In-situ Height Change Measurements during Potential Cycling of Layered Ruthenic Acid

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Layered Ruthenic Acid ($H_{0.2}RuO_{2.1}\cdot nH_2O$)

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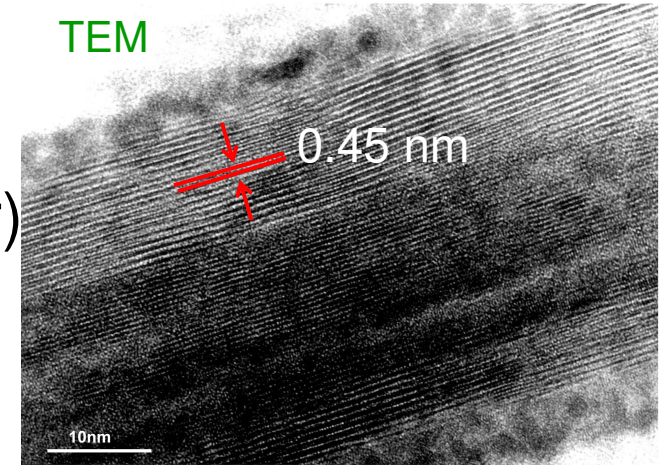
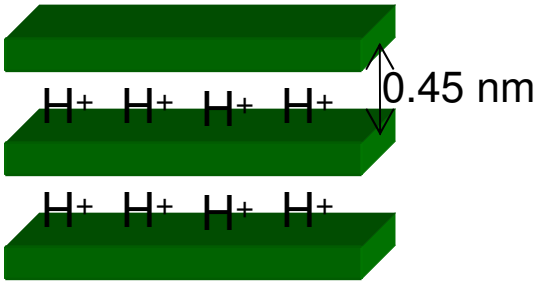
Properties

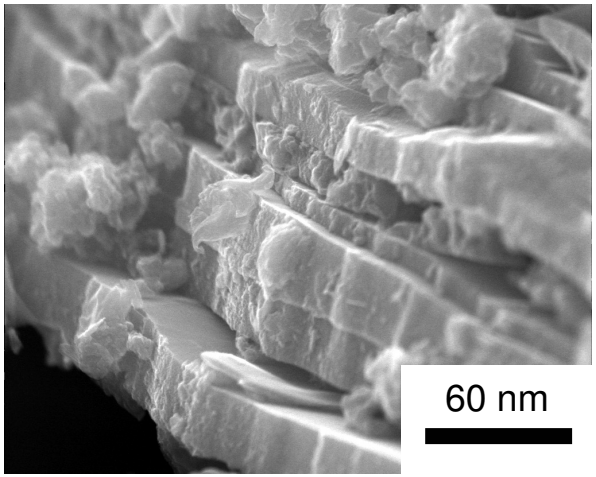
- Layered structure

  (0.4 nm RuO_2 slab & hydrous interlayer)

- Electron & proton mixed conductor
- High EC stability (acid, base, etc.)
- Interlayer is electrochemically active







Layered RuO_2 ($H_{0.2}RuO_{2.1}\cdot nH_2O$)

