results of using 2 wt% VC 1 wt% DTD as additives and concerns.—Figure 3 shows the differential capacity, dQ/dV , versus voltage, V, graph for NMC532/graphite pouch cells during the formation process. These cells used 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC + 1 wt% DTD with different concentrations of intentionally spiked NMP. In Fig. 3, peak 1 is the reduction peak of VC and peak 2 is the reduction peak of DTD. It is very clear that as the concentration of NMP increases, a new peak labeled as 3 becomes intense. Simultaneously, as peak 3 becomes more intense with additional NMP, peak 2 becomes less intense, probably suggesting that the added NMP causes degradation of DTD. It was initially thought that peak 3 was related to the direct electrochemical reduction of NMP, but this was later proved to be wrong as we will discuss later.

Figure 4a shows the EIS measurements for original pouch cells after formation. Figures 4b–4d show the results for the symmetric coin cells made from electrodes extracted from the original pouch cell after formation. Figure 4a shows that as the NMP concentration increases from 0 to 2%, the charge transfer impedance, inferred from

Table I. Concentration of NMP in ppm for the extracted electrolyte from various cells as described in the table. The overfilling method was used.

Cell types	NMP concentration in ppm
120 °C baked LMFP cells without formation	1498
120 °C baked LMFP cells with formation	201
150 °C baked LMFP cells without formation	403
120 °C baked NMC532 cells without formation	/

the large semi-circle of the EIS spectra, roughly doubled which would seriously affect the power performance. To identify which electrode was affected most by the existence of NMP, the EIS spectra of symmetric coin cells made from the electrodes of disassembled pouch cells at 3.8 V were measured. To verify the method of symmetric coin cell construction, the EIS spectra of full coin cells (one positive and one negative electrode) using the same electrodes as the symmetric cells were measured. Figure 4b shows the EIS results for the full coin cells to verify the method of symmetric cell, while Figs. 4c and 4d show the EIS spectra of the cathode/cathode and anode/anode symmetric cells containing electrodes taken from the identical pouch cell, respectively. Figure 4 illustrates that the charge transfer impedance of both the cathode and

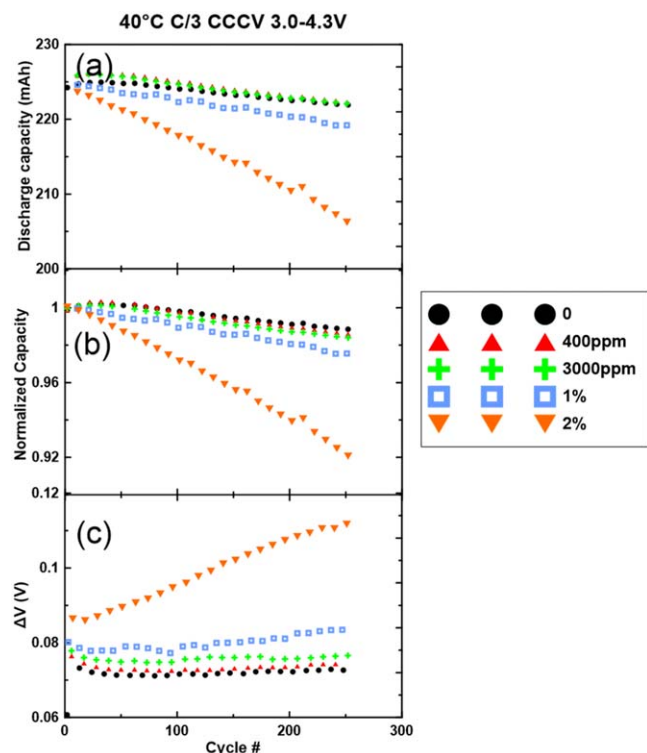


Figure 5. Cycle performance of the NMC 532 pouch cell used electrolyte spiked with different concentration of NMP: (a) Discharge capacity vs cycle number, (b) Normalized discharge capacity vs cycle number and (c) ΔV vs cycle number. Control electrolyte used here was 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC 1 wt% DTD. Cells were tested using a current corresponding to C/3 at 40 °C between 3.0 and 4.3 V.

the anode increased when there was 2 wt% NMP in the electrolyte compared the situation when there was no NMP. R_{ct} for the cathode increased by about a factor of 3.1, while R_{ct} for an anode increased by about a smaller factor of 1.4.

