

## Enhanced Stability of Pt-TiO<sub>2</sub>-CNT Heterostructure Composite Cathodes for Li-O<sub>2</sub> Batteries Studied by High-Resolution AEM

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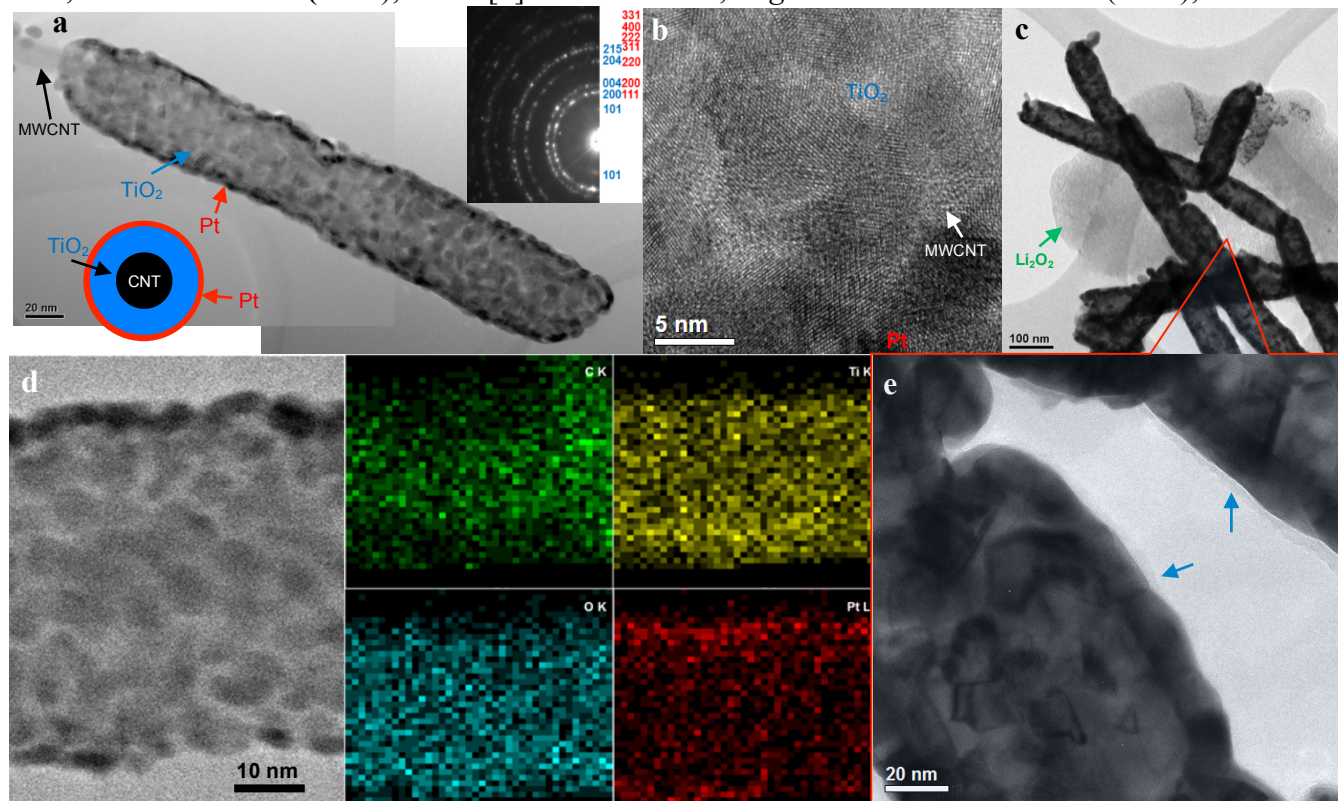
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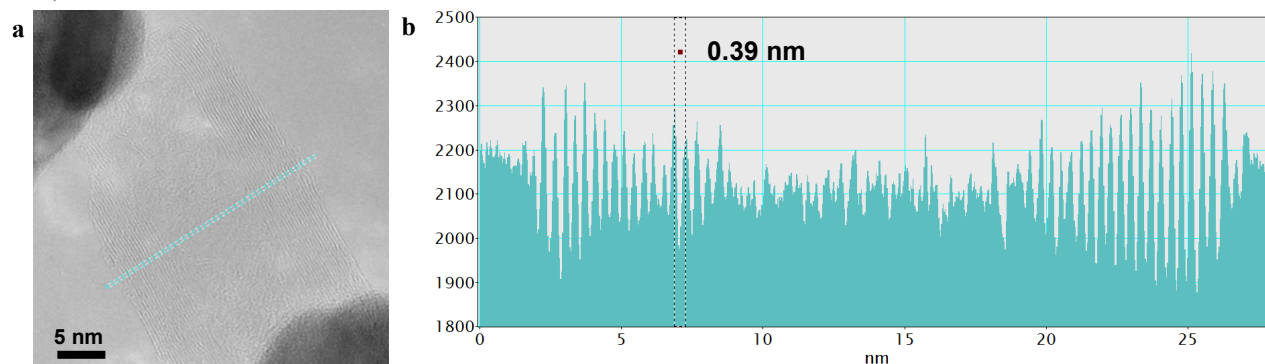
Li-O<sub>2</sub> batteries currently attract a lot of attention due to their super-high theoretical specific energy (~3500 Wh kg<sup>-1</sup>), which is almost an order of magnitude higher than for any Li-ion batteries (~380 Wh kg<sup>-1</sup>). Combined with the ability to use ambient oxygen as a “fuel”, Li-O<sub>2</sub>-based rechargeable electrochemical batteries show high promise in emerging pollution-free applications for long-range electric vehicles (>550 km) and in stationary grid energy storage [1]. One of the obstacles for the practical realization of Li-O<sub>2</sub> battery technology is, however, poor (electro)chemical stability of a cathode material under cell operating conditions. High surface area carbon-based cathodes have been shown high gravimetric capacities, but are hindered in terms of long term stability due to the reactivity of the carbonaceous electrode [1,2] In this work, we demonstrate using high-resolution analytical scanning/transmission electron microscopy (AS/TEM) that conjugation of effective protection and subsequent catalytic functionalization of the carbon surface provides a pathway toward harnessing the excellent current collector properties and high surface area of the carbon scaffold without risking known reactivity issues. A multi-walled carbon nanotube (MWCNT) sponge was chosen as the cathode scaffold for studies due to its excellent electronic conductivity, high surface area with mesoporosity, and lightweight. 3D mesoporous networks of CNTs exhibit a promise as O<sub>2</sub> electrodes [3] as a result of an open, high surface area structure conducive to reduction product formation and storage, as well as diffusion of active species, even at significant depths of discharge. While sp<sup>2</sup> hybridized carbon materials are generally considered the most viable carbon-based cathode scaffolds, during cell operation the CNTs are oxidized, leading to capacity fading and poor cycling stability. The stabilization modes were accomplished with a conformal double TiO<sub>2</sub> core - Pt shell nanolaminate structure as confirmed by conventional TEM, selected-area electron diffraction (SAED), HRTEM and STEM – energy-dispersive X-ray spectroscopic imaging (STEM-EDXS SI, FIG. 1). An inner TiO<sub>2</sub> layer was dedicated to protection of the carbon surface from oxidation, and an outer oxygen Pt electrocatalyst layer was utilized to improve surface reaction kinetics and decrease the oxygen evolution reaction/oxygen reduction reaction (OER/ORR) overpotential. A thin (5 nm), conformal coating layer of TiO<sub>2</sub> was grown on the MWCNTs by atomic layer deposition (ALD). In HRTEM image of the as-fabricated cathode structure (FIG. 1b), 0.23 nm (111) and 0.20 nm (200) lattice fringes from 5-10 nm Pt nanocrystallites overlap with 0.35 nm (101), 0.25 nm (004), and 0.20 nm (200) lattice fringes from the anatase protective shell over barely visible ~0.4 nm coarse graphitic-like interlayer spacings from a MWCNT core. Electrochemical performance of the stabilized MWCNT@TiO<sub>2</sub>@Pt cathode was tested via galvanostatic cycling with a normalized discharge capacity (150 mAhg<sup>-1</sup>) and current density (100 mA g<sup>-1</sup>), and a fixed voltage window of operation (2-4.1 V vs. Li/Li<sup>+</sup>). The baseline pristine MWCNT sponge could deliver only 5 discharge/charge cycles under such conditions before failure due to an oxidation-induced decrease in the electronic conductivity of the MWCNTs. The stabilized MWCNT@TiO<sub>2</sub>@Pt configuration has delivered 75 cycles demonstrating the effectiveness of a 5 nm TiO<sub>2</sub> ALD coating as a protection layer (FIGs. 1c, 1e and 2) and superior ORR activity, shifting the onset potential for oxygen

