Investigation of Aging Mechanism in Lithium-Ion Cell Simulated LEO Satellite Operation Using Electrode Structure Analysis and Surface Characterization

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1. Introduction

☐ Solid electrolyte interphase (SEI)

plays an important role in normal operation of lithium-ion cells
for on-ground applications

- High taper voltage
- High charge (discharge) rate
- Wide ambient temperature
- Lower cycle life requirement
- Long shelf life at various SOCs

1. Introduction

Special requirements

for an on-board lithium-ion cell

- Long cycle life
- Charge-discharge duration limited by orbit

For a LEO satellite

.60-minute charge and 30-minute discharge without interruption

.30,000-cycle operation (five years)

1. Introduction

Moderate operation conditions

different from those used on ground

For a lithium-ion cell

- Low DOD (smaller than 40%)
- Optimum temperature range (10ºC to 20ºC)
- Low charge and discharge rates (smaller than 1 C)
- Low taper voltage (lower than 4.1 V)

1. Introduction

Aging mechanism
of a lithium-ion cell for space applications
differs from those used on ground

?

1. Introduction

Objective

- Investigation on aging mechanism of commercial laminated lithium-ion cells with $LiCoO_2$ cathode and graphite anode in a simulated LEO satellite operation

1. Introduction

Approach

- Electrode structure analysis (XRD, NRM) and surface characterization (FTIR, XPS) of the aged and fresh lithium-ion cells

.less change in separator and electrolyte with cycling in our experience

1. Introduction

Cell specification (1)

Nominal		Materials			Weight g
Voltage V	Capacity Ah	Anode	Cathode	Electrolyte type	
3.7	0.68	Graphite	$LiCoO_2$	Liquid	14.3

1. Introduction

Cell specification (2)

- **Aged cell**
  - 4350-cycle experience in a simulated LEO operation (DOD: 40%)
  - Cell capacity: decline to 0.53 Ah
- **Fresh cell**
  - Same lot with the aged cell
  - Serve as a control
  - Cell capacity: 0.62 Ah

2. Destructive analysis (DPA)

Cell state before DPA

Fully discharged in CC mode at 0.5 C to 2.75 V before DPA

Analytic sample

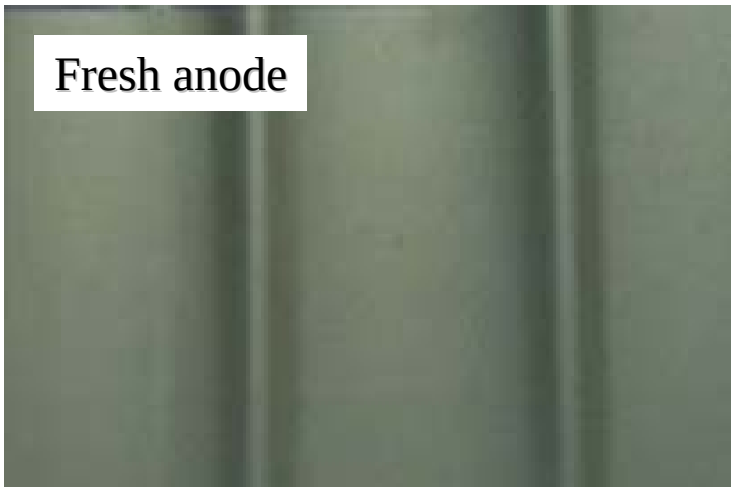
Collected from the inner part of wounded electrode stack under argon atmosphere

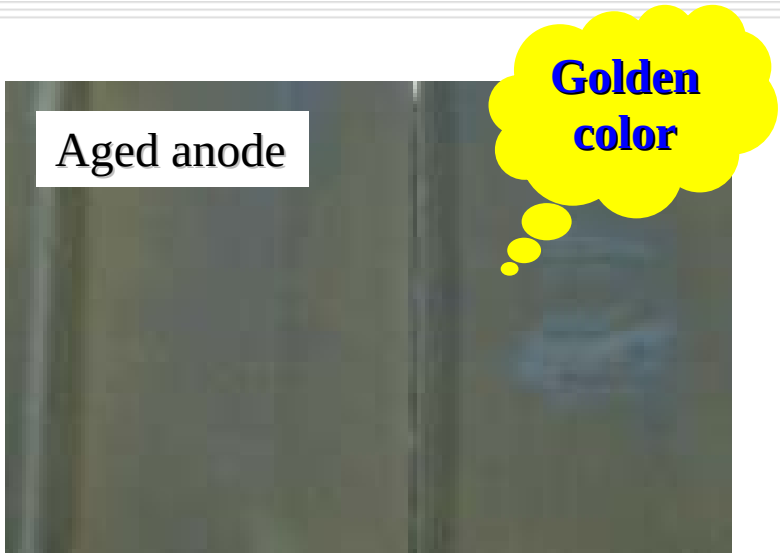
Sample treatment

Do not wash before structure analysis and surface characteristics

2. Destructive analysis (DPA)

Photograph comparison





A part of lithium ion was reserved in graphite anode with cycling and could not reversibly take part in the charge-discharge process again