Figure 5 shows the results of charge-discharge cycling tests on NMC532/graphite pouch cells at 40 °C using charge and discharge currents corresponding to C/3. The upper cut-off voltage was 4.3 V. The cells used an electrolyte of 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC + 1 wt% DTD spiked with different NMP concentrations. Figures 5a and 5b shows that low concentrations of NMP did not obviously impact capacity retention during the first 250 cycles. However, consistent with the EIS results, Fig. 5c shows that the

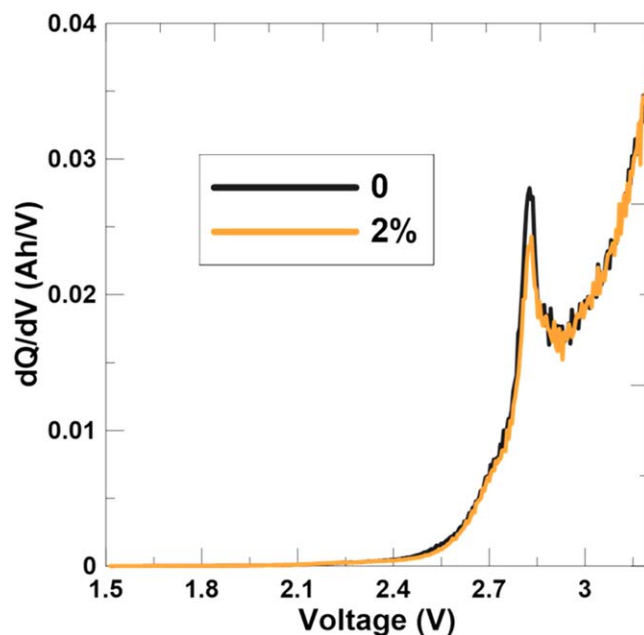


Figure 7. Differential capacity versus voltage during the formation of NMC532/graphite cells. The cells used an electrolyte of 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC with and without 2 wt%NMP. The formation was done at 40 °C at a current corresponding to C/20.

voltage polarization increased as the NMP content increased due to the increased charge transfer resistance at the electrodes. When the concentration of NMP increased to 2%, capacity retention of the pouch cells degraded markedly and the voltage polarization continued to increase with cycle count.

We now return to explain the peaks A and B which appeared in Figs. 1a and 2b–2c. Figure 6 shows the ¹H NMR spectrum for electrolyte mixed in an argon-filled glove box and then simply aged for 15 days. Peaks A and B appearing in the aged electrolyte verified that cell formation is not required to cause peaks A and B. This suggests a reaction between NMP and DTD, which produces something responsible for peaks A and B. To prove that idea, 0.1 g of DTD was added into 1 g of NMP in a small aluminum bottle followed by a quick shake for 5 s, and the mixed solvent was immediately transferred into the NMR tubes. Figure 6c clearly illustrates the solvent change simply by mixing NMP and DTD through the operation described in an argon-filled glove box. The transparent solvent changes to a gelatinous masses after 60 min of storage in an argon-filled glove box at room temperature.