W. Sugimoto et al., *Angew. Chem. Int. Ed.*, **42**, 4092 (2003)

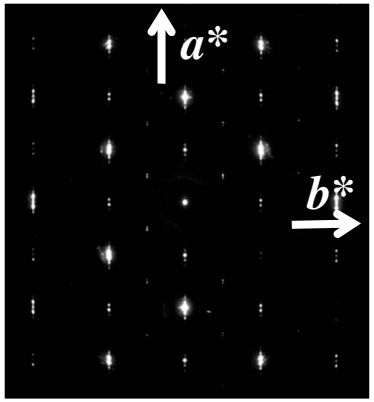
$5\ K_2CO_3 + 8\ RuO_2$

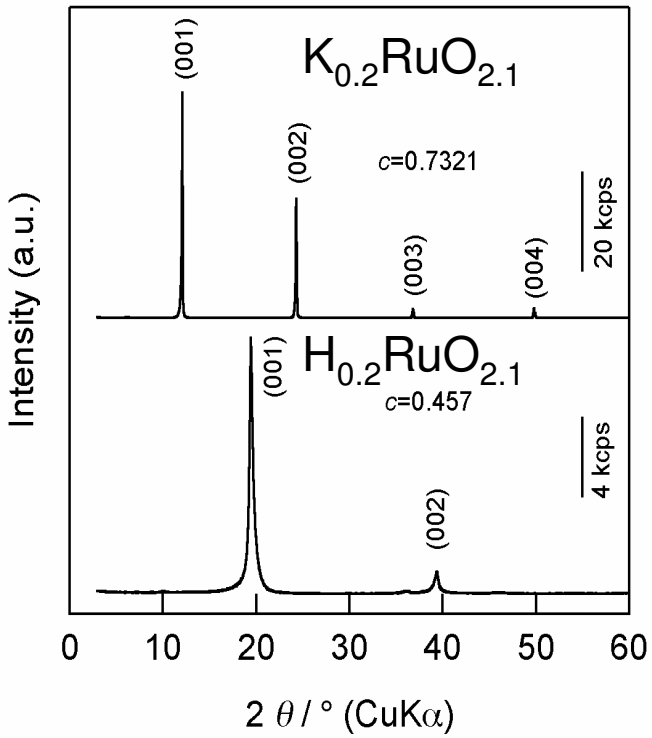
↓ calcination (850°C, 12 h, Ar flow)
grind, H_2O wash, dry (120°C)

$K_{0.2}RuO_{2.1}$

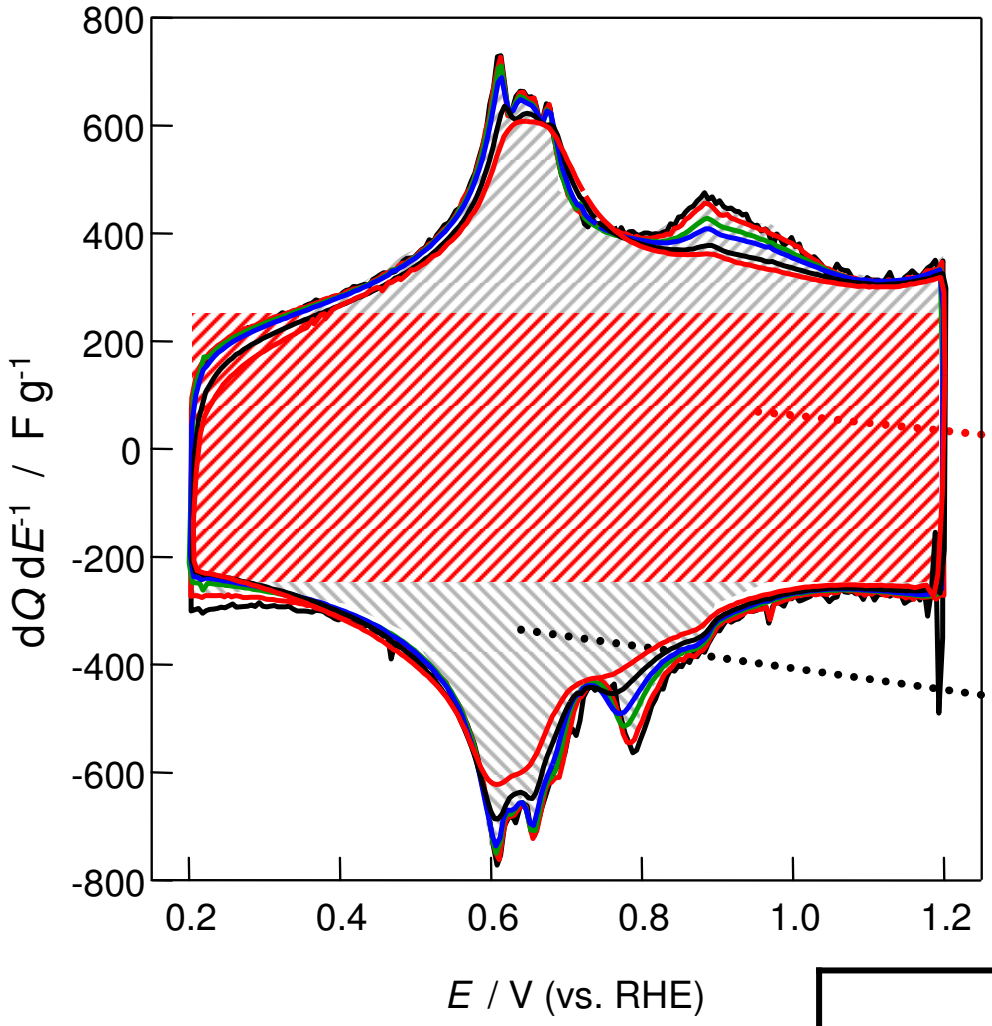
↓ proton exchange (1 M HCl, 60°C)
H_2O wash, dry (120°C)

