Modified Linear Combination Fitting for Large-Area Two-Dimensional Chemical State Mapping

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Back ground :

Recently, 2D or 3D maps of chemical state of elements performed with XAFS measurement are often reported for important targets, i.e., electrodes of battery cells. Usually such measurements are performed with x-ray beams of rather wide cross section and 2D detectors to record information in 2D area at once. In such cases, the size of the map is limited by the size of the beam which is usually not so large as 1mm square order. In order to realize the map larger than the beam size, it is necessary to scan samples mechanically, and it requires undesirable long time to measure XAFS spectra at each point.

In this work :

- We tried to develop a **modified linear combination fitting (MLCF)** technique which can be conducted on spectrum data measured at limited energy points, typically five or six points, to **reduce the measurement time**.
- With such XANES/XAFS spectra measured at several energy points, conventional linear combination fitting is hard to conduct, because it is difficult to find pre-/post-edge lines and to evaluate edge jumps to normalize the spectra.
- In order to obtain 2D maps using MLCF, samples are scanned several times to get maps of absorption coefficient, changing the incident x-ray energy for each scan. The few data sets are enough to analyze chemical state by MLCF.

Developing Modified LCF

Conventional :
1. Prepare spectra of target and standard samples.
2. Normalize the spectra finding pre/post-edge lines.
3. Find the mixture ratio of standard spectra.

Modified :
1. Prepare spectra of target and standard samples.
2. Normalize the **standard spectra only**.
3. Find the **mixture ratio** and the **parameters to normalize the target spectrum at once**.
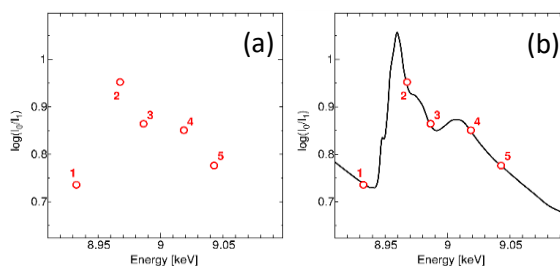
At first glance, you may feel it's impossible to analyze the data shown in fig 1-(a) to find the valence of the sample, don't you ?

MLCF is a problem to find a set of mixture ratio among the standard spectra which represent the spectrum of the target sample (slid line in (b)), when the target spectrum is given on only a few energy points (red circles in (a)).

How to (The method of MLCF)

Inputs Standards : $R^k(E)$, Target : maps of M_i

k : Index of the standard samples.

R^k : Standard spectra normalized by edge-jump $\Delta\mu^k$ after subtracting pre-edge line. $R_i^k \overset{def}{=} R^k(E_i)$

M_i : Measured $\log\{I_0/I_1\}$ for target sample at energy E_i.

· When we assume the state of target element in the target sample can be explained as mixture of the standard materials with ratios α^k,

   M at E_i should be calculated as $M(E_i) = \sum_k \alpha^k \mu_i^k t + BG(E_i)$, where $BG(E_i)$ is back ground, e.g., $BG(E_i) = C_0 + C_1 E_i$, and μ_i^k is given as $\mu_i^k = R_i^k/t^k$.

· When we take the mean thickness of the standards $\bar{t^k}$ as unit of thickness, all other thicknesses can be represented as $t = t_r \bar{t^k}$ for target and $t^k = t_r^k \bar{t^k}$ for standards.

   It is important that t_r^k can be given preliminarily as $t_r^k = \Delta\mu^k/\overline{\Delta\mu^k}$.

· By using the t_r and t_r^k, $M(E_i) = \sum_k \alpha^k (t_r/t_r^k) R_i^k + BG(E_i)$. Replacing $\alpha^k(t_r/t_r^k)$ by A^k, we obtain $M(E_i) = \sum_k A^k R_i^k + BG(E_i)$.

· Then by solving a least square problem to make $\sum_i \{M_i - M(E_i)\}^2$ minimum, values of the parameters A^k and $C_0, C_1,...$ can be decided.

   It means that we can conduct LCF and the process to decide back ground line at once.

