

## ACE 1100 IMR-MS application Note

Main target compound : Off-gas from Litium Ion Battery

### Application fields : Battery Industry

## Background

**Lithium-ion batteries are** widely used in various applications such as electric vehicle and mobile phone batteries due to their advantages in energy use efficiency, and their demand is gradually increasing as the main component of energy storage systems (ESS). On the other hand, in recent years, fires and explosions have been continuously occurring in energy storage devices and electric vehicles, which has become a social issue. It is known that when abnormal mechanical, thermal, and electrical conditions occur in lithium-ion batteries, thermal runaway occurs, which causes explosions and fires. As a result, the thermal runaway phenomenon of lithium-ion batteries is detected at an early stage, Fire prevention is emerging as an important issue.

A lithium-ion battery consists of an anode that provides lithium ions, a cathode that stores lithium ions, a separator that prevents internal short circuits so that electrons generated from the anode and cathode can pass through the external circuit, and an electrolyte that provides space and environment for lithium ions to move.

### Off-gas generation mechanism of lithium-ion battery

Off-gas : Flammable vapors and gases generated from lithium-ion batteries

When a battery is constantly subjected to mechanical, thermal, and electrical stress, the temperature inside the battery rises, and the electrolyte vaporizes, increasing the pressure inside the battery. The gas generated inside escapes through a vent position made for safe discharge when the internal pressure increases, which is called off-gas.

Off-gas components

Contains gases generated when electrolyte and internal materials of lithium-ion batteries decompose and react with each other due to high pressure and heat.

Electrolytes	Compounds by degradation or reaction
Ethylene carbonate(EC)	CO
Diethyl carbonate(DEC)	H <sub>2</sub>
Ethyl methyl carbonate(EMC)	CO <sub>2</sub>
Methyl ethyl carbonate(MEC)	CH <sub>4</sub>

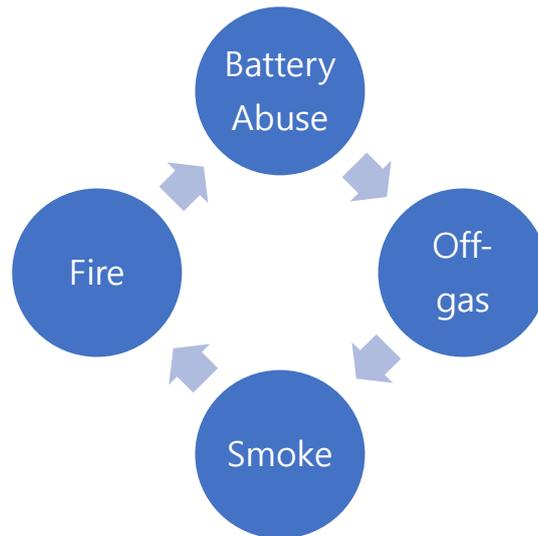
Electrolytes	Compounds by degradation or reaction
Electrolyte composition	Degradation/side-reaction components
Ethylene carbonate(EC)	CO
Diethyl carbonate(DEC)	

### Battery Gas Compounds

Chemical name	Chemical formula	CAS No.	Exact mass	k(H3O+)	k(NO+)	k(O2+)
Argon	Ar	7440-37-1	39.95	-	-	-
Carbon oxide	CO	630-08-0	28.01	-	-	-
Carbon dioxide	CO2	124-38-9	44.01	-	-	-
Methyl fluoride	CH3F	593-53-3	34.03	-	-	<b>2.50E-09</b>
<b>Ethylene</b>	<b>C2H4</b>	<b>74-85-1</b>	<b>28.05</b>	<b>6.30E-11</b>	<b>1.00E-12</b>	<b>1.00E-09</b>
Acetylene	C2H2	74-86-2	26.04	1.10E-11	1.00E-12	<b>1.10E-09</b>
Ethane	C2H6	74-84-0	30.07	-	-	<b>1.10E-09</b>
Ethyl fluoride	C2H5F	353-36-6	48.06	-	-	-
Propylene	C3H6	115-07-1	42.08	<b>1.50E-09</b>	6.30E-11	1.30E-09
<b>Methanol</b>	<b>CH4O</b>	<b>67-56-1</b>	<b>32.04</b>	<b>2.70E-09</b>	<b>1.00E-11</b>	<b>1.00E-09</b>
<b>Methyl formate</b>	<b>C2H4O2</b>	<b>107-31-3</b>	<b>60.05</b>	<b>2.70E-09</b>	<b>5.00E-10</b>	<b>2.20E-09</b>
<b>Acetone</b>	<b>C3H6O</b>	<b>67-64-1</b>	<b>58.08</b>	<b>3.90E-09</b>	<b>1.20E-09</b>	<b>2.70E-09</b>
Methoxyethanol	C3H8O2	109-86-4	76.09	<b>3.50E-09</b>	2.60E-09	2.60E-09
Methyl acetate	C3H6O2	79-20-9	74.08	<b>2.80E-09</b>	1.60E-09	2.40E-09
Dimethyl carbonate	C3H6O3	616-38-6	90.08	-	-	-
2-Methyl-1,3-dioxolane	C4H8O2	497-26-7	88.11	-	-	-
Methyl acetate	C3H6O2	79-20-9	74.08	<b>2.80E-09</b>	1.60E-09	2.40E-09
1,4-Dioxane	C4H8O2	123-91-1	88.11	<b>1.90E-09</b>	1.60E-09	1.50E-09
Ethyl methyl carbonate	C4H8O3	623-53-0	104.10	-	-	-
Dimethyl carbonate	C3H6O3	616-38-6	90.08	-	-	-