$H_{0.2}RuO_{2.1}\cdot nH_2O$





CV of Layered RuO_2



Overall capacitance
500 ⇒ 2 mV s^{-1}
330 ⇒ 390 F g^{-1}

Electric Double Layer Charge
=> Inner&Outer Helmholtz
~200 F g^{-1}
E_{SA}=250 m^2 g^{-1}

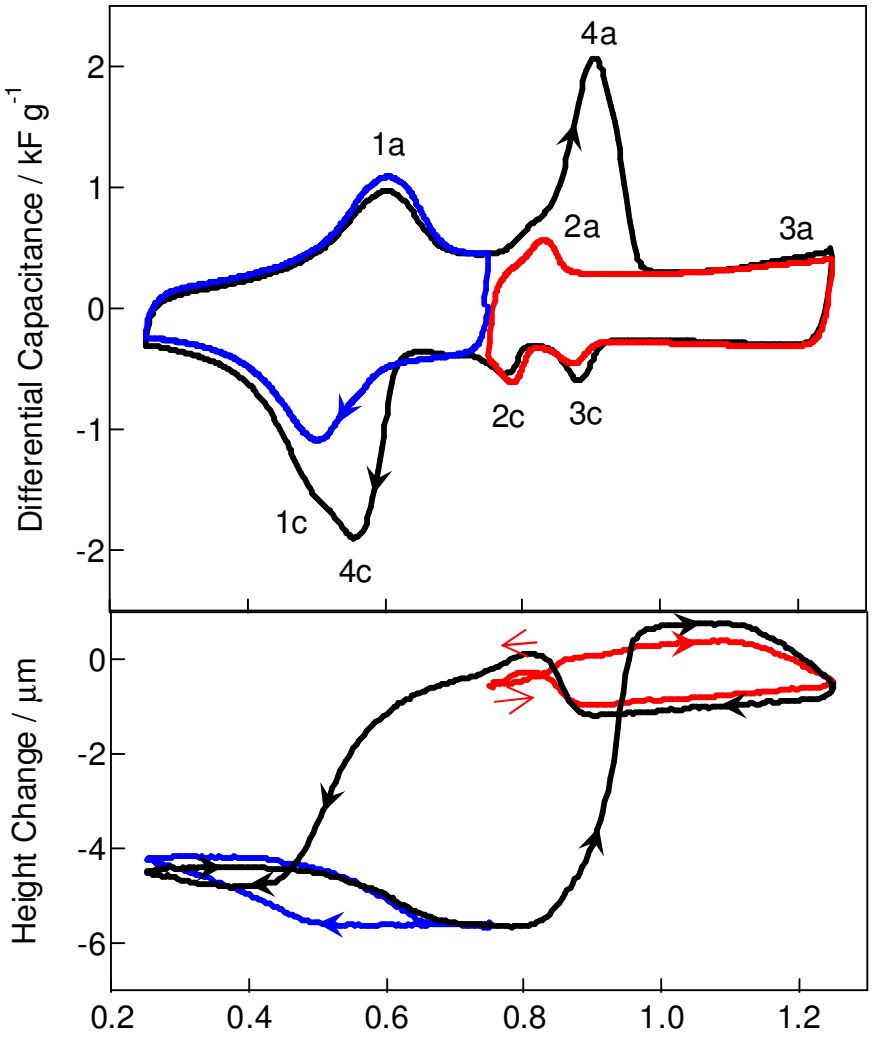
Surface Redox
~100-200 F g^{-1}

40 µg material on GC
0.5 M H_2SO_4 (25ºC)

	Layered RuO_2	anhydrous RuO_2
particle size	Submicron	10 nm
Capacitance	330-390 F/g	< 40-70 F/g
Active surface	250 m^2/g	50 m^2/g

