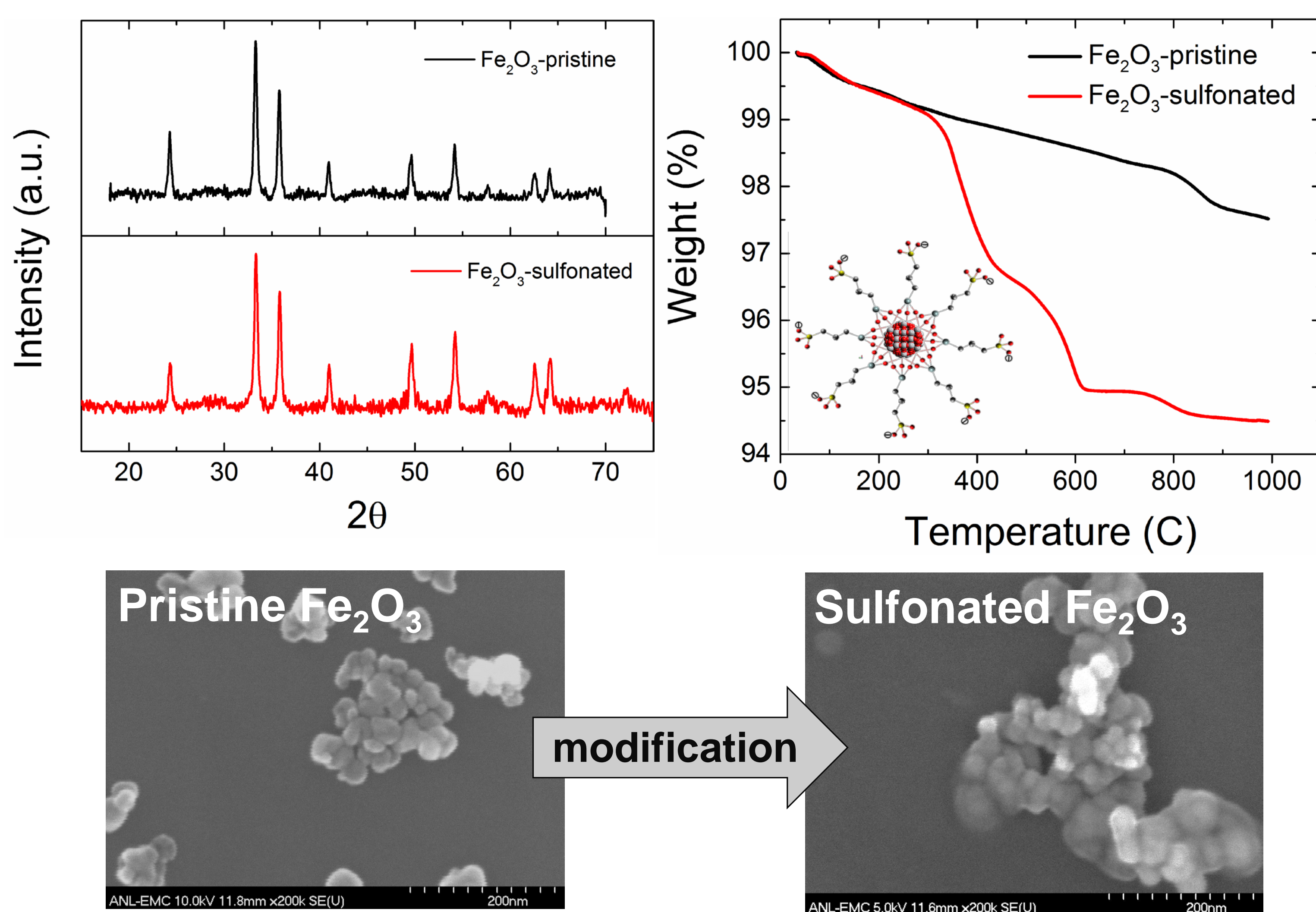


## Introduction

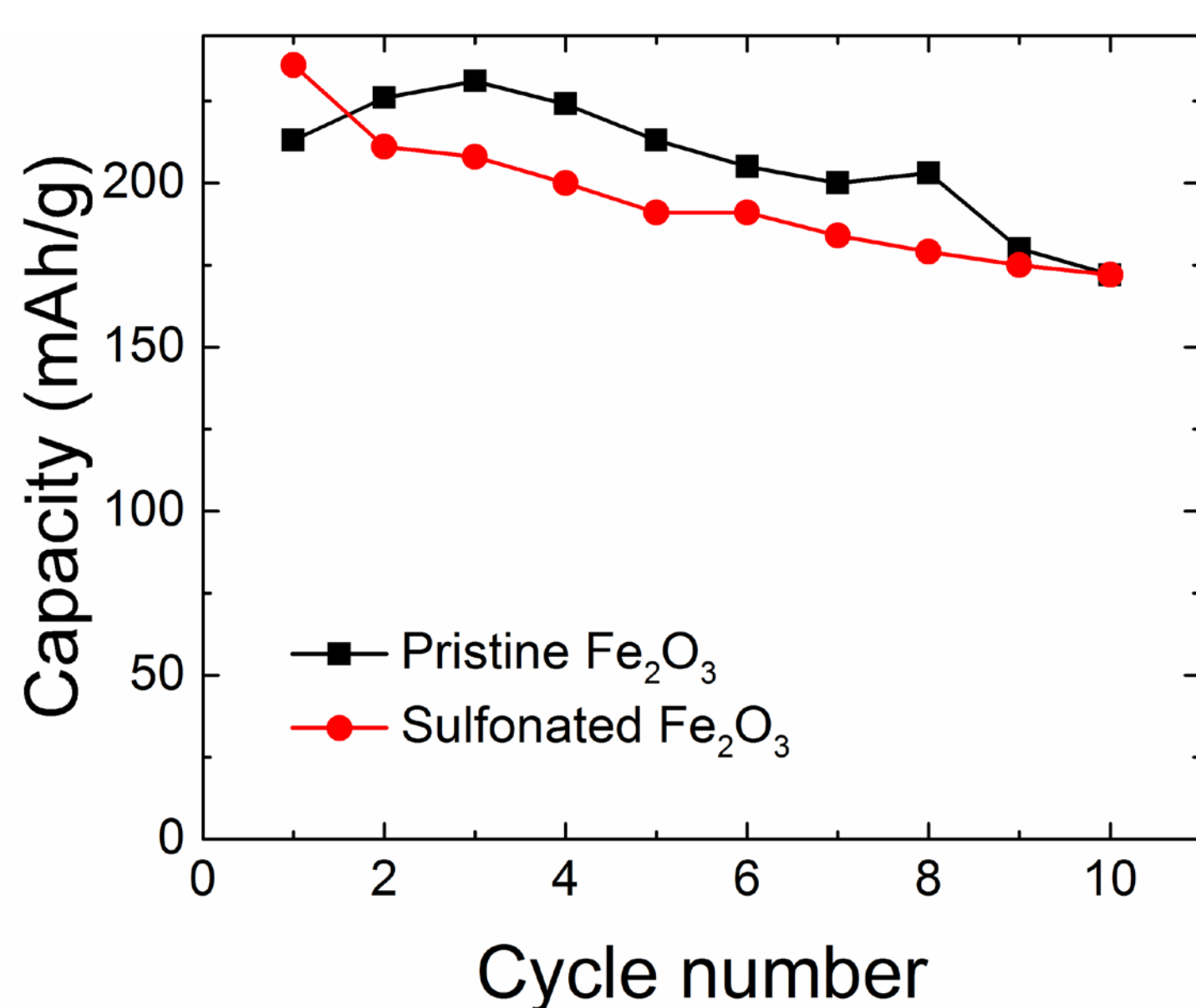
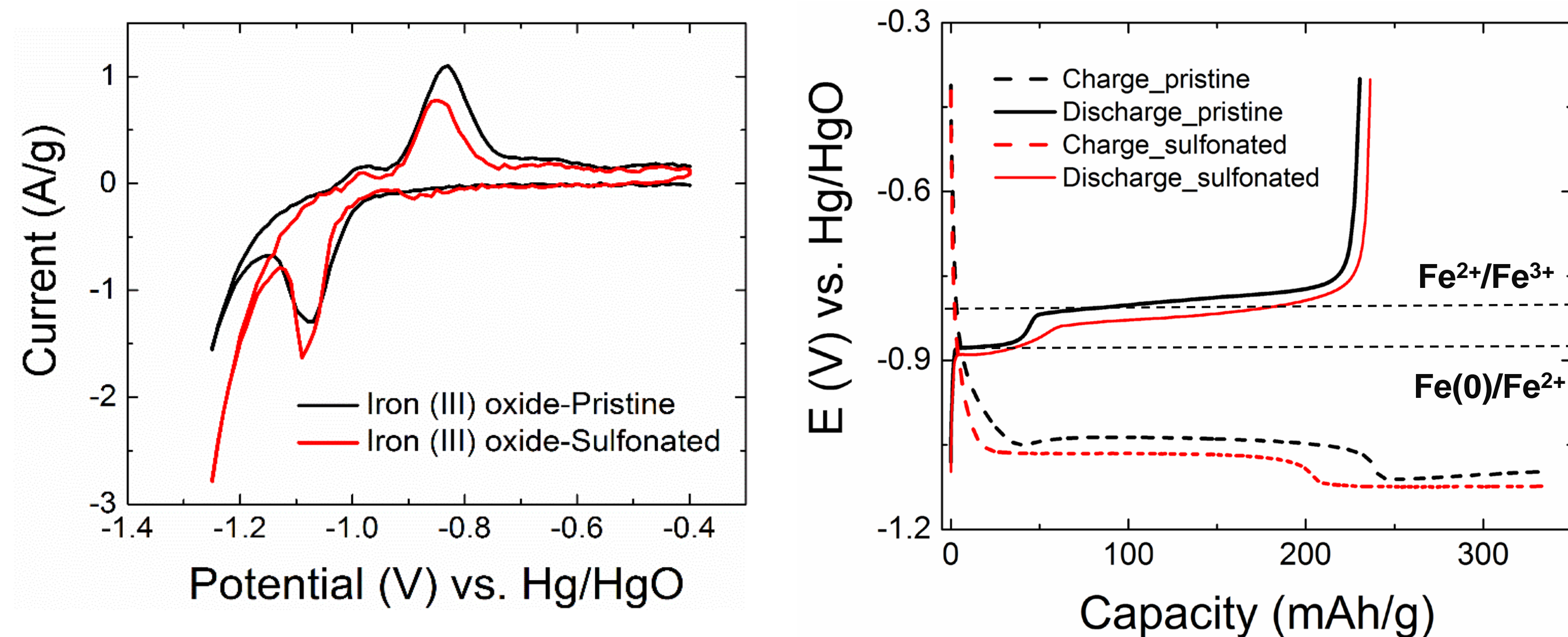
Iron oxides are considered as high capacity anode materials due to multiple redox transitions:  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $\text{Fe}^{2+}/\text{Fe}^0$ , which also can be accompanied by lithium ion intercalation. The nature of the redox event varies with several factors such as electrolyte composition and concentration, rate of charge/discharge and cycling history. Understanding the nature of the redox transition during electrochemical cycling is critical for optimization of the system capacity. We use in-situ X-ray absorption spectroscopy (XAS) combined with post-mortem characterization of electrode morphology with scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX) to study the redox chemistry of Iron (III) oxide ( $\alpha\text{-Fe}_2\text{O}_3$ , hematite) nanoparticles in aqueous electrolytes, and establish the role of  $\text{Li}^+$  ions and correlate redox events with coulombic input. We also investigated the effect of surface modification of  $\text{Fe}_2\text{O}_3$  nanoparticles on capacity and cycling performance.