3. Capacity check

Cell structure

Sandwich-type half cell (electrode area 12.5 cm^2)

Charge-discharge condition

Charge: CC-CV, 2.0 mA, 1 mV or 4.2 V, 8 hours

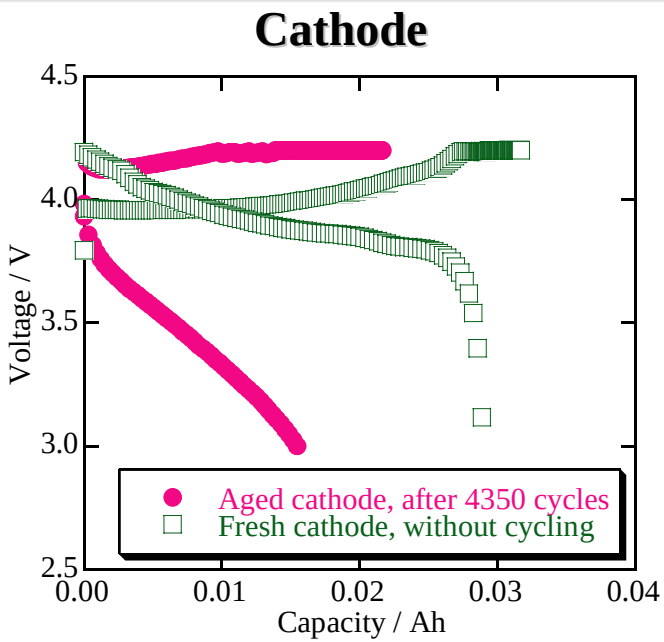
Discharge: CC, 2.0 mA, 1.5 V or 3.0 V

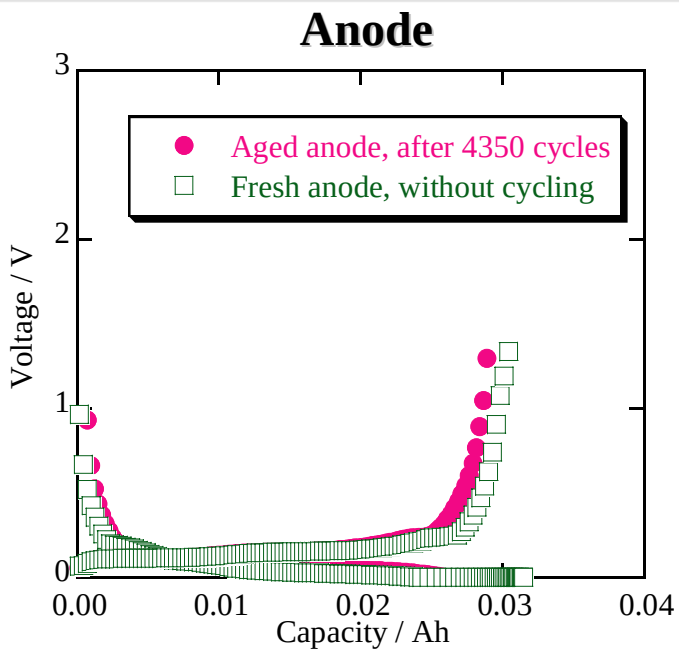
AC impedance measurement

Amplitude: 5 mV from OCV. Frequency: 10 kHz – 10 mHz

3. Capacity check

Charge-discharge curves



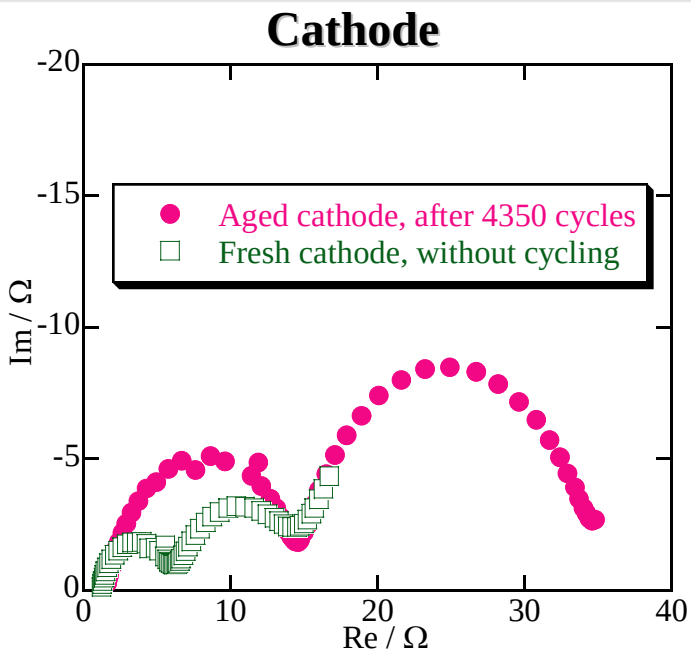


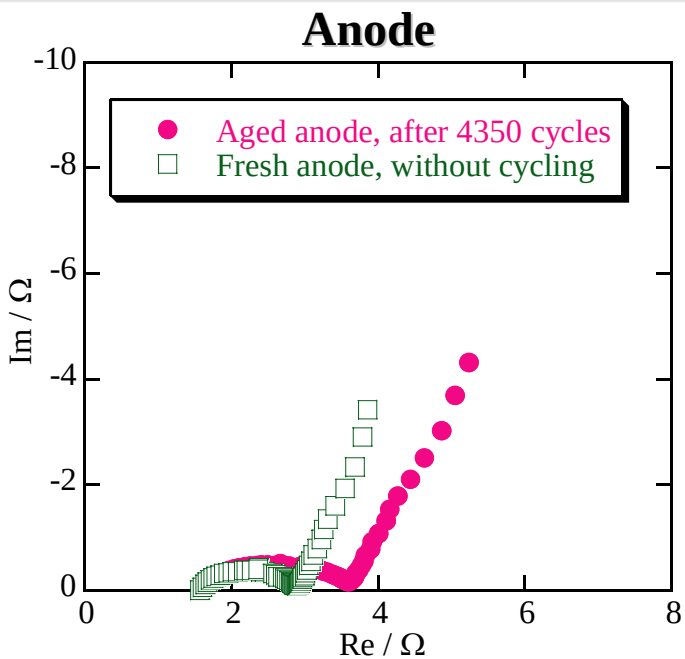
The aged $LiCoO_2$ cathode:

a steep decrease in discharge capacity as compared with that of the fresh cell

3. Capacity check

☐ AC impedance





The aged $LiCoO_2$ cathode:

a sharp increase in impedance as compared with that of the fresh cell

3. Capacity check

☐ Summary

$LiCoO_2$ cathode,
rather than graphite anode,
is responsible for cell-performance degradation
of the aged cell with cycling

4. XRD study

Analytic sample

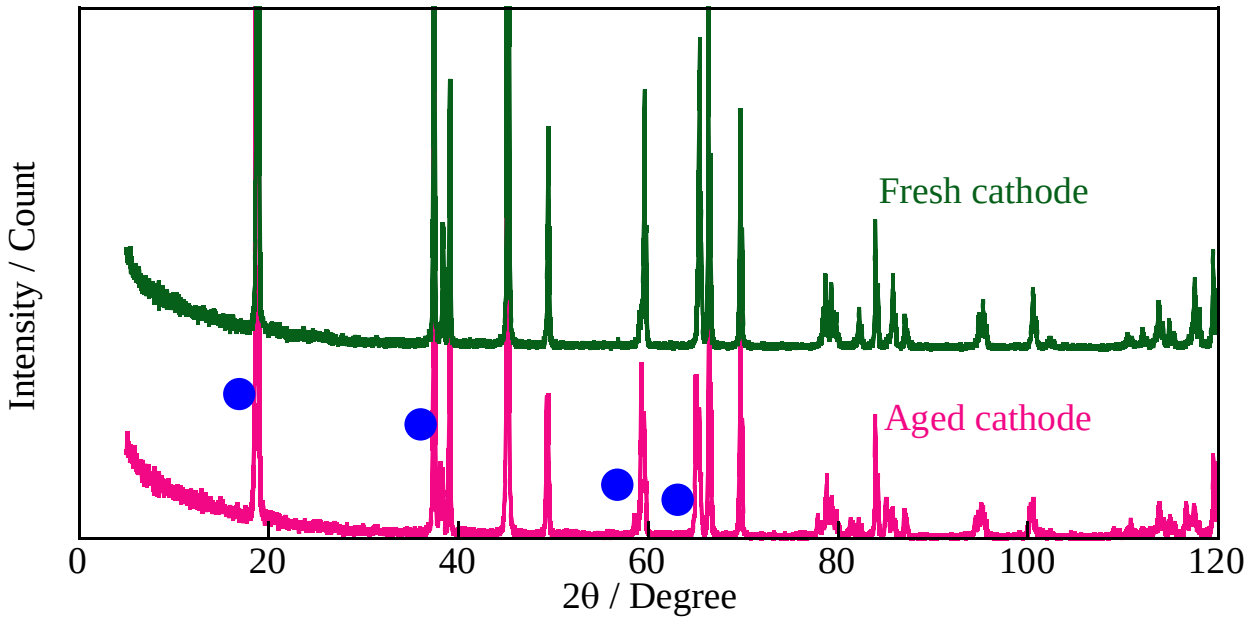
Graphite anode and $LiCoO_2$ cathode

Experimental

Crystal-structure investigation by powder X-ray diffraction (XRD) under air atmosphere