Angew. Chem. Int. Ed., 42, 4092, 2003.

Dilatometric Study of Layered HRO

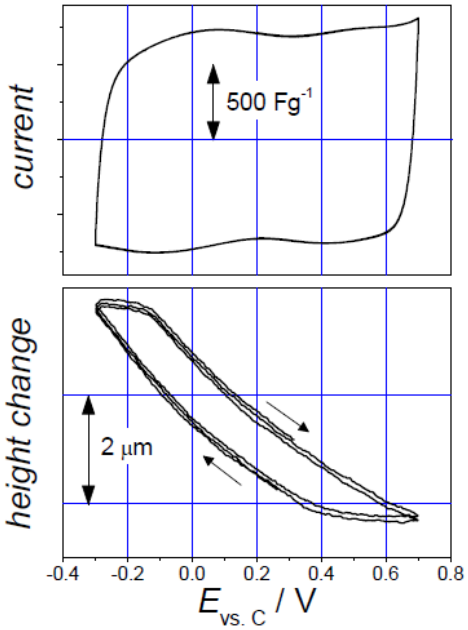


0.5 M $HClO_4$ (25ºC)
v=0.5 mV s^{-1}
2.0 mg, h_0~180 µm

maximum of ~ 4 % change in height

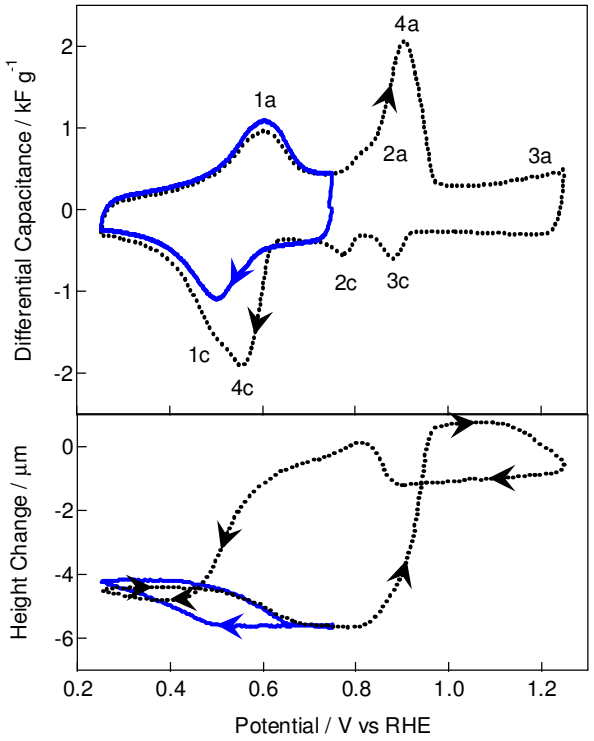
for RuO_2 nH_2O: ~1.8% change

$RuO_2 \cdot nH_2O$



0.5 M $HClO_4$ (25ºC)
v=0.5 mV s^{-1}
3.7 mg, h_0~220 µm

Indetificaton of Peak 1



change in height (~1 %)
cathodic: 0.50 → 0.25 V (↑ in *h*)
anodic: 0.45 → 0.65 V (↓ in *h*)