## Surface modification

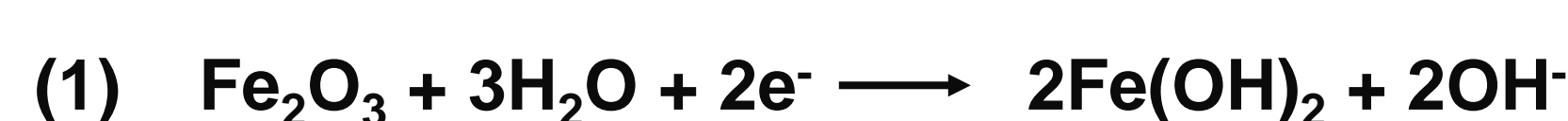
For surface modification, pristine  $\text{Fe}_2\text{O}_3$  (hematite) was treated with a silane based grafting moiety in aqueous media to obtain sulfonated  $\text{Fe}_2\text{O}_3$ . Thermogravimetric (TGA) analysis revealed a 3 wt.% loading of the grafting moiety, which corresponds to a near monolayer coverage. XRD analysis showed no change in the crystalline structure of the hematite due to the surface modification procedure. SEM imaging shows obvious presence of a coating on the surface of individual nanoparticles.



Cyclic voltammogram of solid casted electrodes of both pristine and surface modified  $\text{Fe}_2\text{O}_3$  reveal reversible redox transition occurs at -0.9V vs. Hg/HgO in aqueous 5.5 M LiOH. Potentiometric testing of the same electrodes (C/3 charge; C/6 discharge) revealed a comparable maximum discharge capacity of ~230 mAh/g (assuming theoretical capacity of 335 mAh/g for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in  $\text{Fe}_2\text{O}_3$ ). Capacity fading was observed in both systems.



