Typical measurements of parasitic heat flow in lithium-ion cells can determine the magnitude of heat flow but cannot differentiate between different types of reactions. This causes difficulty when comparing cells that contain different coatings and solvent systems, which may affect parasitic reaction pathways. In this work, a new technique to measure the net enthalpy change ($\Delta H$) of parasitic reactions in lithium ion cells is introduced. Isothermal microcalorimetry and precision current measurements are used to make in-situ, non-destructive measurements of heat flow and parasitic current during high-voltage holds. The results are used to determine $\Delta H$ of parasitic processes in NMC532/graphite pouch cells. Effects of positive electrode coating, solvent, and upper cutoff voltage are explored. Solvent systems of organic carbonates with and without methyl acetate, and fluorinated carbonates are also investigated. Each solvent system yielded a unique trend of $\Delta H$ with increased voltage, and results were consistent between pair cells. Cells with organic carbonates showed consistent $\Delta H$ between voltages, while cells containing methyl acetate showed decreasing $\Delta H$. Cells containing fluorinated carbonates showed increasing $\Delta H$ with increased voltage. The observed trends in $\Delta H$ and solvent systems as well as future developments of this method are discussed.

However, this work is to introduce a method that is capable of both determining the magnitude of parasitic reactions as well as the net enthalpy change of parasitic reactions in cells. This technique allows for the same information to be collected as with previous cycling methods in addition to information about the types of chemical processes occurring in cells. First, a proof-of-concept study was performed using stable, reversible redox shuttle molecules, which demonstrates the capability of isothermal microcalorimetry to accurately measure the expected zero net enthalpy of reaction for the redox shuttle, within error. We then employed the technique to probe the enthalpies of parasitic reactions in cells with different positive electrode coatings and electrolytes at varying potentials.

**Experimental**

**Pouch cells.**—Dry, sealed single-crystal NMC532/artificial graphite 402035-sized pouch cells (230 mAh, balanced to 4.4 V) from Li-Fun Technology (Zhuzhou City, Hunan Province, PRC) were used in this work. Cells used in shuttle experiments had no coating on the positive electrode. For voltage-hold experiments, cells with both coated and uncoated NMC532 were used. The details of the coating were not disclosed by the manufacturer, but were recently studied using X-ray photoelectron spectroscopy and electron energy-loss spectroscopy by Ma et al. 7 The results show the coating on the materials is Ti-based and may be TiO2. Electrolytes contained 1.2 M LiPF6 (BASE; purity 99.94%, water content 14 ppm) in various solvents. Cells used in shuttle experiments either contained 0.1 M 1,4-di-tert-butyl-2,5-dimethoxybenzene (DBB), (purchased from Keystone Scientific, then crystallized from ethanol to obtain a white solid), or 1,4-dimethyl-2,5-dimethoxybenzene (DMB) (synthesized following a published procedure Reference 10) in ethylene
carbonate (EC):ethyl methyl carbonate (EMC):dimethyl carbonate (DMC) (25:5:70 wt ratio) (BASF). Cells used for voltage holds contained either EC:EMC:DMC (25:5:70 wt ratio), (EC:EMC:DMC):methyl acetate (MA) (60:40 wt ratio) (BASF, 99.99%) or fluoroethylene carbonate:bis(2,2,2-trifluoroethyl)carbonate (FEC:TFEC) (30:70 wt ratio) (FEC: BASF, 99.94%; TFEC: HSC Corp., China, 99.8%). Cells containing EC:EMC:DMC with and without MA also contained 2 wt% vinylene carbonate (VC) (BASF, > 99.8%, water content < 100 ppm) and 1% PES + 1% DTD. Table I summarizes the cells used in each experiment in this work by positive electrode type (coated or uncoated NMC 532) and corresponding electrolytes.

Before filling, cells were cut beneath the heat seal and heated under vacuum for 14 h at 100 °C to remove residual moisture. The cells were then transferred into an argon-filled glove box without exposure to air, filled with 0.84 mL of electrolyte, and sealed with a compact vacuum sealer (MSK-115A, MTI Corp.) for 4 s at 165 °C, −90 kPa. Cells were then clamped between rubber spacers to displace any gas formed in the electrode stack during formation and held at 1.5 V for 24 h at room temperature to ensure complete electrode wetting. A Maccor 4000 series cycler (Maccor Inc.) was used for the formation cycle: Cells were charged at 10 mA (~C/20) to 4.2 V, held at top of charge for 1 h, then discharged to 3.8 V and held for 1 h. Cells used in shuttle experiments were charged to 3.5 V and held for 1 h so as not to activate the shuttle molecules. Cells were then transferred back into the argon glove box, cut open to release any gas formed, and vacuum sealed again using the same sealing conditions.