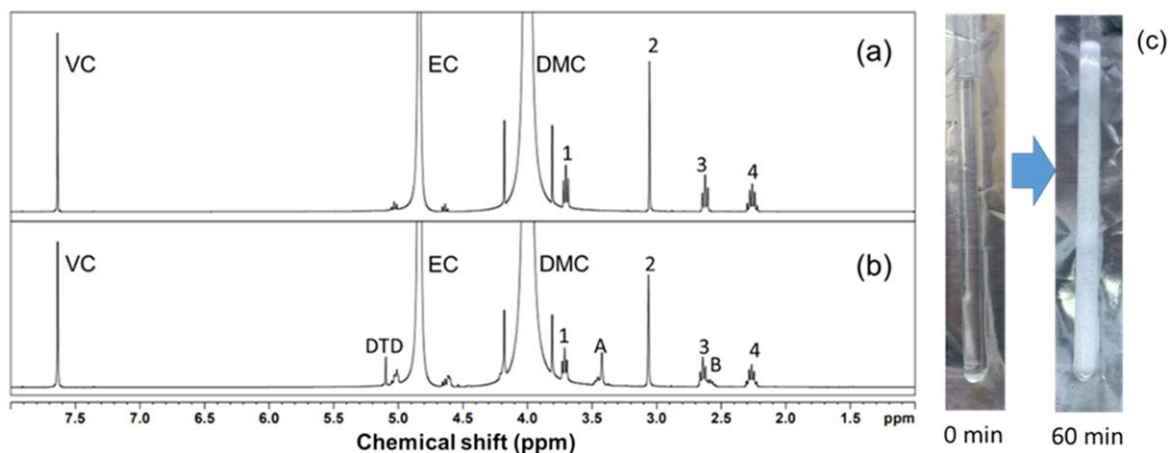


Figure 6. Results which show the reaction between DTD and NMP: (a) ¹H NMR spectrum of 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC with 2 wt% NMP electrolyte aged for 15 days, (b) ¹H NMR spectrum of 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC 1 wt% DTD with 2 wt% NMP electrolyte aged for 15 days and (c) Photographs showing the change of the solvent containing 1 g NMP and 0.1 g DTD.

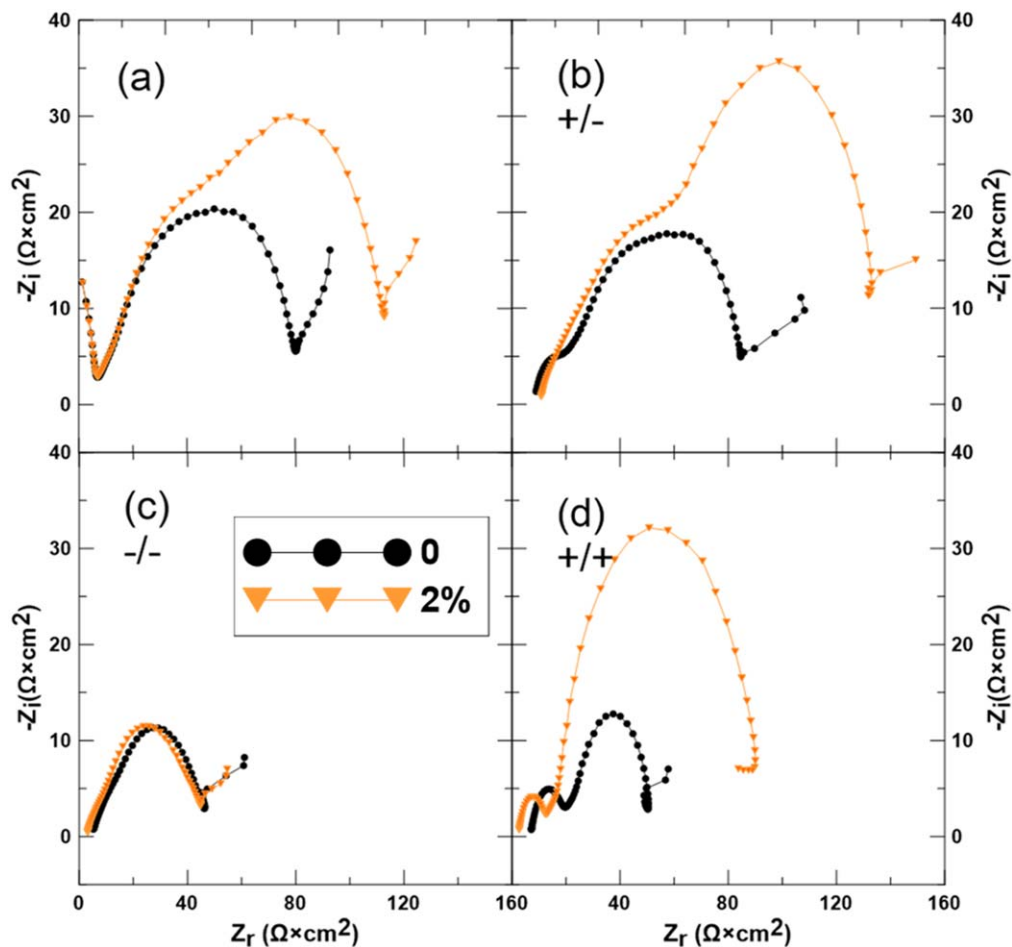


Figure 8. Nyquist plots of the (a) pouch cell, (b) corresponding full coin cell, (c) anode symmetric cell divided by 2 and (d) cathode symmetric cell divided by 2. Electrolyte used in the pouch cells was 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC spiked with and without 2 wt% NMP. The spectra were measured at 10 °C.