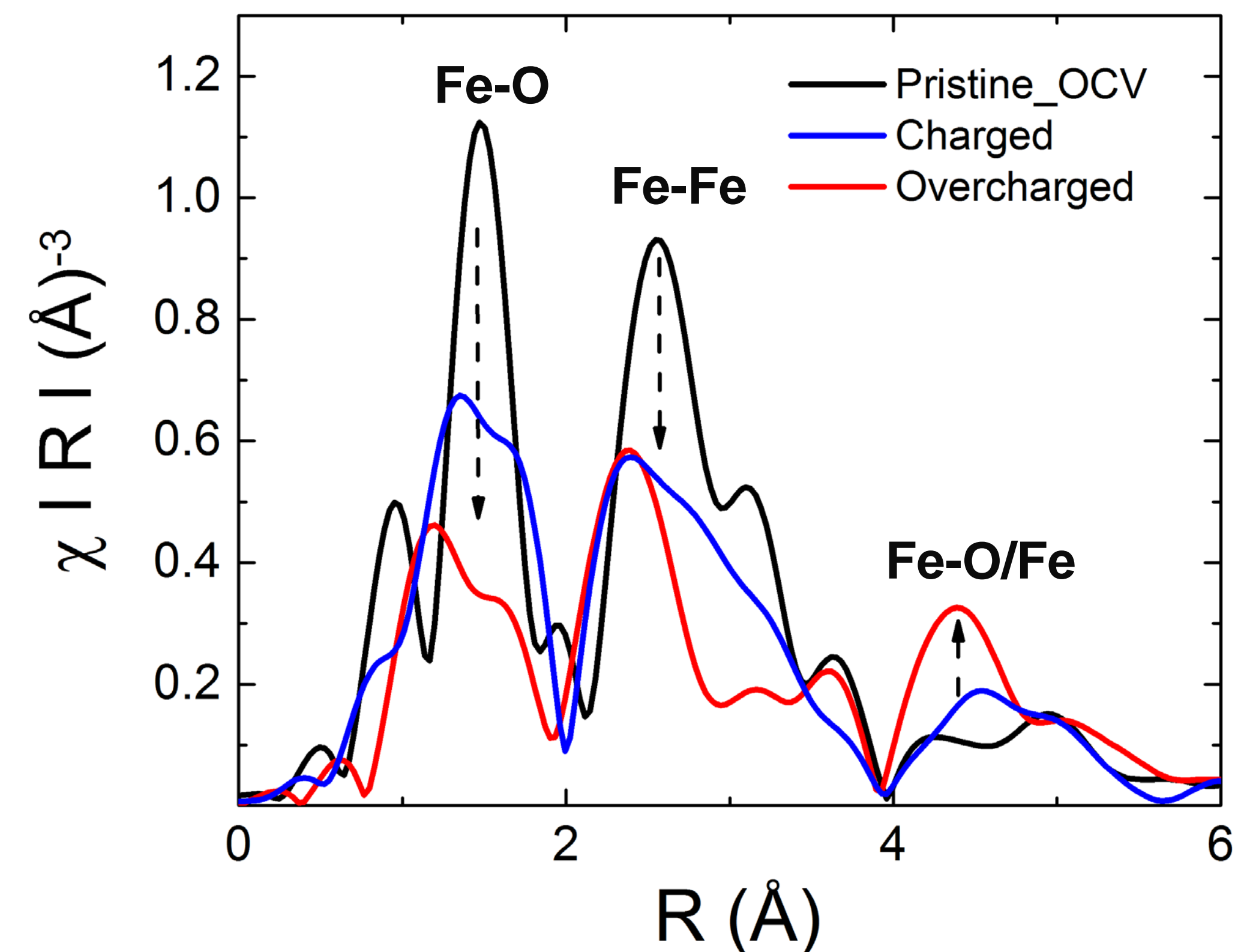
Charging reaction : 335 mAh/g



Over-charging reaction : 670 mAh/g



## In-situ XAS characterization of anode

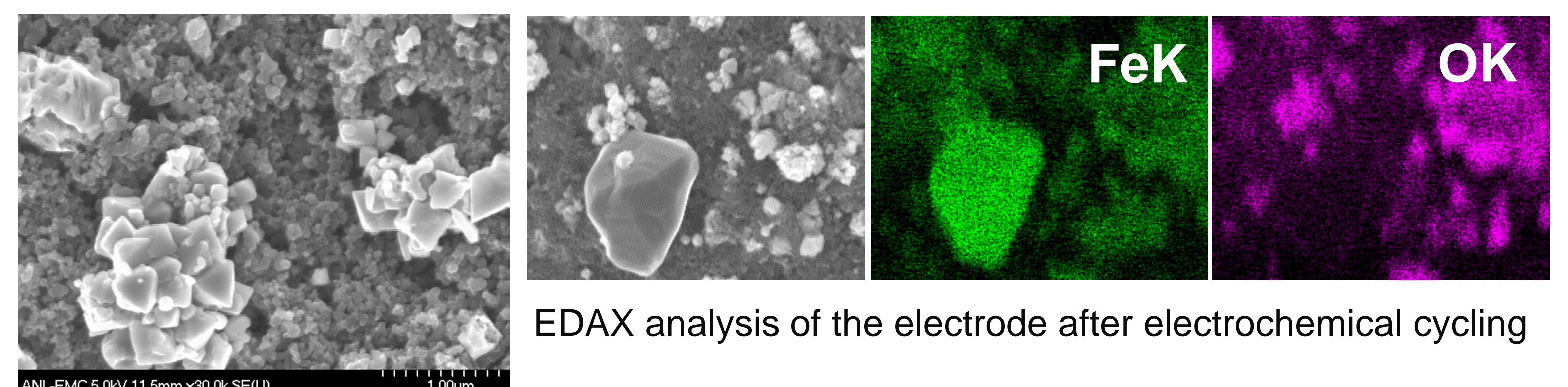


In-situ XAS characterization was performed on a solid casted pristine  $\text{Fe}_2\text{O}_3$  electrode in aqueous 5.5M LiOH. R-space plots in different states of charge reveal significant changes in Fe-O and Fe-Fe bond distances and peak intensities. Charging to 335 mAh/g (equation 1) leads to a marked decrease in Fe-O and Fe-Fe peak intensities. Further *overcharging* to 1005 mAh/g (equation 2) leads to a further drop in the Fe-O intensity but little change in Fe-Fe peak intensity. Growth of peaks  $>4\text{\AA}$  suggests increasing long-range order metallic interactions

## Morphological changes after cycling

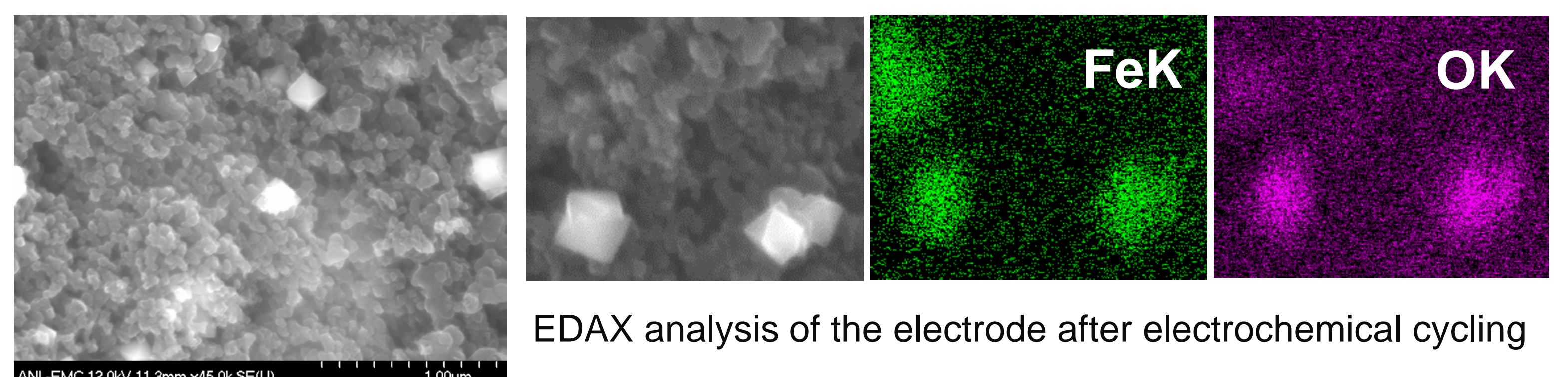
Examination of the pristine electrodes after cycling in the *discharged state* using SEM and EDX revealed significant changes in morphology, in particular formation of large metallic iron crystallites. Repeated electrochemical cycling leads to growth of large micron sized Fe crystals, No oxygen atoms are present in the same area.

### Pristine $\text{Fe}_2\text{O}_3$



Electrodes prepared with surface modified particles on the contrary, show minimal change in morphology with even distribution of both iron and oxygen atoms throughout the electrode

### Sulfonated $\text{Fe}_2\text{O}_3$



## Summary

A simple one-step modification method was used to functionalize the surface of  $\text{Fe}_2\text{O}_3$  hematite nanoparticles with sulfonate groups. This procedure suppressed the morphological changes in electrode during charge/discharge cycles and prevented growth of Fe crystallites, while exhibiting similar discharge capacity. Ongoing efforts for XAFS modeling of charged and discharged states will reveal more on redox transitions and role of Li-intercalation in both electrodes.

## Acknowledgements

This project is supported by DOE ARPA-E RANGE program. Electron Microscopy Center (EMC) and XAS was conducted at MRCAT beamlines at Advanced Photon Source (APS), both at Argonne National Laboratory and supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DEAC02-06CH11357. MRCAT operations are supported by the Department of Energy and the MRCAT member institutions.