### Isothermal microcalorimetry

After formation, cells for isothermal microcalorimetry measurements were inserted into a TAM III Microcalorimeter at 40.0 °C (TA Instruments: stability ± 0.0001 °C, accuracy ± 1 μW, precision ± 1 nW) and connected to a Maccor 4000 series cycler. All specifications and information regarding microcalorimetry calibration, cell connections, and operation procedures can be found in a previous publication. Cells were cycled 4 times from 3.0 V to 4.2 V to ensure a well-formed SEI was present. Cells were then charged between 4.0 V and different upper cutoff limits: 4.2 V (twice), 4.4 V (twice), and again to 4.2 V at 1.5 mA to compare previous cycling methods to voltage holds. Afterward, cells were connected to Keithley 2602B source meters (Keithley Instruments Inc.) and underwent voltage holds at 3.8 V, 4.2 V, 4.3 V, and 4.4 V for 100 h while in the microcalorimeter. After the series of holds, some cells were connected to a Novonix 5V, 2A High Precision Cycler (Novonix, 177 Bluewater Road, Bedford, NS, Canada) and held at 4.4 V for 95 h while in the calorimeter.

Cells used for shuttle experiments were inserted into the calorimeter and connected to the Maccor cycler, charged to 3.7 V at 10 mA, then charged at 2 mA until the end of the experiment. A description of the analysis techniques is provided in the Results and discussion section.

### Results and Discussion

#### Reversible redox shuttle

To investigate whether isothermal calorimetry could be used to accurately measure reaction enthalpies in a real cell, redox shuttle molecules with varying stability were used: 1,4-di-tert-butyl-2,5-dimethoxybenzene (DDB), 1,3-di-tert-butyl-2,5-dimethoxybenzene (DDBB), and 1,4-diethyl-2,5-dimethoxybenzene (DBDB). DDB was found by Moshurchak et al. to have a shorter lifetime of ~24 overcharge cycles under the same conditions. Moshurchak found that DMB also has limited stability, lasting 13 overcharge cycles. Figure 1a shows a schematic of an activated redox shuttle operating in a Li-ion cell under open circuit conditions. When the positive electrode of a cell is at a sufficiently high potential, the shuttle molecule, S, oxidizes to its radical cation form, S⁺. Upon migration to the negative electrode, S⁺ reduces back to S, yielding a net reaction enthalpy change of 0 kJ mol⁻¹. In open circuit voltage (OCV) conditions, this electron transfer causes an internal charge migration to the negative electrode, S⁺ + e⁻ → S.

![Figure 1](image_url)

**Figure 1.** A redox shuttle process in a) open circuit voltage conditions b) closed circuit with electrode equilibrium, and c) closed circuit charge. Ic and Ip correspond to cell charging current and shuttle current, respectively.
The internal current formed by the charge transfer is called the parasitic current, \( I_p \). In these cases, the redox shuttle does not ‘harm’ the cell but is still a non-ideal electrochemical process within the cell. In closed circuit conditions, such as when charging the cell, the charge balance due to the redox shuttle is supplied through the external circuit, as shown in Figure 1b.

The heat flow due to all non-ideal reactions in a cell (including redox shuttle reactions) is defined as the parasitic heat flow. When current is applied to a cell during charge and discharge, the heat flow is given by

\[
\dot{q} = |\eta| + \frac{T I}{e} \left[ \left( \frac{d x}{d x} \right)_\text{a} - \left( \frac{d x}{d x} \right)_\text{s} \right] + \dot{q}_p \quad [1]
\]

where \( I \) is the applied current, \( \eta \) is the cell overpotential, \( e \) is the electron charge, \( T \) is the temperature, \( x_a \) and \( x_s \) are the positive and negative electrode entropies, respectively, \( x \) is the stoichiometric content of lithium in the electrode materials, and \( \dot{q}_p \) is the parasitic heat flow.\(^{15}\) In the absence of hysteresis, the cell overpotential is the applied current multiplied by the internal resistance of the cell (IR). The first two terms in Equation 1 are then proportional to \( \sim I^2 \) and \( I \), respectively. Thus, the heat flow, \( \dot{q} \), of a cell with negligible current \( I \) actively charging or discharging the cell (such as open circuit, voltage hold) equivalent to the parasitic heat flow, \( \dot{q}_p \). The parasitic heat flow has contributions from the parasitic current, \( I_p \), and the change in enthalpies of each parasitic process, given by

\[
\dot{q}_p = I_p V + \sum_i k_i (-\Delta_i H) \quad [2]
\]

where \( V \) is the cell voltage and \( k_i \) and \( \Delta_i H \) are the rate and enthalpy change of each reaction pathway.\(^{16}\) Since the enthalpy change for a reversible redox shuttle is 0 kJ mol\(^{-1}\), the parasitic heat flow from cells in Figures 1a or 1b should be \( I_p V \).