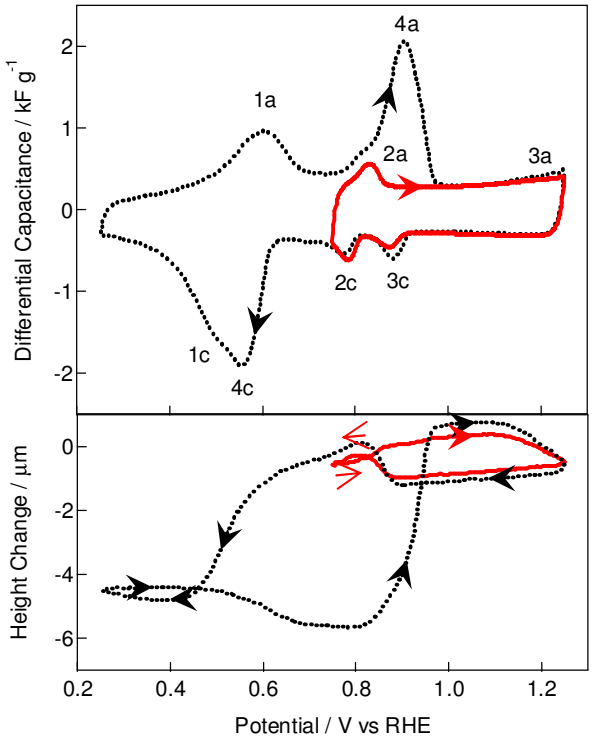
Change in *h* for peak 1 is ~1% (<2 µm/180 µm).
From the *d* spacing of HRO (*d*=0.5 nm), the height change per each sheet would be 0.5 nm to 0.505 nm. A change of 5 pm is too small to consider anion adsorption in the interlayer. Redox reaction most likely condifined to the outermost surface of the particles.

<u>Peak 1 => specific anion sorption</u>
Observed only in H_2SO_4 and $HClO_4$.[]
Decrease in *h* on the anodic scan -> desorption of specifically adsorbed anions.
Probable anodic reaction:

$$H_{0.2+x}Ru^{(4-x)+}O_{2.1}\cdot(SO_4^{2-})_y \rightarrow H_{0.2+x}Ru^{(4-x)+}O_{2.1} + y(SO_4^{2-}) - 2ye^-$$

0.5 M $HClO_4$ (25ºC)
v=0.5 mV s^{-1}
2.0 mg, h_0~180 µm

Identification of Peak 2



change in height (~0.5 %)

Peak 2
cathodic: 0.82 → 0.75 V (↓ in *h*)
anodic: 0.75 → 0.87 V (↑ in *h*)

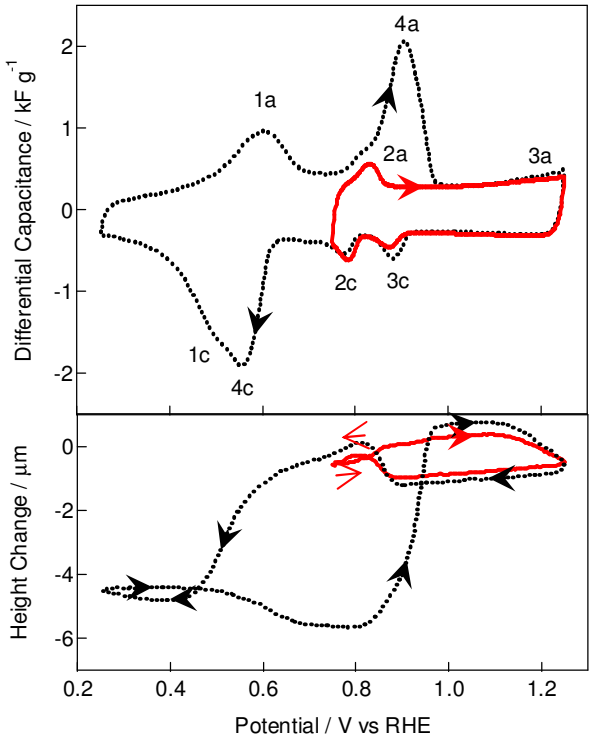
Change in *h* for peak 2 is <1% (~1 µm/180 µm).
From the *d* spacing of HRO (*d*=0.5 nm), the height change per each sheet would be 0.5 nm to 0.505 nm. A change of 5 pm is too small to consider anion adsorption in the interlayer. Redox reaction most likely condifined to the outermost surface of the particles.