Results of using 2 wt% VC single as additives.—After understanding the potential of NMP to react with DTD, the question of whether NMP affects the impedance and cycle performance of pouch cells that do not contain DTD needs to be addressed. Consequently, the same experiments were conducted using 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC without DTD. Figure 7 shows the dQ/dV versus voltage graph of the NMC532/graphite pouch cells during formation and there is only a single reduction peak which is caused by VC. This finding illustrates that the new reduction peak labeled as 3 in Fig. 3 which appears in cells with both NMP and DTD disappeared in the cells without DTD.

However, even without the electrochemical reaction caused by the reaction product between DTD and NMP, the impedance of pouch cells still increases when NMP is added to cells with VC only as shown in Fig. 8a. Figure 8b shows the EIS results for the full coin cells while Figs. 8c and 8d show the EIS spectra of the cathode/cathode and anode/anode symmetric cells, respectively. Figures 8c–8d show that, the anode charge transfer impedance was not affected by NMP additions when DTD is not present while the cathode charge transfer impedance increased by about a factor of 2.5, suggesting that NMP itself has the potential to poison the cathode.

Figure 9 shows the charge-discharge cycling results for NMC532/graphite pouch cells using electrolytes of 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC with and without 2 wt% NMP. The same testing temperature (40 °C) and cycling protocol (C/3 3.0–4.3 V) as used for the cells described in Fig. 5 were selected for the cells without DTD. Similar to the results in Fig. 5 for the cells containing DTD, the capacity retention of the cells with 2% NMP

was degraded. With 2 wt% NMP the voltage polarization not only had a much larger initial value but also continues increasing with cycle number. As a result, NMP itself has the potential to increase the impedance of pouch cells and accelerate the capacity loss.

After 200 cycles, the electrolyte in these pouch cells was extracted for analysis to determine whether all the NMP was consumed or not. The MA extraction method was used to extract the electrolyte for NMR testing. Figure 10b shows that there are 2 peaks that are caused by MA. The relative peak height of NMP decreased after the cycling test. With the assumption that the concentration of the main solvent DMC used in the electrolyte was unchanged, the concentration of NMP was calculated through the main peak area ratio between NMP and DMC and the corresponding numbers of protons for each peak. The data suggests that the NMP concentration dropped from 1.97 wt% to 0.78 wt% in the electrolyte during the cycling.

Discussion.—Figures 11 and 12 show the EIS and cycle performance of LMFP/graphite pouch cells using an electrolyte of 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC + 1 wt% DTD as mentioned before. As shown previously in Table 1, the residual concentrations of NMP in these LMFP/graphite pouch cells that were vacuum dried for 14 h at either 120 °C or 150 °C were about 1500 ppm and 200 ppm, respectively, in cells overfilled with ~2 ml of electrolyte. As a result, in a normal fill of ~1 ml of electrolyte for these pouch cells, the actual concentrations of NMP would be doubled about 3000 ppm and 400 ppm, respectively. Based on the experimental results in NMC532/graphite pouch cells, the existence