The shuttle molecules used in this study had reported oxidation potentials of 3.85 V to 4.1 V vs Li/Li\(^+\), or approximately 3.6 V to 4.0 V vs graphite, depending on the state of charge of the graphitic electrode.\(^{14}\) Cells were charged using a constant current (CC) rate of 10 mA (C/20) to 3.7 V, at which time a CC rate of C/100 (2 mA) was applied. If all 2 mA of supplied current went into redox shuttle cycling when operated at above 3.7 V, the heat flow would be approximately 7.4 mW. If a portion \( x \) of the current acted to further charge the cell and the remainder \( y \) was used by the shuttle, a situation shown in Figure 1c would arise, where \( I_p \) is the cell charging current, \( I_p \) is the shuttle current, and the measured heat flow would be \( I_p V < 7.4 \) mW.

Figures 2a, 2b, and 2c show the results from cells containing DDB, DBDB, and DMB, respectively, in the columns. Voltage vs time plots are shown in row i) for each cell after shuttle activation (black). In these experiments, the cell voltage increased slowly, indicating that a portion of the supplied current was charging the cell, while the majority of the current was used in redox shuttle cycling. The voltage increase was less for DDB and DBDB compared to DMB, indicating that DMB is less stable compared to DDB and DBDB. For comparison, voltage vs time data for a cell without shuttle molecules is shown in row i) as a dashed green line in each panel. The charging current, \( I_c \), does not contribute to the shuttle heat flow (\( I_p V \)) and is calculated using the differential capacity (dQ/dV\(^{-1}\)) of a control cell (same cell and electrolyte without DDB) charged at a rate of C/20. The differential voltage (dV dt\(^{-1}\)) of the DDB-containing cell by

\[
I_c = \left( \frac{dQ}{dt} \right)_c = \left( \frac{dQ}{dV} \right)_\text{control} \left( \frac{dV}{dt} \right)_\text{shuttle} \quad [3]
\]

\( I_c \) was then subtracted from the total current of 2 mA to calculate \( I_p V \). Row ii) in Figure 2 shows the theoretical \( IV \) in blue, corrected \( I_p V \) in black, and the measured heat flow in red. \( I_p \) was approximately 5% of the charge current, or 0.1 mA for DDB and DBDB and ~20% (0.4 mA) for DMB. At this rate, the entropic heat flow of electrode materials and overpotential heat flow due to charging the cell would be

**Figure 2.** a-i) Voltage versus time during a 2 mA (C/200) charge for a cell with the DDB redox shuttle activated (black) and a cell without DDB (dashed green). ii) Calculated \( IV \) (blue), measured heat flow (red), and \( I_p V \) (black). iii) Calculated enthalpy per mole of electrons supplied to the shuttle. These plots are shown for DBDB and DMB in columns b and c, respectively.
on the order of 1 pW, a value within the calorimeter’s uncertainty, and is three orders of magnitude smaller than the measured heat flow.\textsuperscript{8,16} The net enthalpy per mole of electrons transferred by \( I_p \) will be referred to as \( \Delta H_e \) and is a measure of the net reaction enthalpy of all reactions occurring in the cell per mole of electrons in the parasitic current. \( \Delta H_e \) was then calculated from Equation 2 as the difference between the measured heat flow and \( I_p V \) divided by the rate of electron transfer (\( I_p \) is proportional to the rate of reaction, \( k \), by the one-electron redox process):

\[
\Delta H_e = \frac{I_p V - \dot{q}}{I_p} F
\]

where \( \dot{q} \) is the total heat flow and \( F \) is Faraday’s constant. The calculated enthalpy per mole of electrons is shown in row iii) of Figure 2. DDB and DBDB showed enthalpies near 0 kJ mol\(^{-1}\), while the enthalpy of DMB was \( \sim 30 \pm 10 \) kJ mol\(^{-1}\). In this case, a non-zero enthalpy does not yield the enthalpy of reaction for the decomposition of a shuttle molecule. To calculate \( \Delta H \) for a single decomposition, one would need to know the number of transits a single molecule made on average before decomposition. A smaller \( \Delta H \) indicates greater shuttle stability. No electrolyte additives were used in these cells, meaning there could be a small amount of parasitic reactions occurring (especially in DDB with a higher redox potential) in addition to the redox shuttles, which would contribute to heat flow and further offset the net enthalpy. Shuttlles that were previously reported to be more stable had close to the expected net enthalpy of 0 kJ mol\(^{-1}\), while less stable DMB had a value slightly higher than expected. The observed value of \( \sim 10 \pm 10 \) kJ mol\(^{-1}\) for the more stable shuttle molecules was assumed to be reasonable for this proof-of-concept experiment. The uncertainty in the shuttle enthalpy can be considered when evaluating other cells when parasitic reactions with non-zero enthalpy are analyzed.