4. XRD study

Cathode pattern

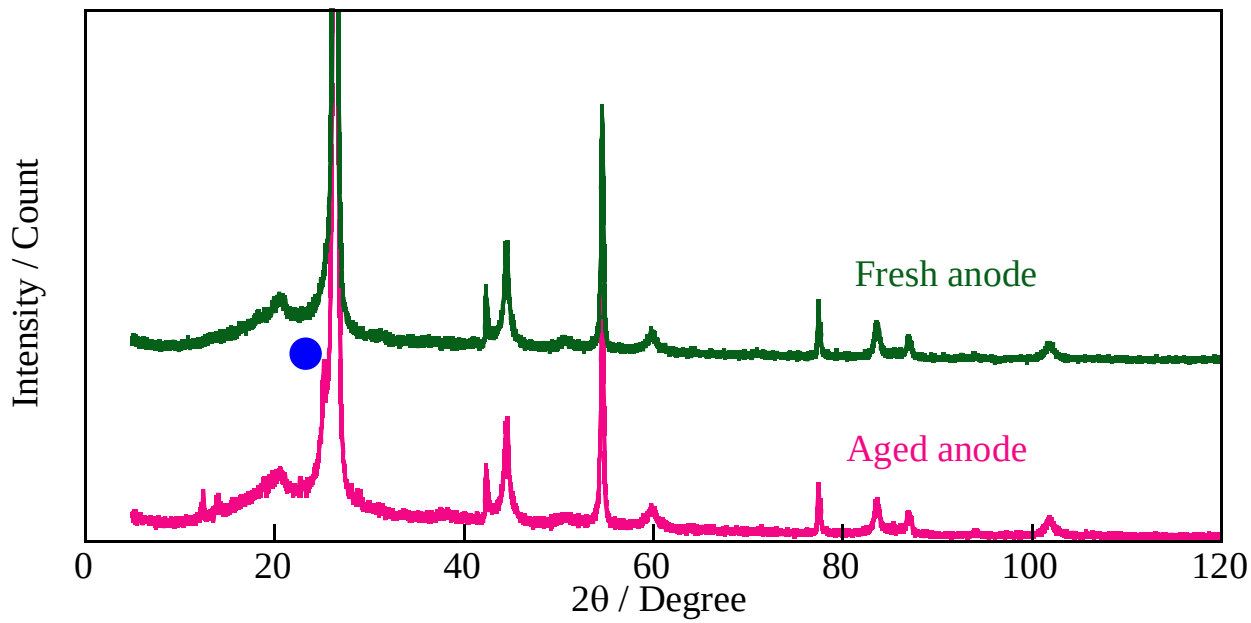


Peak split of aged $LiCoO_2$ cathode:

indicating crystalline structure change of $LiCoO_2$ with cycling.

4. XRD study

Anode pattern



Aged graphite anode:

less crystalline structure change than cathode.

4. XRD study

☐ Lattice constant

Sample		Crystalline Phase	Lattice Constant (Å)	Note
Cathode	Aged	Hexagonal	a=2.814, **c=14.189**	New structure
			a=2.815, c=14.070	
	Fresh		a=2.816, **c=14.063**	
Anode	Aged	Hexagonal	a=2.462, c=6.721	
			c=7.07	New structure
	Fresh		a=2.463, **c=6.719**	

C-axis increase at new structures of both aged electrodes:

indicating lithium-ion reservation at aged anode and deficiency at aged cathode

4. XRD study

Summary

The structure destruction of $LiCoO_2$ may be one of the factors causing cell-performance degradation