Peak 2 => cation sorption.
Increase in h on anodic scan => simultaneous desorption of protons and injection of H_2O.
Possible anodic reaction:

$$H_{0.2+x}Ru^{(4-x)+}O_{2.1} \bullet (m+n)H_2O \rightarrow \; H_{0.2}Ru^{4+}O_{2.1} \bullet mH_2O + nH_2O - xe^- - xH^+$$

0.5 M $HClO_4$ (25ºC)
v=0.5 mV s^{-1}
2.0 mg, h_0~180 µm

Identification of Peak 3



change in height (~0.5 %)

Peak 2
cathodic: 0.90 → 0.82 V (↑ in *h*)
anodic: 1.10 → 1.25 V (↓ in *h*)

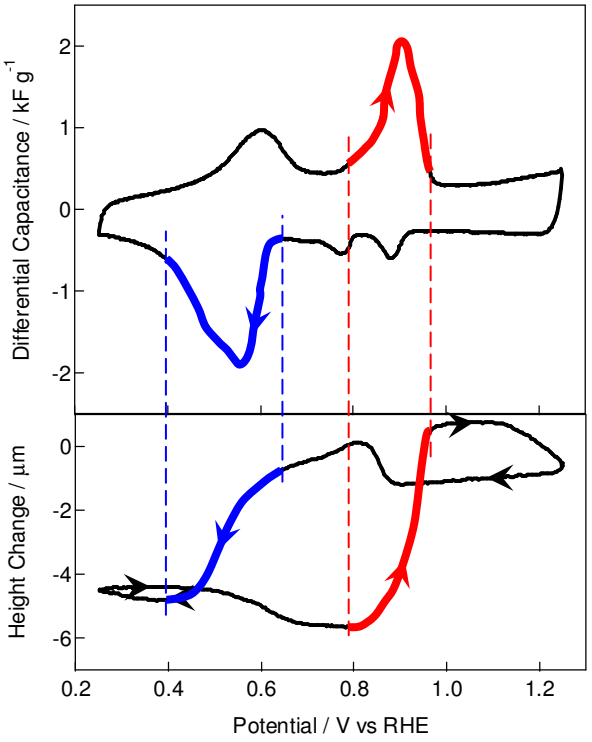
Change in *h* for peak 3 is <1% (~1 µm/180 µm).
From the *d* spacing of HRO (*d*=0.5 nm), the height change per each sheet would be 0.5 nm to 0.505 nm. A change of 5 pm is too small to consider anion adsorption in the interlayer. Redox reaction most likely condifined to the outermost surface of the particles.