reduction from  $\sim 2.7\text{V}$  to  $\sim 2.8\text{V}$  as well. The Pt decorated cathode also showed the decrease in the overpotential of OER as compared to the pristine MWCNT and MWCNT@TiO<sub>2</sub>, and significantly more capacity was recovered under 4.1 V.

References: [1] M.A. Schroeder et al, *ACS Appl. Mater. Interfaces* **7** (2015), 11402. [2] M.A. Schroeder et al, *Chem. Mater.* **27** (2015), 5305. [3] H.D. Lim et al, *Angew. Chemie - Int. Ed.* **53** (2013), 3926.



**Figure 1.** BF-TEM montage, (a) a MWCNT@TiO<sub>2</sub>@Pt cathode and its schematic (bottom inset). The SAED pattern (top inset) shows discrete ring reflections assigned to superimposed anatase phase (blue) and fcc Pt (red). (b) HRTEM, an enlarged cathode fragment (see text for details). (c) A discharged cathode and an amorphous Li<sub>2</sub>O<sub>2</sub> phase accumulated during cycling. (d) STEM-EDX-SI, BF-STEM, composite cathode (left) and corresponding CK $\alpha$ , TiK $\alpha$ , OK $\alpha$ , and PtL $\alpha$  X-ray maps (right top and bottom), respectively. (e) An enlarged view of the discharged cathode reveals a 3-5 nm-thick solid electrolyte interface (SEI) layer on its surface (blue arrows).



**Figure 2.** HRTEM, (a) a discharged MWCNT@TiO<sub>2</sub>@Pt cathode, a 22-shell MWCNT preserved its structure after cycling. (b) An integrated line profile along the rectangular box in (a) with 0.39 nm graphitic-like interlayer spacing from the MWCNT fragment.