5. NMR analysis

Analytic sample

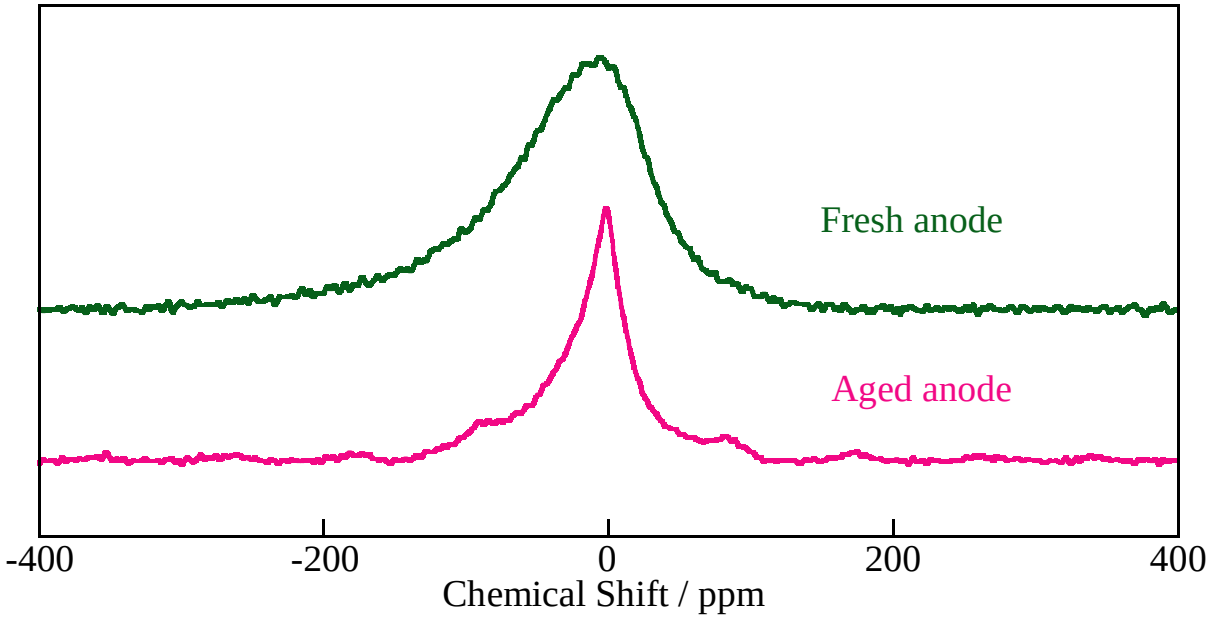
Graphite anode

Experimental

Lithium-ion-state investigation by 7Li magic angle spinning (MAS) NMR under dry nitrogen

5. NMR analysis

Spectrum comparison



Aged graphite anode:

peak shift corresponding to different lithium-ion states.

5. NMR analysis

Peak separation

Sample	Chemical shift	Lithium-ion state
Aged cell	0 ppm	Restricted lithium ion
	-10 ppm	Lithium salt
Fresh cell	From 0 ppm to -51 ppm	Dilute (a phase before stage structure formation)

Lithium-ion reservation in aged graphite anode;
very little lithium ion in fresh graphite anode.

5. NMR analysis

☐ Summary

NMR analysis of the aged graphite anode detected lithium ions that were irreversibly reserved inside graphite layer.

6. FTIR spectroscopy

Analytic sample

Graphite anode and $LiCoO_2$ cathode

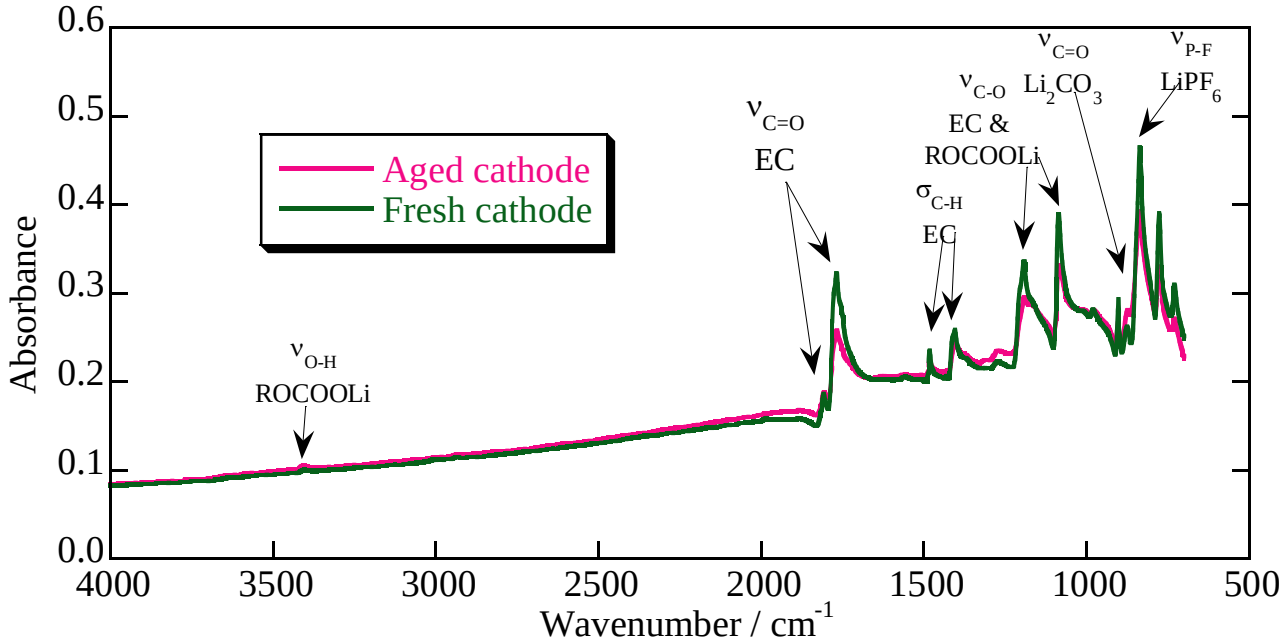
2.0 mm diameter area pressed against the Ge crystal

Experimental

Incidence angle: 40º (0.76 μm depth)