**Parasitic heat flow**—To investigate the enthalpy of parasitic reactions in lithium-ion electrolytes at different voltages, three electrolyte solvent mixtures and two cell types were used. Work in a previous publication by Glazier et al. showed that changing the positive electrode cell chemistry or positive electrode coatings had a substantial effect on parasitic heat flow in cells, but capacity retention in long-term cycling did not necessarily follow the observed trend in parasitic heat flow.\textsuperscript{5} The authors hypothesized that positive electrode coatings may have contributed to different parasitic chemical pathways. Therefore, here we decided to investigate both coated and uncoated single-crystal NMC532/artificial graphite cells. The effects of different coatings, compositions, and morphologies can be evaluated in future studies. The solvent blends of EC:EMC:DMC (25:5:70 wt ratio) and EC:EMC:DMC:MA (15:3:42:40 wt ratio) were chosen to explore changes in enthalpy when adding a co-solvent to a known system, particularly with increased voltage. When added as a co-solvent, MA can lead to a small reduction in capacity retention during long-term cycling compared to cells with EC:EMC:DMC electrolytes.\textsuperscript{7,17} The studies suggested that MA leads to increased electrolyte oxidation and gas production at the positive electrode at lower voltages than cells without MA, indicating a difference in parasitic reaction processes. We hypothesized that a solvent system with an entirely different composition would yield different reaction enthalpies. Thus, FEC:TFEC was studied in comparison to the organic carbonate system. Fluorinated carbonates can improve capacity retention and lower parasitic heat flow at high voltages, but perform poorly in lower voltage ranges.\textsuperscript{16,18-20} To create robust SEI layers and simplify or reduce the number of possible reaction pathways, additive combinations of 2% VC and 1% DTD (for EC:EMC:DMC with and without MA) and 2% PES and 1% DTD (for FEC:TFEC) were chosen.

Before measuring the enthalpies of reactions, cells underwent slow (1.5 mA, ~C/130) charge-discharge cycles, from 4.0 V to 4.2 V and 4.4 V, to extract the magnitude of the parasitic heat flow as a function of voltage. The methods used here are outlined in previous publications, and utilize the reversibility of heat flow due to entropy between charge and discharge (Equation 1) to obtain an average parasitic heat flow as a function of cell voltage during each charge-discharge process.\textsuperscript{7,8} This method has demonstrated that normally increased magnitude of parasitic heat flow directly correlates to decreased capacity retention during cycling, as well as decreased coulombic efficiency and higher charge end point capacity slippage. However, this correlation may not exist when many chemical parameters are changed and compared at once, potentially changing the contribution of reaction enthalpy to the parasitic heat flow in Equation 2.

Figure 3 shows the parasitic heat flow during two cycles to 4.2 V and two cycles to 4.4 V (Figures 3a, 3b and Figures 3c, 3d, respectively). Heat flows from cells with coated NMC532 are shown as solid lines, and from cells with uncoated NMC532 as shown as dashed lines. Heat flows from cells with EC:EMC:DMC are shown in black, EC:EMC:DMC:MA in blue, and FEC:TFEC in red. This color scheme is repeated through the rest of this work. Cells containing MA showed significantly more parasitic heat flow than cells with EC:EMC:DMC, as we expected based on the results of previous studies.\textsuperscript{7,17} Cells with FEC:TFEC demonstrated an inconsistent trend between coated and uncoated cells during the two cycles at 4.4 V, and showed higher parasitic heat flow at lower voltages, consistent with previous findings.\textsuperscript{16,19} However, only qualitative comparisons can be made between organic carbonates and fluorinated carbonates using the charge-discharge method without knowing if the enthalpies of the parasitic reactions differ. In cells with EC:EMC:DMC, both with and without MA, the cells containing coated NMC532 showed lower parasitic heat flow than those containing uncoated NMC532.

Figure 4 shows a summary of the mean parasitic heat flow per cycle for all of the voltage windows studied. Parasitic heat flow often decreases over the course of an experiment due to a buildup of SEI products from parasitic reactions. Although the rate of these reactions decreases over time, the cell impedance rises with continued SEI formation. Sometimes, however, this is not the case. Cells with an uncoated NMC532 positive electrode with EC:EMC:DMC:MA and both coated and uncoated NMC532 with FEC:TFEC-based electrolytes had higher parasitic heat flow during the last cycle to 4.2 V than during the second cycle to 4.2 V, indicating less passivating SEI layers. Additionally, parasitic heat flow increased between subsequent cycles to 4.4 V in uncoated cells with FEC:TFEC electrolytes, but decreased in coated cells. Therefore, it was apparent there were differences in the types of reactions occurring in cells with different coatings but otherwise identical chemistries.

