

In summary, a facile strategy based on rapid reconstruction of amorphous nanofilm precursors is proposed for the exploration of catalysts free of precious metal and with satisfactory electronic conductivity, ultrahigh activity and robust stability. The rapidly reconstructed SCFP bifunctional catalysts show ultrahigh mass activity and protracted operational stability, significantly over-performing precious-metal catalysts at the state of the art. (Reported by Yan-Gu Lin)

This report features the work of Zongping Shao and his co-workers published in Adv. Mater. 30, 1804333 (2018).

TLS 11A1 BM – (Dragon) MCD, XAS

- MCD, PES, XPS, XAS
- Condensed-matter Physics, Materials Science

Reference

1. G. Chen, Z. Hu, Y. Zhu, B. Gu, Y. Zhong, H.-J. Lin, C.-T. Chen, W. Zhou, and Z. Shao, Adv. Mater. **30**, 1804333 (2018).

Neutrons See the Mechanism of an Energy Material Without Destroying the Component

The advantages of neutrons as a probe are utilized, i.e. with sensitivity to Li and the ability to penetrate through the battery as a whole. Neutron diffraction has served in an investigation of the structural changes of the anode and cathode materials, with the focus on the former, that take place during charging and discharging.

Two mainstream advanced-energy storage systems are well known and are under development for end-user applications. Lithium-ion secondary batteries (LIB) have already become practical as small power supplies for devices such as mobile telephones and notebook computers, but for large power supplies, such as grid energy storage, the weight of the material that increases cost, environmental impact and cost performance, becomes the top priority instead of energy density. One candidate for the next generation of secondary batteries that has been proposed to meet this demand for large-scale energy storage is the sodium-ion secondary battery (SIB), that uses sodium instead of lithium as the charge carrier.¹

For this application, there is no doubt that safety during discharging and efficiency upon charging are the most urgent issues for the lithium-ion batteries, especially at low temperature. Investigations of the phenomena on an atomic scale are essential for a full understanding of the processes during battery operation. Also, batteries are operated within a broad temperature range, both below and above room temperature, and temperature change affects the performance and safety limits. Li-plating, i.e. forma-

tion of lithium metal on the graphite anode, severely degrades the performance of the battery, including loss of capacity, increased impedance, slowed activity and accelerated aging. Neutron diffraction has been used to investigate the structural changes of the anode and cathode materials, with the focus on the former, that occur during charging and discharging.² Chun-Ming Wu (NSRRC) utilized the advantages of neutrons as a probe, i.e. the sensitivity to Li and an ability to penetrate through the battery as a whole, to undertake an investigation *in operando* on an LIB of 18650 type at and below ambient temperature with the first Taiwan cold-triple axis spectrometer — SIKA at OPAL, ANSTO.³

Figure 1 shows the temporal evolution of neutron diffraction patterns over scattering angle 2θ in the range 35° to 42° in monitoring the LiC_x from the LiC_6 phase transition to the graphite phase for the discharging or the opposite transition for the charging state at varied temperature. The five stages in **Fig. 1** show the substantial loss of capacity at low temperature, especially at -20°C at which the capacity was found to decrease to 229.5 mAh, which is one seventh that at ambient temperature (stage 1). Stage 4 at ambient temperature was tested to verify whether