6. FTIR spectroscopy

Cathode spectra

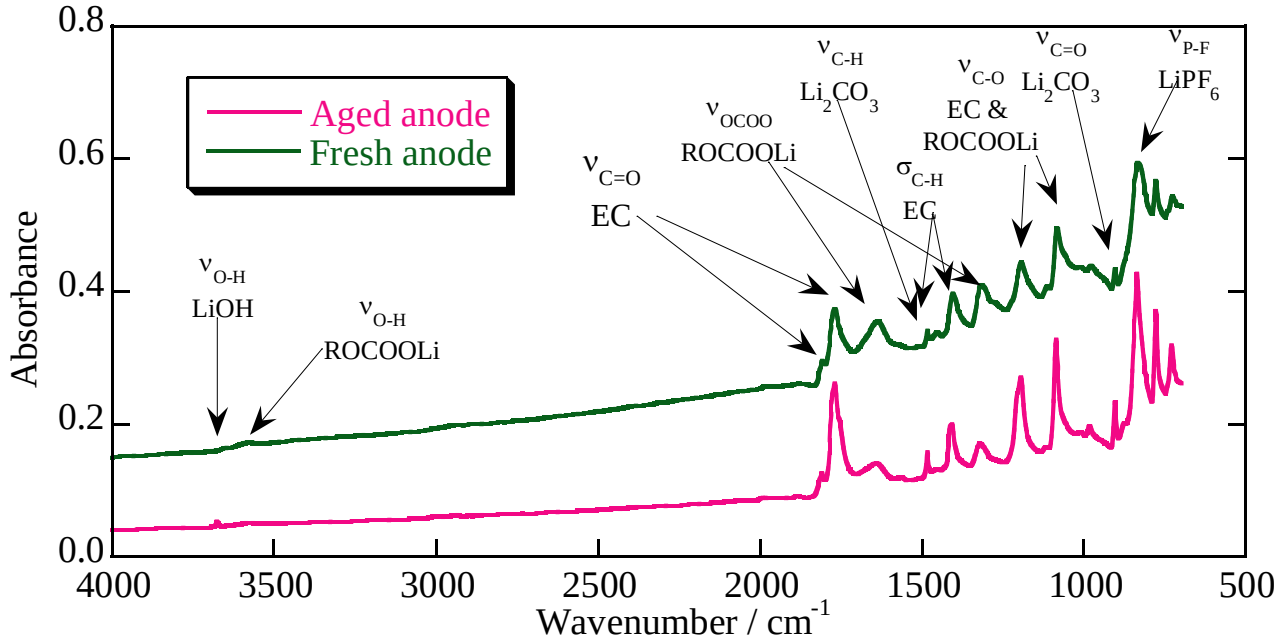


$LiCoO_2$ cathode:

less change in surface species with cycling.

6. FTIR spectroscopy

Anode spectra



Aged graphite anode:

new component of LiOH besides the common surface species.

6. FTIR spectroscopy

Peak intensity ratio

Representative surface species to EC (1770 cm^{-1})

Graphite Anode	ROCOOLi	LiOH
	1640 cm^{-1}	3680 cm^{-1}
Aged	0.18	0.05
Fresh	0.64	0

Aged graphite anode:

amount of organic component decreased, in contrast to inorganic one increase

6. FTIR spectroscopy

Summary

1) Graphite anode had a larger change in surface chemistry than that of the $LiCoO_2$ cathode

2) The amount of organic component decreased, in contrast to the increase of inorganic one.

7. XPS measurement

Analytic sample

Graphite anode and $LiCoO_2$ cathode

Elliptic sharp of 1000x1750 mm^2 for surface analysis or 300x525 mm^2 for depth profiling

Depth profile

Ar ion-beam sputtering (3 keV); 3.7~4.0 nm/min for a SiO_2/Si film

7. XPS measurement

☐ Surface composition

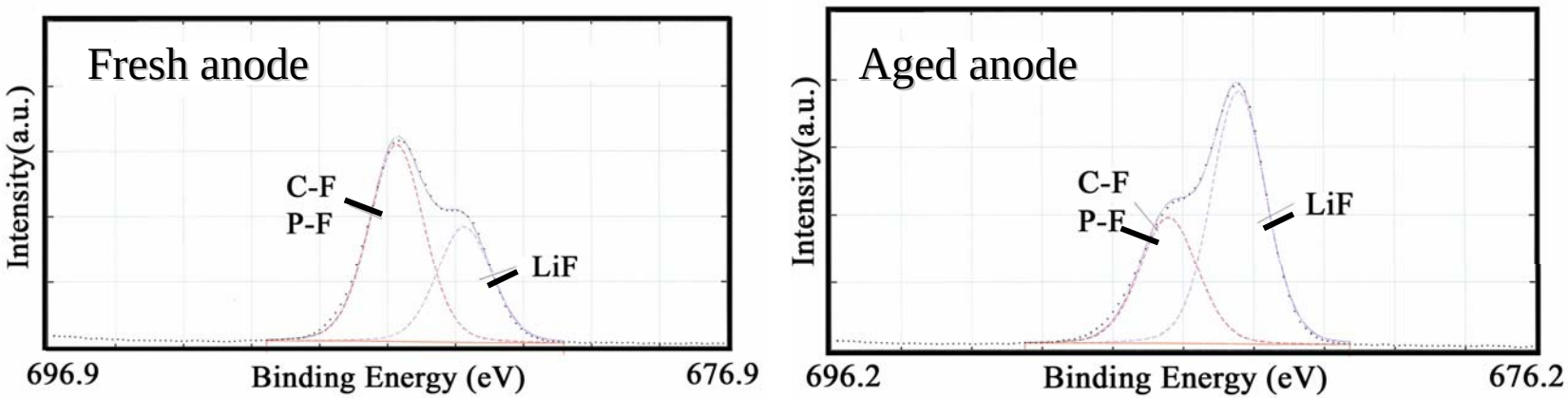
Atomic percentage of various elements on surface layer