Consider Figure 5a, in which electrolyte species S oxidizes at the positive electrode to form S\(^{2-}\), then reduces at the negative electrode into new species X, rather than returning to S, in an irreversible fashion. This is an example of a “cross-talk” reaction, and here the net enthalpy of this reaction could be non-zero. The process leads to an internal current, \( I_p \), and a self-discharge process maintains charge balance in the cell. Assuming only the cross-talk process is present in a cell, the parasitic heat flow would be given by

\[
\dot{q}_p = I_p V + k \Delta H
\]

where \( I_p \) is the parasitic current, \( k \) is the rate of the cross-talk reaction and \( \Delta H \) is the reaction enthalpy. When in closed circuit (such as during a voltage-hold shown in Figure 5b), the result is the same, but the charge balance can be applied to the cell through the external circuit. \( I_p \) is then known, and the parasitic reaction enthalpy per mole of electrons in the parasitic current (\( \Delta H_e \)) can be calculated as

\[
\Delta H_e = \frac{(I_p V - \dot{q}_p)}{I_p} F
\]

Equation 6 is an oversimplification, as numerous reactions could occur in a real cell, and not all parasitic reactions produce a parasitic current. For example, Figures 5c to 5d demonstrate examples of parasitic reactions that produce a parasitic current: c) transition metal dissolution and d) solvent oxidation at the positive electrode. Figures 5e and 5f demonstrate examples of reactions that do not produce a parasitic current: e) a solvent-oxygen reaction and f) solvent reduction. The case

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Figure 3. Calculated parasitic heat flow of cells with EC:EMC:DMC-based electrolytes (black), EC:EMC:DMC:MA-based electrolytes (blue), and FEC:TFEC-based electrolytes (red) cells during two cycles at 4.2 V (a,b) and 4.4 V (c,d). Results for cells with coated NMC532 are shown as a solid line and cells with uncoated NMC532 are shown as a dashed line.

Figure 4. Mean parasitic heat flow per cycle for cells containing EC:EMC:DMC-based electrolytes (black), EC:EMC:DMC:MA-based electrolytes (blue), and FEC:TFEC-based electrolytes (red). Results for cells with coated NMC532 are shown as a solid line and cells with uncoated NMC532 are shown as a dashed line.

In Figure 5f will lead to no parasitic current, even under closed circuit conditions, if the graphite electrode is in a two-phase plateau (e.g. stage 1 LiC₆ and stage 2 LiC₁₂) where the potential remains constant despite differing lithium content. Equation 6 does not directly account for reactions that do not produce a parasitic current, i.e. the proposed reduction of EC with lithium ions and electrons to make lithium ethylene dicarbonate and ethylene at the negative electrode.²¹⁻²³ The treatment of Equation 6 must be considered carefully, and the effects of the different reactions in Figure 5 will be investigated in future work. In this work, the measurable quantity is defined as the net enthalpy of all reactions occurring in the cell per mole of electrons in the parasitic current, called ΔHₑ. Therefore, changes in the calculated enthalpies can either be due to different reaction pathways or to changes in the ratio of different reactions. For example, if the rate of some endothermic solvent reduction reaction, as pictured in Figure 5f, increases more than a solvent oxidation reaction in Figure 5d in a cell, the magnitude of the net enthalpy per mole of electrons will increase disproportionately due to the increase in rate of reduction without a change in parasitic current.

Voltage-hold experiments.—Cells in the calorimeter were connected to Keithley source-meters controlled with in-house software. Cells were charged to 3.8 V and held for 100 h. Then cells were charged to 4.22 V, held for 24 h and then held at 4.2 V for 100 h. Before each subsequent 100-h hold at 4.3 V and 4.4 V, cells were also charged to 20 mV higher than the hold voltage and held for 24 h. This 24-h charge-hold aimed to ensure the lithium concentration in the electrodes would reach equilibrium early in the 100 h hold. Figure 6 shows the measured heat flow (red) and IV (black) for each voltage-hold in cells having EC:EMC:DMC-based electrolytes with and without MA. The high IV noise level is due to large fluctuations in current supplied to the cells. Each data point represents the average of measurements recorded every 5 s over 3 min intervals. Without this...
averaging of 36 data points, the noise level in the current was 75 μA, leading to a noise in \( I_pV \) of approximately 300 μW. It was observed that cells with MA had higher parasitic heat flow and a larger parasitic current than cells without MA, especially at high voltage. It was also observed that the majority of the measured heat flow was due to the \( IV \) term. This could help justify the use of the previous charge-discharge methods if the difference in parasitic heat flow between cells is significant, as observed in the case of adding MA. Similar voltage-hold measurements (not paired with calorimetry) performed by Vadivel et al. on coin cells showed that cross-talk-like reactions accounted for a large portion of the parasitic current at high voltage.\(^{24}\)