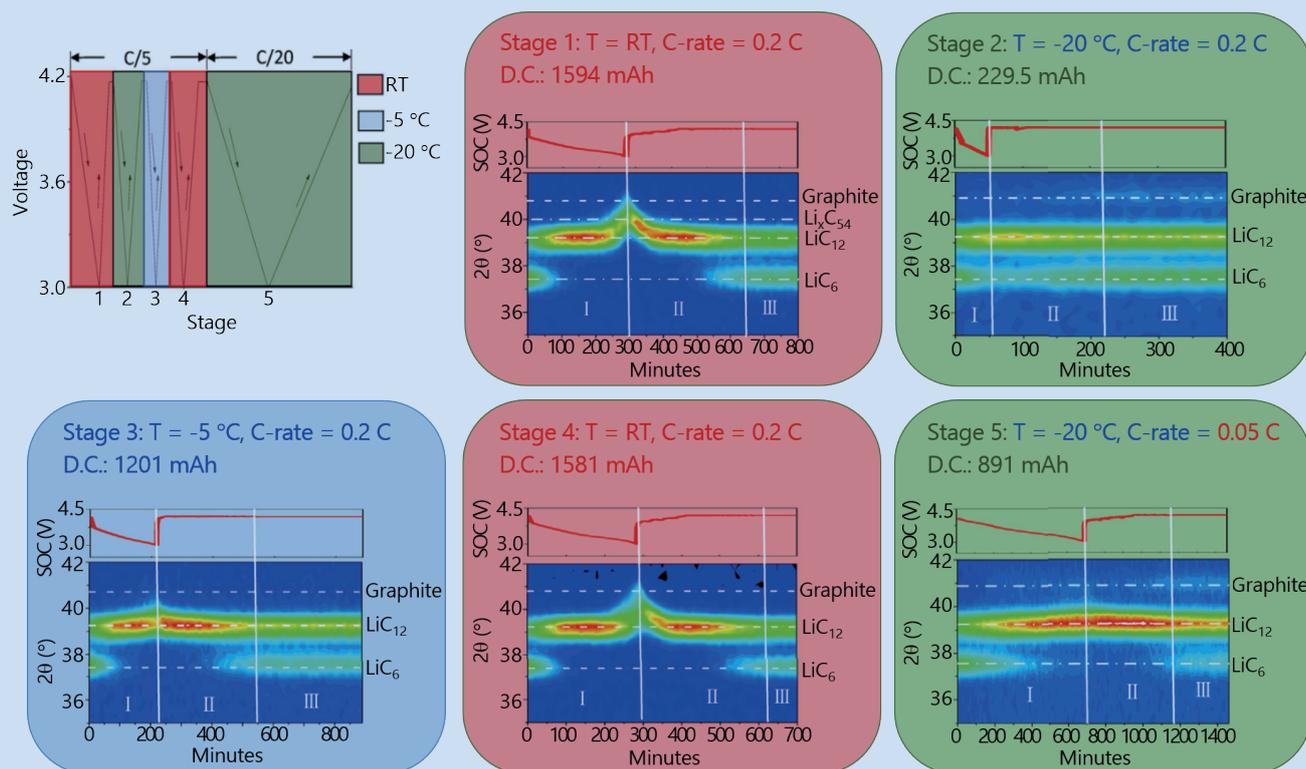


Fig. 1: Temporal evolution of neutron-diffraction patterns collected for a 18650 cell with the NMC cathode corresponding to the state of charging (voltage) at five stages of temperature and current rates: (1) discharge phase (CC), (2) is the charge phase (CC) and (3) is the relaxation phase (CV) in the battery operation. [Reproduced from Ref. 3]

the battery returns to the original state, *i.e.* the rate of Li extraction and recovery of capacity after cooling the battery to $-20\text{ }^{\circ}\text{C}$. The data indicated that the battery showed only a negligible memory effect, $\sim 3\%$, as discussed in the article.

A concept similar to the neutron technique was conducted by Chia-Ching Chang (National University of Taiwan) who investigated the Na^+ ion deintercalation in the charging stage of the first cycle. As shown in **Fig. 2 and 3**, the lattice spacing of (002) (d_{200}) expanded from 4.755 to $4.806\text{ }\text{\AA}$ with cell voltage from 2.0 to $\sim 3.9\text{ V}$. On increasing voltage further to 4.3 V , d_{200} maintained $4.806\text{ }\text{\AA}$. A plateau of lattice spacing between 3.9 and 4.3 V implies a large energy barrier for the diffusion of Na^+ ions. During charging, the polarization curve shows a profile similar to that of a distribution of diffusion-controlled ion concentration in a solid-state crystal, with capacity increasing from 0 to 300 mA h . In this curve, an inflection point for different slopes of a plot for capacity vs voltage was found, implying an interface for the ion diffusion barrier at 3.9 V .⁴

Chang's group observed a region of slow exchange from Na^+ to defect site, in the decreased capacity to voltage slope at a voltage greater than 3.9 V . In this voltage range, a slight decrease of d_{102} from 2.420 to

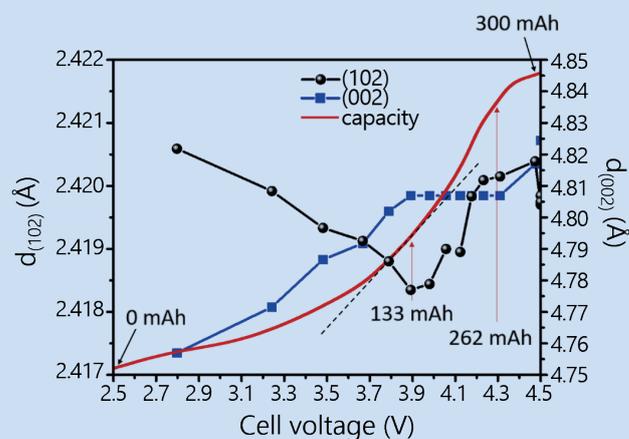


Fig. 2: Neutron diffraction results *in operando* and the corresponding polarization curve of a 18650 cell operating between 2.0 and 4.5 V during charging. [Reproduced from Ref. 4]

$2.418\text{ }\text{\AA}$ resembled a local compression or distortion in lattice planes intersecting with plane (002). An expansion might be attributed to a local distortion mostly at Fe sites. On increasing the cell voltage to 4.5 V , d_{002} expanded to $4.825\text{ }\text{\AA}$. In this stage d_{102} shifted back to its original width, revealing a relaxation of the local distortion upon the completion of ion diffusion channels in NFMO. According to the neutron diffraction *in operando* conducted by Echidna in ANSTO, the scenarios for Na^+ deintercalation behavior in the