### Off-gas Detection Algorithm

A fire caused by a battery is caused by a thermal runaway of a single lithium-ion battery and spreads, and it occurs in a certain stage. Therefore, it is very important to detect the generated gas quickly at the off-gas generation stage and remove the stressor on the battery to prevent thermal runaway.



The fire of a lithium-ion battery is caused by a chain reaction as shown above, and the fire from one battery spreads continuously, leading to a large-scale fire. Recognition of abnormal phenomena through early detection in the off-gas generation stage can prevent the spread of fire and secondary damage by cutting off the intermediate link of the chain reaction by freeing time to remove the stressors that are quickly applied.

### **Real time Analysis Method**

-ACE 1100 IMR-MS

### **Problems with Conventional Analysis Methods**

- Analysis time: In the case of GC, it takes a long time because the separation of components must be preceded by the use of columns.
- Real-time analysis of off-gas generation source through equipment movement is not possible
- After collecting samples from the source, move them to the laboratory for analysis – Unable to respond quickly, accuracy is reduced
- Gas sensor: fast and highly mobile, but requires a separate sensor for each material, and low accuracy accuracy

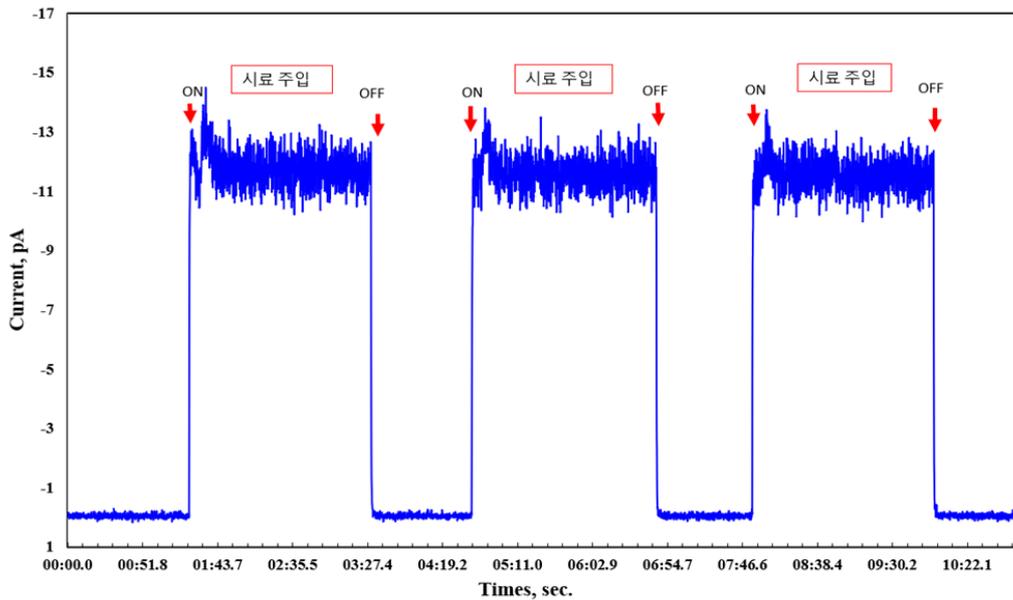
### **ACE 1100 IMR-MS Advantages**

- Analysis time : No GC required, analysis time is drastically shortened by direct injection of sample