Approximately 50 h into each hold, the current appeared to reach a decay rate comparable to the decay rate of the heat flow: When \( IV \) decays faster than heat flow some current is still charging the cell to reach a homogeneous Li concentration in the electrodes. After 50 h it was assumed all current was used in parasitic reaction charge balance such that \( I = I_p \) and therefore \( \dot{q} = \dot{q}_p \). In each case \( I_pV \) was larger than the measured heat flow. Since less heat flow was measured than produced by \( I_pV \), the parasitic reaction enthalpies must be net endothermic (positive \( \Delta H_e \)). The noise level shown in Figure 6 is too large to deduce any quantitative information from this representation of the data. However, since the accuracy of the Keithley current sources are better than 0.1%, integrating \( I_pV \) over the final 50 h of each hold can be used to accurately represent the parasitic energy produced by maintaining charge balance at each voltage.\(^{25}\) The integrated \( I_pV \) over time, which we term cumulative \( IV \) energy (\( E_{IV} \)), and the integrated \( \dot{q} \), here called cumulative parasitic energy (\( E_p \)), can be used to reduce the noise over the length of the hold and obtain quantities with relatable units to enthalpy. The total charge supplied during the voltage hold is the parasitic capacity (\( Q_p \)). Equation 6 can then be rewritten to obtain the net enthalpy per mole of electrons

\[
\Delta H_e = \frac{\int I_pV dt - \int \dot{q} dt}{\int I_p dt} F = \frac{E_{IV} - E_p}{Q_p} F
\]  

Figure 5. Simplified parasitic reaction schemes: a) open-circuit oxidation/reduction cross-talk. Diagrams b) to d) are shown in voltage hold conditions: b) oxidation/reduction cross-talk, c) transition metal dissolution, d) solvent oxidation at the positive electrode. Diagrams e) and f) involve no internal current in voltage hold (self-discharge in OCV): e) solvent-oxygen reaction, f) solvent reduction at the negative electrode.

Figure 6. \( IV \) (black) and measured heat flow (red) in cells with coated NMC532 with EC:EMC:DMC-based electrolytes (left column) and with EC:EMC:DMC:MA-based electrolytes (right column) cells at different upper cutoff voltages: 3.8 V (a,b), 4.2 V (c,d), 4.3 V (e,f), and 4.4 V (g,h).
Figure 7 shows the integrated results starting after 50 h during each voltage hold. Figures 7a, 7b, 7c and 7d show $E_p$, $E_{IV}$, the difference between these energies, termed the cumulative reaction energy ($E_r$), and $\Delta H_r$, respectively. Results are plotted after the 60 h point since the noise introduced in $\Delta H_r$ was large during the first 10 h of the integration when fewer data points were used. Columns i, ii, iii, and iv correspond to voltage holds at 3.8 V, 4.2 V, 4.3 V, and 4.4 V, respectively. In almost every case cells with coated NMC532 showed lower $E_p$ than cells with uncoated NMC532, largely due to the smaller parasitic current present in these cells, observed in row b of Figure 7. In the case of cells with MA, at 4.4 V the pair cells with coated NMC532 yielded inconsistent results for $E_p$ and $E_{IV}$; otherwise there was very good agreement between pair cells. Results for $\Delta H_r$ became more consistent between pair cells as the hold voltage increased, due to the higher signal to noise ratio in $I_p$. Regardless, good qualitative agreement exists between $\Delta H_r$ for pair cells at each voltage. Although MA-containing cells with coated NMC532 at 4.4 V yielded inconsistent results for $E_p$ and $E_{IV}$, the calculated $\Delta H_r$ was the same. This result suggests that the rate of reactions in one MA cell increased significantly over the other, but the reaction processes were the same in both cells. MA has been found to produce significant amounts of gas in cells, so this may have been due to gas in part of the electrode stack in one cell, decreasing the active surface area of that cell. The agreement in $\Delta H_r$ between pair cells at high voltage and consistent $\Delta H_r$ between pair cells with different rates of reactions was quite encouraging, considering the noise level in $I_p$. Another notable observation was the large difference in $\Delta H_r$ at 3.8 V between organic carbonate cells and fluorinated carbonate cells. As voltage increased, the enthalpy changed for some compositions while others appeared to stay the same. To make more quantitative trends at low voltages, a higher precision measurement of $I_p$ is needed.

To investigate whether trends could be found in the integrated data and $\Delta H_r$, Figure 8 shows a summarized view of the curves in Figure 7. Figure 8a shows the cumulative $E_p$ between 50 and 100 h. Figure 8b shows the cumulative $E_{IV}$ and the cumulative $E_r$ over the same time interval (which total to $E_p$) and Figure 8c shows $\Delta H_r$. Cells with coated NMC532 are shown as dark, narrow bars, and cells with uncoated NMC532 are wide, lighter bars behind the data for the cells with coated NMC532. Values for the energies represent the total integration over the final 50 h of each hold, and values for $\Delta H_r$ in Figure 8c are representative of the average value of $\Delta H_r$ during the final 40 h of each voltage hold. The first 10 h were not included in this average due to the noise level at the beginning of the integration. Error bars represent the range of values between pair cells, and again show very good agreement.