NFMO crystal with respect to voltage change in the SIB charging process include (1) Na⁺ ions relocating from lattice points to ion channels from 2.0 to 3.9 V. In this stage, Na⁺ ions tend to accumulate in the lattice planes perpendicular to axis *c* as revealed by expansion of d_{002} from 4.755 to 4.806 Å. In this event, Na⁺ intercalation generated a lateral expansion in plane (002) and thus compressed the lattice spacing of intersecting lattice planes (*i.e.*, (102)). (2) from 3.9 to 4.3 V, the capacity increased from 133 to 267 mAh. In the absence of d_{000} expansion, Na⁺ relocation occurred without generating additional distortion in planes (002) and was mainly in ion channels. Increasing voltage further from 4.3 to 4.5 V slightly expanded d_{002} to 4.825 Å, which accounts for further Na⁺ intercalation and a structural alignment in the ion channels. In this event, expansion of d_{102} (*i.e.*, relaxation of lateral strain in ion channels) to its original value complementary explains the interplays of lattice strains between intersecting lattice planes from 3.9 to 4.5 V. We cross-referred the obtained results also with X-ray absorption spectra and X-ray diffraction. Our results reveal that the local structural distortion appears at Fe sites but is absent at Mn sites of NFMO crystals in the first charging process. After 100 cycles, the transformation of octahedral to tetragonal symmetry proves a chemical interaction of Fe sites in the NFMO crystal. Such a transformation can be attributed to a formation of amorphous NaFeO_x structures, but the Mn sites showed a greater affinity for Na⁺ storage relative to the Fe sites and maintained their local symmetry unaltered, hence suppressing the capacity reversibility in a SIB. (Reported by Chun-Ming Wu)

This report features the work of Chun-Ming Wu, Chia-Ching Chang and their collaborators, published in (1) *Physica B: Condensed Matter* **551**, 305 (2018), and (2) *J. Phys. Chem. C* **122**(24), 12623 (2018).

ANSTO-CG4 SIKA – Cold Neutron Triple-axis Spectrometer

ANSTO-TG1 ECHIDNA – High-resolution Powder Diffractometer

- Elastic/Inelastic Neutron Scattering, Neutron Powder Diffraction
- Single Crystal, Superconductivity, Magnetism, Energy Materials, Material Structure

References

1. S. Komaba, W. Murata, T. Ishikawa, N. Yabuuchi, T. Ozeki, T. Nakayama, A. Ogata, K. Gotoh, K. Fujiwara, *Adv. Funct. Mater.*, **21** (20), 3859 (2011).
2. A. Senyshyn, O. Dolotko, M.J. Mühlbauer, K. Nikolowski, H. Fuess, H. Ehrenberg, *J. Electrochem. Soc.* **160** (5), A3198 (2013).
3. C. M. Wu, C. C. Chang, M. Avdeev, P. I. Pan, W. H. Li, *Physica B: Condensed Matter* **551**, 305 (2018).
4. T. Y. Chen, B. Han, C. W. Hu, Y. F. Su, Y. X. Zhou, H. Y. Chen, P. I. Pan, C. M. Wu, A. Hu, J. J. Kai, Y. D. Juang, C. C. Chang, *J. Phys. Chem. C*, **122** (24), 12623 (2018).

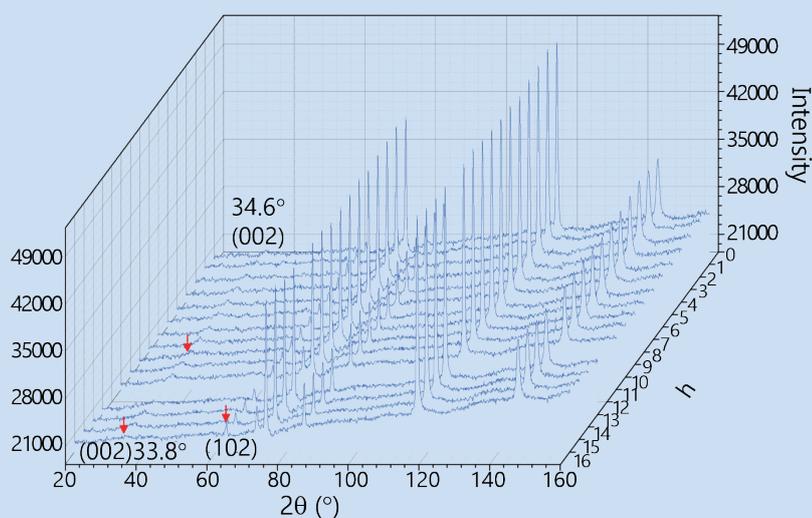


Fig. 3: Neutron-diffraction pattern *in operando* of a NFMO cathode in a 18650 cell operating from 2.0 to 4.5 V. [Reproduced from Ref. 4]