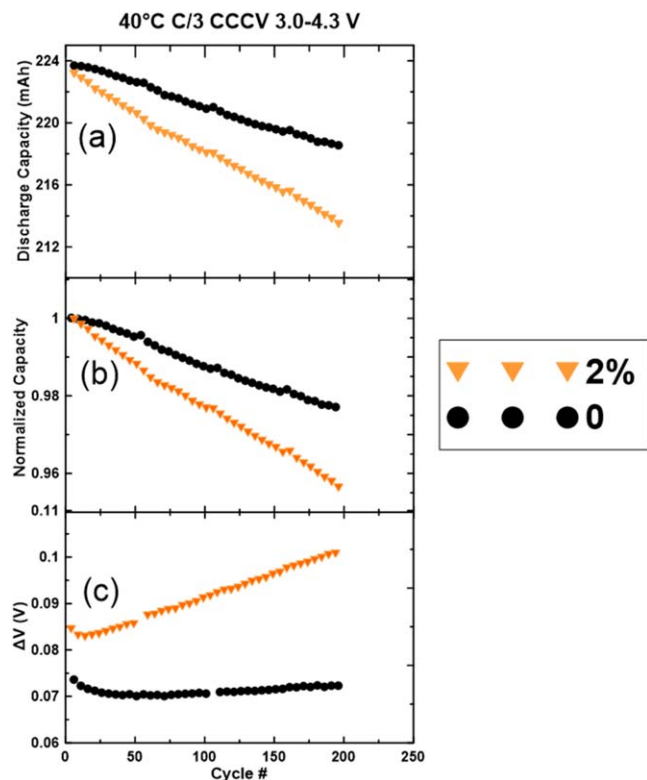


Figure 9. Cycle performance of the NMC 532 pouch cell used electrolyte with and without 2 wt% NMP: (a) Discharge capacity vs cycle number, (b) Normalized discharge capacity vs cycle number and (c) ΔV vs cycle number. Control electrolyte used here was 1.5 M LiPF_6 EC: DMC (3:7) + 2 wt% VC. Cells were tested with a current corresponding to C/3 at 40 °C between 3.0 and 4.3 V.

of trace amounts of NMP in the electrolyte will increase the impedance and not affect the capacity retention obviously in limited cycle numbers. This expectation matches the results for the LMFP/graphite pouch cells (Figs. 11 and 12) very well.

In a research laboratory, if cathodes are not dried correctly (perhaps due to haste of a researcher to get cells built before the end of the day, for example), the residual amount of NMP could poison the cathode and negatively impact testing results. For mass

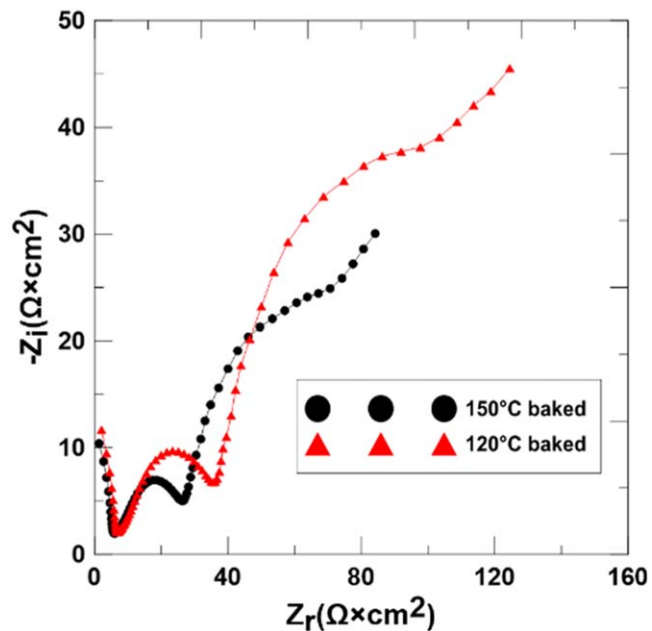


Figure 11. Nyquist plots of LMFP/graphite pouch cells using electrolyte of 1.5 M LiPF_6 EC: DMC (3:7) + 2 wt% VC + 1 wt% DTD. One cell was vacuum dried at 120 °C and the other was vacuum dried at 150 °C before electrolyte filling. The impedance data was measured at 10 °C and 50% SOC after the formation cycle of the cells.

production, attention must also be given to ensure minimal NMP remains, especially, in electrodes of high specific surface area like LMFP.

Conclusions

In this work, we first identified the existence of NMP and its instability during formation of LMFP/graphite pouch cells which have extremely high cathode specific surface area. To investigate the potential impact of NMP on lithium-ion cells, NMP-free NMC532/graphite cells were selected. After the investigation of the NMC532 pouch cells using electrolytes of 1.5 M LiPF_6 EC: DMC (3:7) + 2 wt% VC + 1 wt% DTD spiked with different concentrations of NMP, it was found that NMP has the potential to increase both cathode and anode impedance and react with the DTD.