In every case in Figure 8c, $\Delta H_r$ was lower for cells with uncoated NMC532 than for cells with coated NMC532. This may give cells with uncoated NMC532 a disadvantage when comparing cycling
heat flow results, as any reactions that occur in cells with uncoated NMC532 are less endothermic. At 3.8 V, cells with coated and uncoated NMC532 having EC:EMC:DMC-based electrolytes had very similar $\Delta H_\text{r}$ around 225 kJ mol$^{-1}$. Above 4.2 V cells with uncoated NMC532 showed a much less endothermic $\Delta H_\text{r}$ than coated cells by about 100 kJ mol$^{-1}$. The coating on the positive electrode may suppress oxidation processes responsible for the more endothermic $\Delta H_\text{r}$ seen in the cells with coated NMC532. In both cells with coated and uncoated NMC532 having EC:EMC:DMC-based electrolytes, $\Delta H_\text{r}$ was approximately the same from 4.2 V to 4.4 V (175 kJ mol$^{-1}$ in cells with coated NMC532, and 75 kJ mol$^{-1}$ in cells with uncoated NMC532), suggesting that although the rate of reactions increased with increased voltage, the reaction processes in each cell type stayed the same. However, in cells with MA, $\Delta H_\text{r}$ was similar to that of cells with EC:EMC:DMC-based electrolytes at 3.8 V, then as the hold voltage increased, $\Delta H_\text{r}$ decreased. Therefore, the addition of MA must have changed the total parasitic reaction processes, becoming less endothermic. The change could have been due to the introduction of at least one additional, less endothermic process, as the rate of this process increased with high voltage faster than the rate of reactions in cells with EC:EMC:DMC-based electrolyte alone. Previous works suggest that MA is responsible for a significant increase in electrolyte oxidation at high voltage that produces gas and increases cell impedance over time, but does not significantly affect the graphite negative electrode.$^7,17$ The results here suggest this gas-producing oxidation process is likely to be exothermic. Conversely, $\Delta H_\text{r}$ increases in FEC:TFEC cells as the voltage is increased, suggesting multiple reaction pathways are present, the rates of which also vary differently with voltage. At 3.8 V $\Delta H_\text{r}$ was 0 kJ mol$^{-1}$ in FEC:TFEC cells, suggesting either a shuttle reaction was occurring, or multiple reaction pathways with coincidentally net zero $\Delta H_\text{r}$ were occurring. Due to the reductive nature of FEC and reported performance in the literature, the latter is more probable.

Cresce et al.$^{26}$, Xu et al.$^{27,28}$ and Islam et al.$^{19}$ have suggested that species coordinated to $\text{Li}^+$ (typically EC in the EC:EMC:DMC-based electrolyte) preferentially react at the electrodes. In the cells with EC:EMC:DMC-based electrolyte here, it could be that EC is preferentially oxidized or reduced in the same way, (just at different rates) with increased voltage, explaining the similar $\Delta H_\text{r}$ over an extended voltage range. MA has been found to reduce the binding energy of solvent to PF$_6^-$ molecules, which is in turn correlated with increased rates of electrolyte oxidation.$^{29}$ This may explain how MA could introduce additional reaction pathways with rapidly increasing rates at higher voltages.

Figure 8 has shown that in some cell chemistries, the rates of different reaction pathways may change independently with voltage. This adds an additional level of uncertainty when only comparing the magnitude of parasitic heat flow between cells with different coatings on the electrodes and different electrolytes. Interestingly, all measured values of $\Delta H_\text{r}$ show net endothermic parasitic processes. However, this result does not suggest every reaction is net endothermic. It is possible that a large, endothermic contribution comes from the origin of lithium involved in parasitic reactions, either from de-solvation of $\text{Li}^+$ from solvent or from deintercalation from electrodes.$^{27,28}$ In cells with MA, the sharply decreasing enthalpy suggests exothermic processes with increasing rates occurred at high voltages. Therefore, it is highly possible that a hold at 4.5 V may have shown a net exothermic $\Delta H_\text{r}$, or a cell containing more MA may yield net exothermic reactions. Due to cell balance (4.4 V) and concerns about exposing the expensive microcalorimeter to cells generating large volumes of gas, neither of these options were explored.

Future works will further explore trends with voltage and may also benefit from exploring how rates and enthalpies depend on cell temperature. The technique shown here would benefit from measurements such as GC-MS to study electrolyte content, XPS to analyze differences in electrode surfaces, and chemical simulations to investigate preferential chemical pathways in different systems. Future work will also utilize higher precision instruments to measure $I_p$. For example, after the sequence of voltage holds summarized in Figure 8, some

Figure 8. Total integrated results from the final 50 h of voltage holds. a) final cumulative parasitic energy, b) final cumulative $IV$ and final cumulative reaction energy, and c) the enthalpy per mole of electrons (average of the final 40 h of voltage hold). Results for cells with coated NMC532 are shown as thin, dark bars, and results for cells with uncoated NMC532 are thick, light bars.
**Figure 9.** $IV$ (black) and measured heat flow (red) from cells with coated NMC532 with EC:EMC:DMC:MA-based electrolyte during a 4.4 V voltage-hold on a) a Keithley 2602B source-meter and b) a Novonix charger.