· Using the preliminarily given t_r^k and the values of A^k, now we can calculate $\sum_k t_r^k A^k$ and it gives t_r, since $\sum_k t_r^k A^k = \sum_k t_r^k \alpha^k (t_r/t_r^k) = t_r \sum_k \alpha^k = t_r$ (note $\sum_k \alpha^k = 1$).
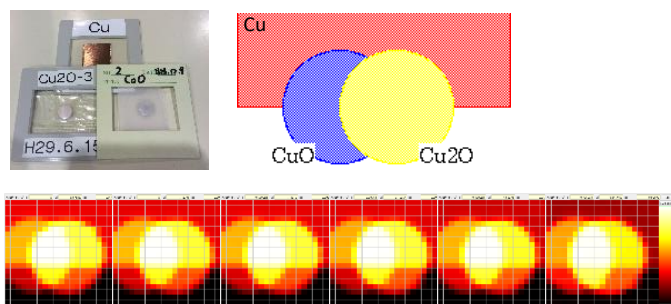
· Finally, we can obtained the mixture ratios as $\alpha^k = A^k t_r^k/t_r$.
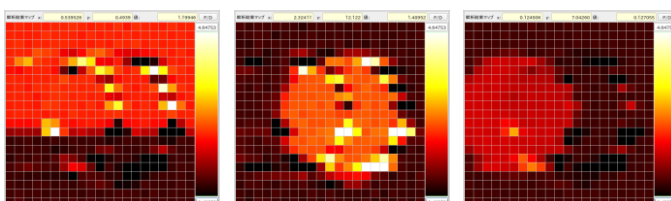
Outputs   Target : maps of α^k, a map of t_r

Examples

### 1. Stacked Cu foil and tablets of Cu2O and CuO.

Measured $M_i = \log(I_0/I_1)$ map on 2x2 cm square at 6 energy points E_i. It spent only a few minutes to take each map.


Calculated distributions of Cu, Cu2O, and Cu. Each map clearly shows where each material is. Note, the MLCF method gives not only the mixture ratios a^k, but also the relative thickness t_r. Thus, equivalent thicknesses of standard materials at each point are also given as $a^k t_r$, in other words, we can find if the material is there, or not.

2. Cathode surface of Ni-MH cell.

60%   100% Charged
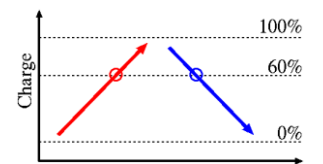

2.0   2.5   3.0
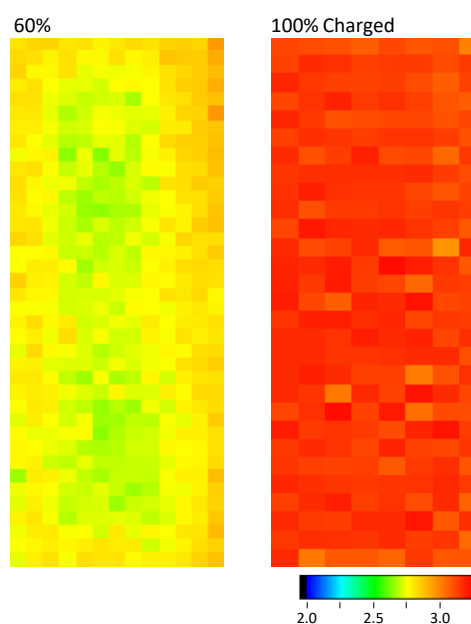
Distributions of Ni valence in 76mm x 26mm area were successfully analyzed from a set of 2D maps measured at 4 energy points, which totally spent about half an hour.

3. Ni valence in sliced cathode of Ni-MH cell.
(Microscopic mapping using capillary)
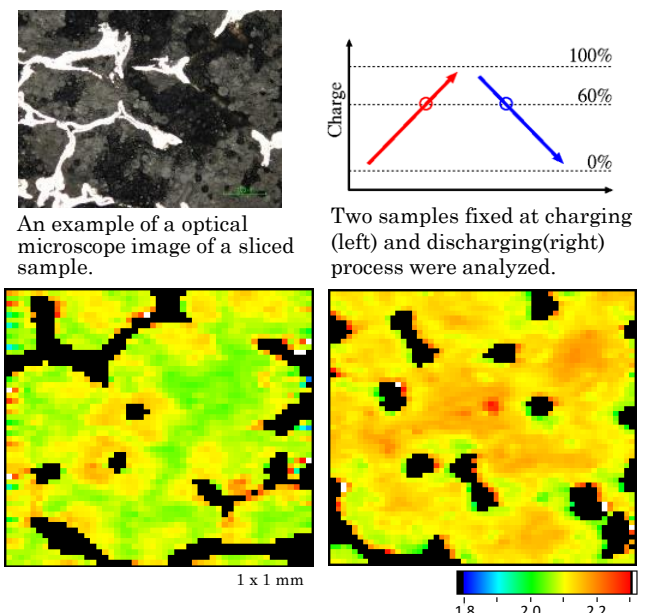
An example of a optical microscope image of a sliced sample.

Two samples fixed at charging (left) and discharging(right) process were analyzed.

1 x 1 mm

1.8   2.0   2.2

It was observed on the charging process, Ni near the electrode (black) showed higher valence, while it showed lower valence on the discharging process.