Sample		Atomic Percentage, %					
		C	F	O	Li	P	Co
Anode	Fresh	29.7	27.5	18.7	20.8	2.9	0.4
	Aged	**20.3**	**31.6**	16.2	**29.0**	2.5	**0.4**
Cathode	Fresh	41.1	28.1	15.2	12.4	0.9	2.3
	Aged	39.3	29.2	15.4	13.4	1.2	**1.5**

Main change with cycling: occur on anode surface

7. XPS measurement

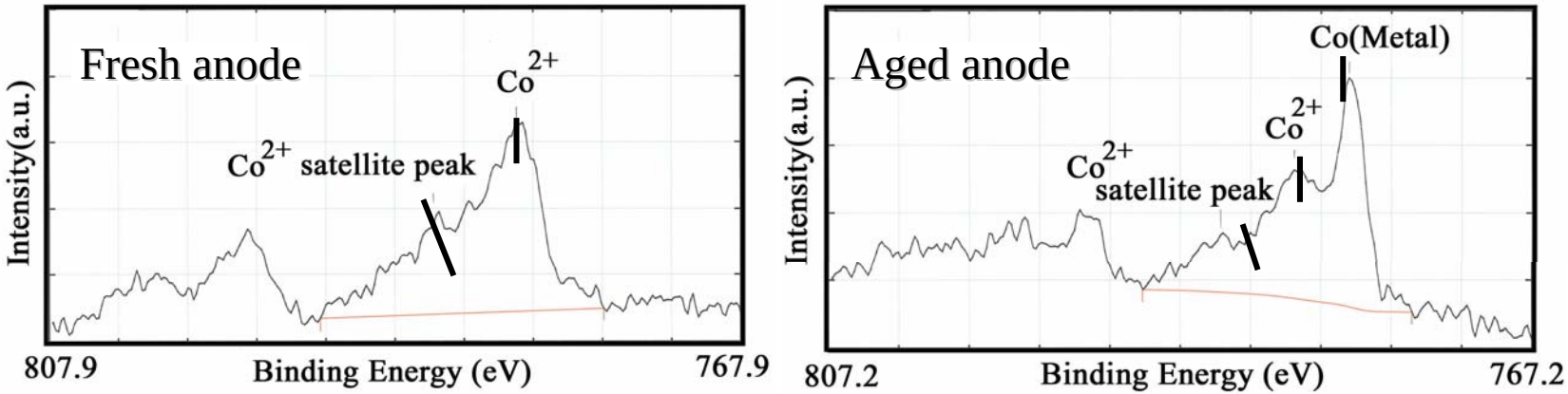
F 1s spectra



High-impedance LiF:
forms at the surface of fresh anode and increases with cycling