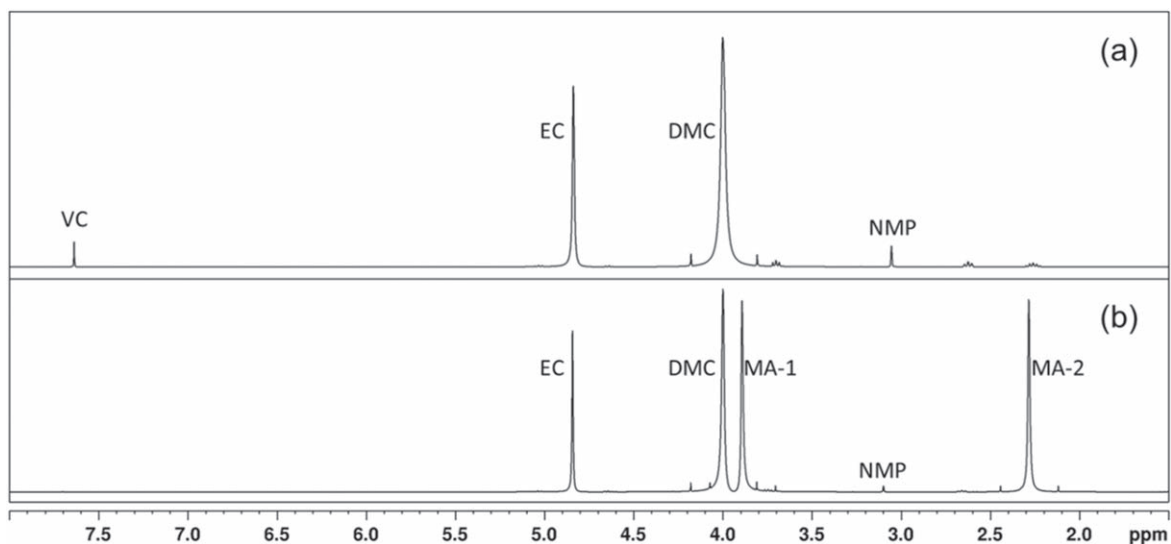


Figure 10. ^1H NMR spectrum from (a) original electrolyte of 1.5 M LiPF_6 EC: DMC (3:7) + 2 wt% VC with 2 wt% NMP and (b) MA extracted electrolyte from NMC532/graphite pouch cells after 200 cycles.

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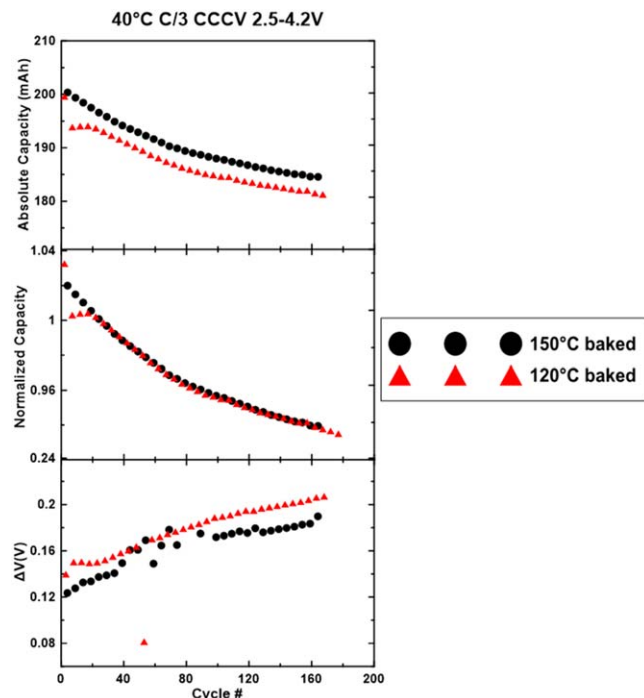


Figure 12. Cycle performance of the LMFP/graphite pouch cells using electrolyte of 1.5 M LiPF₆ EC: DMC (3:7) + 2 wt% VC + 1 wt% DTD: (a) Discharge capacity vs cycle number, (b) Normalized discharge capacity vs cycle number and (c) ΔV vs cycle number. One cell was vacuum dried at 120 °C and the other was vacuum dried at 150 °C before electrolyte filling. Cells were tested with a current corresponding to C/3 at 40 °C between 2.5 and 4.2 V.

Consequently, cells using electrolyte spiked with 2 wt% NMP without DTD were also tested and compared to the control cells. The results of electrochemical impedance spectroscopy on symmetric cells show that NMP itself can independently increase the charge transfer impedance of the cathode, while the impedance increase of anode is due to the reaction product between NMP and DTD. Charge-discharge cycling results show that relatively high concentrations of NMP will cause serious capacity loss in both cases with and without DTD. Even though trace amounts of NMP may not seriously affect the capacity loss in a limited number of cycles, it will still increase the impedance and damage the power performance of cells. As a result, it is crucial to establish the appropriate procedure for completely elimination of NMP residue in lithium-ion batteries, both in laboratory and industrial settings, to mitigate these effects.