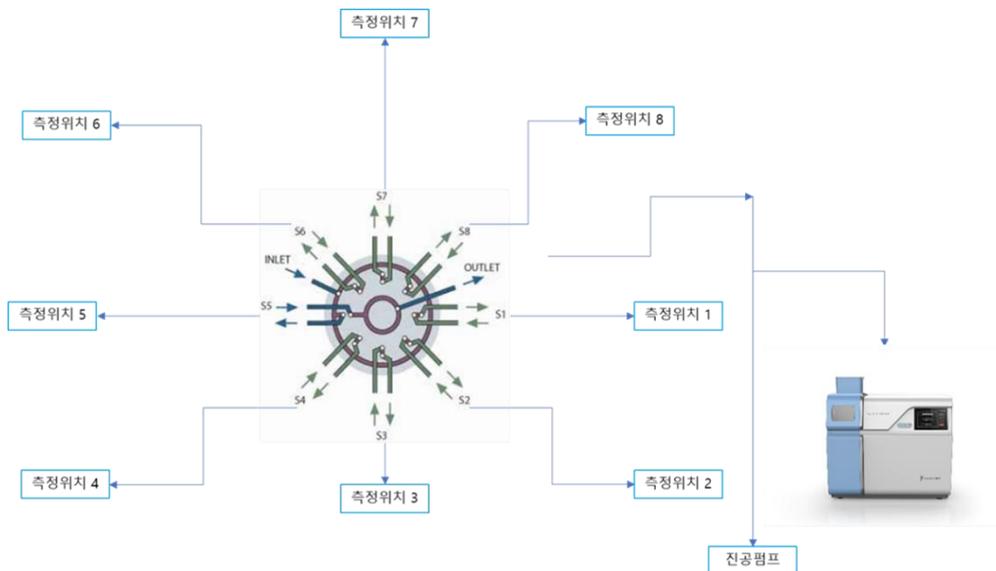
into mass spectrometer

- Real-time analysis : Check the analysis result at the same time as the sample is injected, real-time monitoring of off-gas components is possible

### Sample Gas (Benzene) Response Test



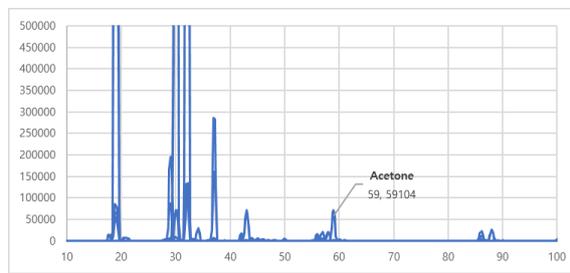
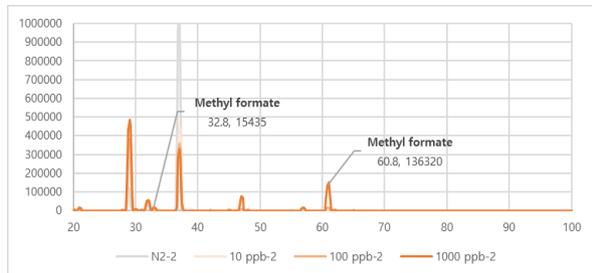
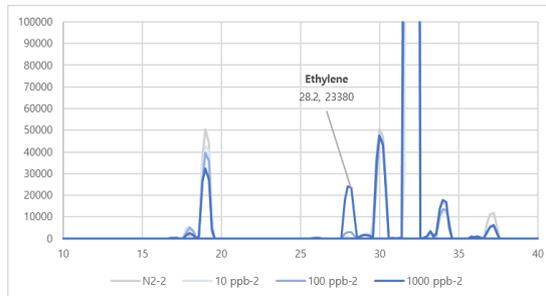
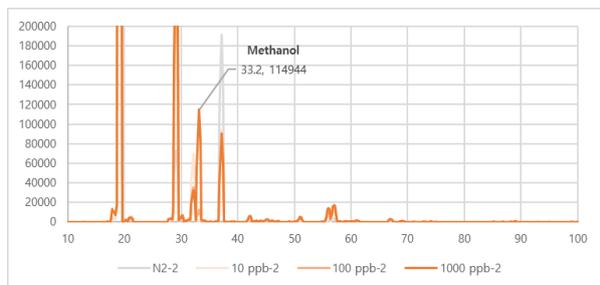
-On-site analysis : On-site analysis is possible at the site where measurement is required, such as off-gas sources (no need to collect samples and travel to the laboratory)



The above figure is a simple diagram of measuring samples from multiple locations with a single instrument, and the actual application in the field requires detailed examination of the valve configuration, number of ports, etc.

The combination of a multi-position valve and a vacuum pump creates a flow path for introducing samples from each point into the instrument.

### Analysis result of some compounds (ACE 1100 IMR-MS)



<b>Compound</b>	<b>Linearity (R<sup>2</sup>)</b>	<b>Sensitivity (cps/ppb)</b>	<b>%RSD (@10 ppb)</b>	<b>%RSD (@100 ppb)</b>	<b>Accuracy (@100 ppb)</b>	<b>LOD (ppb)</b>	<b>LOQ (ppb)</b>
<i>Ethylene</i>	0.9999	39.22	6.58	2.48	79.82%	1.345	2.584
<i>Methyl alcohol</i>	0.9999	148.927	4.65%	1.99%	100%	0.345	0.666
<i>Methyl formate</i>	0.9998	81.205	3.34%	1.05	100%	0.858	1.594
<i>Acetone</i>	0.9975	87.70	2.62%	1.83%	97.1%	0.668	1.191