7. XPS measurement

Co 2p spectra

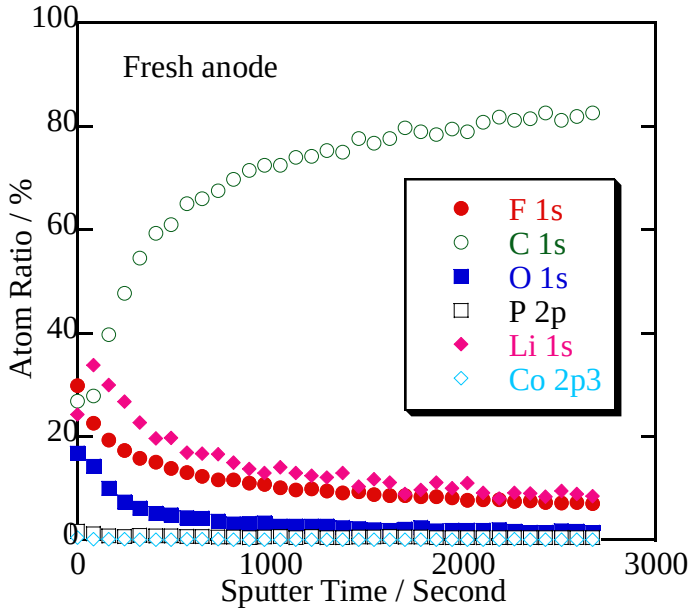


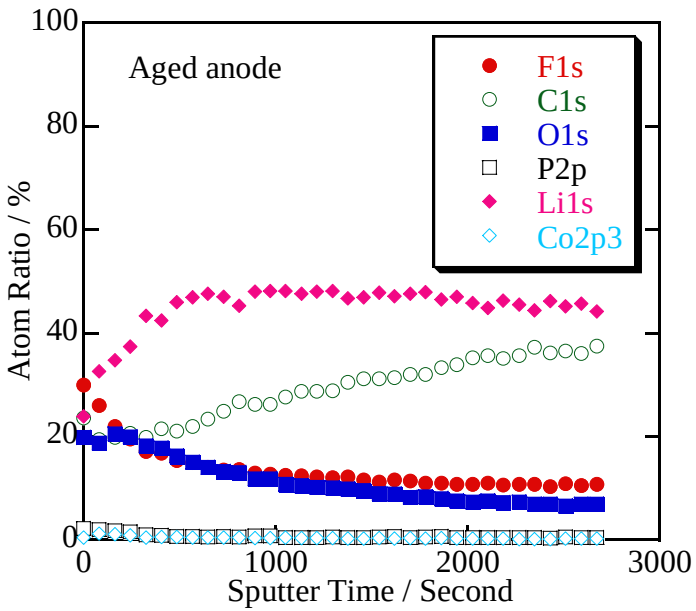
Co^{2+} ion was detected for both anodes;

Co metal existed on the aged graphite-anode surface.

7. XPS measurement

Anode depth profile

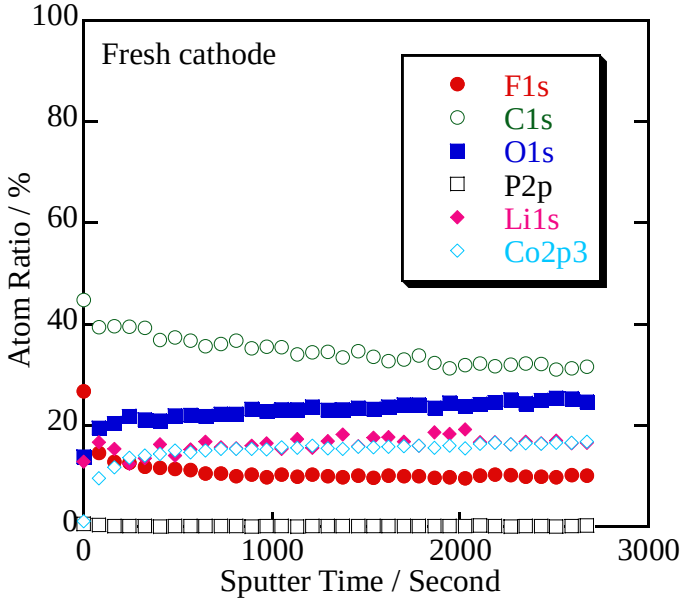


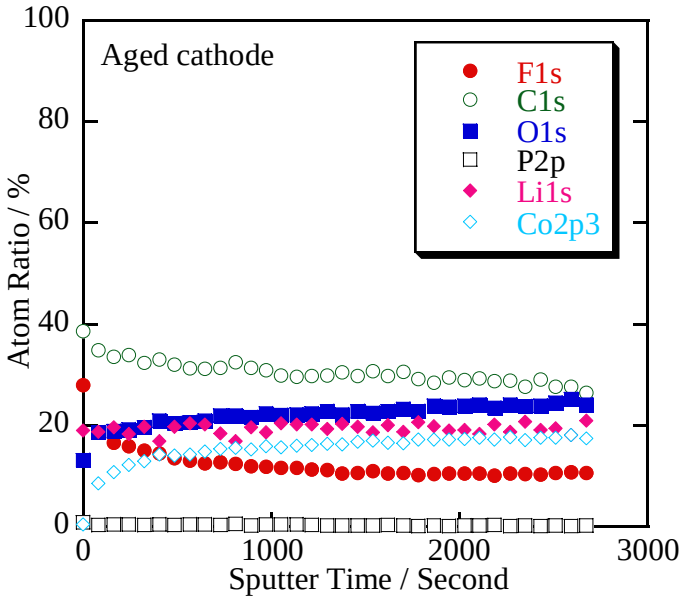


Surface film at anode surface becomes thicker with cycling

7. XPS measurement

Cathode depth profile





No obvious change in cathode surface chemistry

7. XPS measurement

☐ Summary

1) Main change with cycling occurred on anode surface
2) Surface film at graphite anode became thicker with cycling
3) Co metal was detected at the graphite anode surface as a result of prolonged cycling

8. Conclusions (1)

- **Degradation cause of cell performance with cycling**

	Anode	Cathode
Capacity fading	Small	large
Structure destruction	Slight	Serious
Surface chemistry change	Large	Small

8. Conclusions (2)

- **Cathode structure destruction**

Primary performance-degradation cause of lithium-ion cells with $LiCoO_2$ cathode and graphite anode in a simulated LEO operation

9. What can we learn?

- **Space lithium-ion design**

1) Improve structure stability of $LiCoO_2$ materials
2) Use other cathode materials as an alternative to $LiCoO_2$
3) Increase capacity ratio of $LiCoO_2$ cathode to graphite anode, compared with < 0.8 for an on-ground cell