Peak 3 => cation adsorption?
Possible anodic reaction:

$$H_{0.2}Ru^{4+}O_{2.1} \rightarrow Ru^{4.2}O_{2.1} - 0.2e^{-} - 0.2H^{+}$$

0.5 M $HClO_4$ (25ºC)
v=0.5 mV s^{-1}
2.0 mg, h_0~180 µm

Identification of Peak 4



large change in height (~2 %)
cathodic scan 0.6 V → 0.45 V (decrease)
anodic scan 0.8 V → 0.95 V (increase)

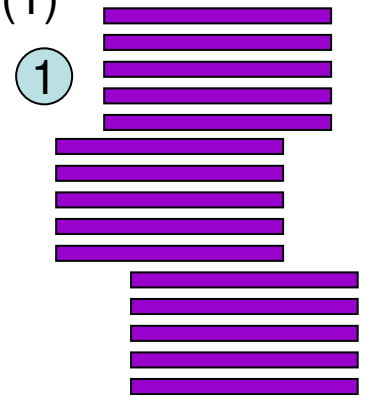
Change in *h* for peak 4 is <3% (~6 µm/180 µm).
From the *d* spacing of HRO (*d*=0.5 nm), the height change per each sheet would be 0.5 nm to 0.505 nm. A change of 5 pm is too small to consider anion adsorption in the interlayer. Redox reaction most likely condifined to the outermost surface of the particles.

Peak 4 => Cation sorption in the interlayer
✓ Large capacitance and height change.
✓ Large difference between E_a and E_c.
✓ Sorption process in the interlayer.
✓ Sensitive to the electrode fabrication process.

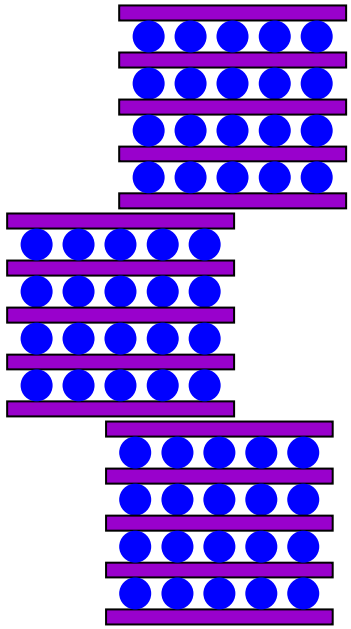
0.5 M $HClO_4$ (25ºC)
v=0.2 mV s^{-1}
5.2 mg, h_0~270 µm

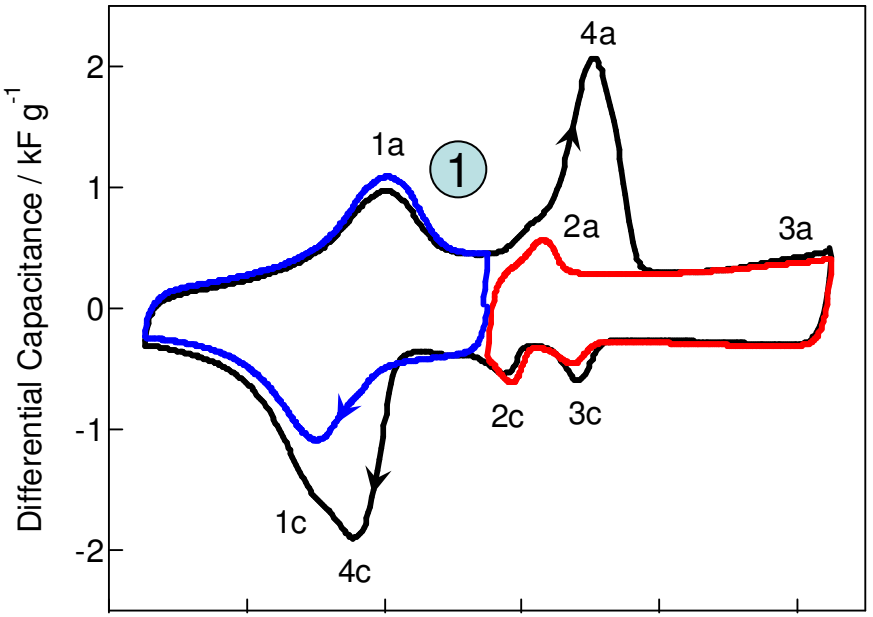
Proposed Redox Process in layered HRO

(1)



(2)





(3)

Proposed Redox Process in layered HRO