**Figure 10.** Integrated total parasitic energy (a,b), $IV$ energy (c,d), reaction energy (e,f), and enthalpy per mole of electrons (g,h) during 4.4 V holds on a Keithley 2602B source-meter (left column), and a Novonix system (right column) for some of the cell types used in this study.
Cells were connected to a Novonix high precision charger and were held at 4.4 V for 90 h after the previous 4.4 V holds experiments. Figures 9a and 9b show the difference between the measurements done in this work using a Keithley source-meter (data taken every 5 s and points averaged over 3 min intervals) and the Novonix system collecting a single data point without averaging every 30 s. Without the 36-point averaging, the noise in the Keithley data was ~300 μW. The Novonix system showed much higher accuracy with a noise level of < 25 μW for single measurements. The voltage hold on the Novonix system was not preceded by a voltage hold at 4.42 V like the first voltage hold, so the cell took longer to reach lithium equilibrium in the cell. Figure 10 shows a comparison between the cumulative parasitic energy, cumulative IV energy, cumulative reaction energy, and ΔHE integrated in the same way as in Figure 7 for all cells tested on both systems. The Novonix data was integrated after 70 h into the hold when the decay in parasitic heat flow was closer to the decay in IP/V. Figures 10g and 10h show that the results for ΔHE were consistent between cycling systems. The Novonix system could be used to increase the accuracy of data collected during low voltage holds. As a side note, the cumulative EIV and the cumulative Ep of cells with EC:EMC:DMC-based electrolytes decreased significantly less than other cells between the two ~100 h 4.4 V holds, suggesting a thickening SEI caused by parasitic reaction products in MA-containing and FEC:TFEC-containing cells.

This work aimed to act as a stepping stone into more quantitative, physical understandings of parasitic reactions in lithium ion cells. Future studies using high precision current sources and combining computational and analytical techniques may be able to help elucidate the fate of electrolyte components in cells, and aid in diagnosing the mechanisms behind cell death, impedance growth, and lithium loss. Future works can use the method developed here to investigate the effects of cell aging under different conditions on the types of reactions that occur. Additionally, combining experimental techniques with computational studies may help in further understanding how surface chemistry and electrode/coating-electrolyte interfaces affect parasitic reaction pathways.

Conclusions

A new technique to measure the rate and net enthalpy of parasitic reactions in lithium ion pouch cells was introduced. The technique employs high precision current sources to obtain the parasitic current during voltage hold conditions, and isothermal microcalorimetry to measure the heat flow of the cell. The technique is capable of measuring the net reaction enthalpy per mole of electrons in the parasitic current (ΔHE). Proof of concept experiments using a reversible shuttle molecule in an NMC532/graphite pouch cell yielded net reaction enthalpies of 10 ± 10 kJ mol⁻¹, close to the expected value of 0 kJ mol⁻¹. Coated and uncoated NMC532/graphite pouch cells were also filled with different solvent systems with 1.2 M LiPF₆ and were studied at 3.8 V, 4.2 V, 4.3 V, and 4.4 V. The majority of the parasitic heat flow at all voltages was found to be due to Joule heating caused by the parasitic current. Cells with an EC:EMC:DMC (25:5:70 wt) solvent showed approximately constant ΔHE from 4.2 V to 4.4 V in each cell type but an increase in reaction rate, suggesting the parasitic reaction pathways were unchanged, but the number of reactions increased with voltage. Cells containing EC:EMC:DMC:MA (15:3:42:40 wt) as a solvent showed a decreasing ΔHE as voltage increased, suggesting higher rates of reaction included additional reaction pathways influenced by the addition of MA. Cells with FEC:TFEC as a solvent showed increasing ΔHE with voltage, again suggesting different reaction pathways were present, with different rate dependencies on voltage. All reactions measured were net endothermic. Cells with coated NMC532 showed higher ΔHE in each case, which suggest coated electrodes were preventing certain reactions. Results for ΔHE were consistent between cell pairs.

This preliminary study shows the importance of understanding the types of reactions in cells, as typical measurements of parasitic heat flow cannot account for differences in reaction enthalpies. This study also directly shows that different reactions in cells can have rates which change independently with voltage. Further studies combining this technique with simulations and compositional analysis of electrolyte, gas, and surface products are suggested. Future studies can focus on comparisons between positive electrode compositions, different negative electrode materials, coatings, additives, and solvent systems. Isothermal microcalorimetry is a unique, powerful tool, and is encouraged to be pursued by researchers in the field to investigate the complexities behind parasitic reactions in lithium ion cells.

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