

Supporting Information

Microstructural Intra-Granular Cracking in $\text{Cu}_2\text{ZnSnS}_4@\text{C}$ Thin Film Anode Enhanced Electrochemical Performance in Lithium-Ion Battery Applications

Boya Venugopal^{a,b,c}, Indrajit Shown^{a,d*}, Satyanarayana Samireddi^c, Zeru Syum^a, Vimal Krishnamoorthy^{e,f}, Heng-Liang Wu^{e,g}, Chih-Wei Chu^h, Chih-Hao Lee^c, Li-Chyong Chen^{e,g}, Kuei-Hsien Chen^{a,e*}

^a Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.

^b Nanoscience and Technology Program, Taiwan International Graduate Program, Academia Sinica, Taipei-115-29, Taiwan.

^c Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30013, Taiwan.

^d Department of Chemistry, Hindustan Institute of Technology and Science, Chennai, 603103, India.

^e Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan.

^f Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 10607, Taiwan.

^g Center of Atomic Initiative for New Materials, National Taiwan University, Taipei 10617, Taiwan.

^h Research Centre for Applied Sciences, Academia Sinica, Taipei-11529, Taiwan.

*Corresponding authors

E-mail addresses: indrajit25@gmail.com (I. Shown), chenkh@pub.iams.sinica.edu.tw (K-H. Chen)

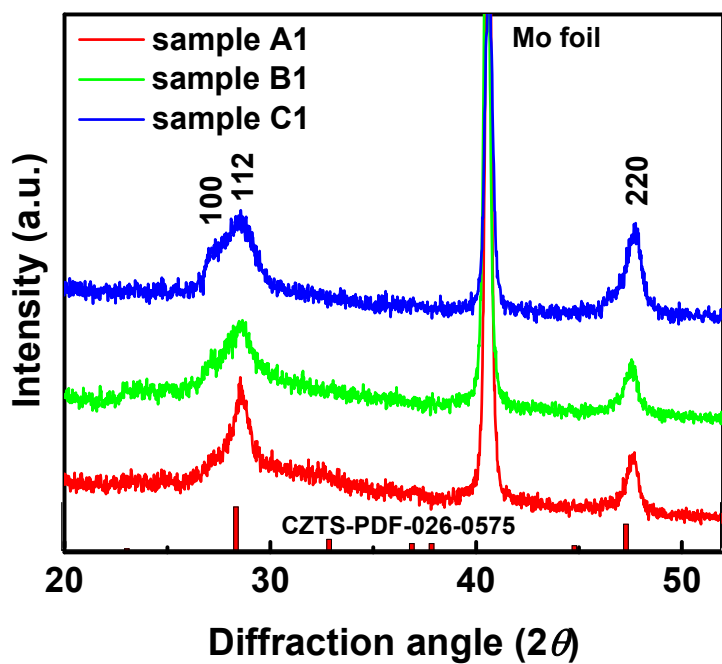


Fig. S1. XRD pattern for pure CZTS thin films deposited on Mo substrate at different time intervals (a) 12 h for sample A1, 24 h for sample B1, 48 h for sample C1

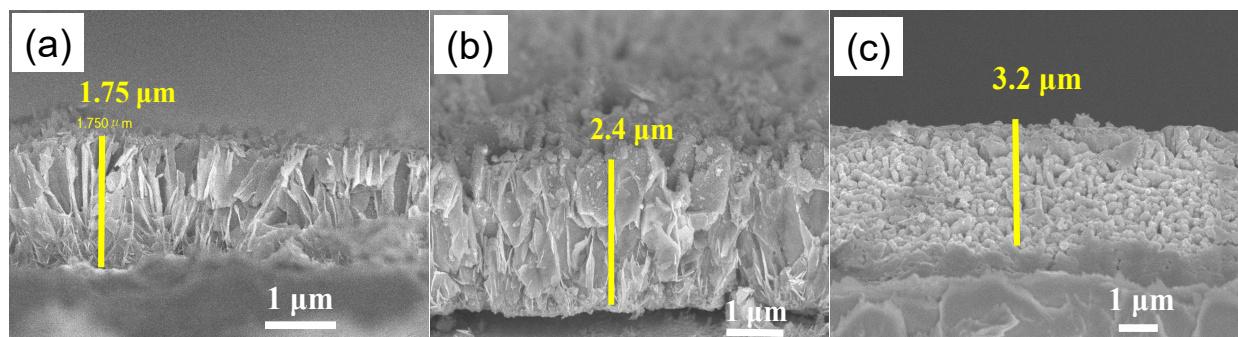


Fig. S2. SEM cross-sectional images of (a) Sample A (b) Sample B and (c) Sample C

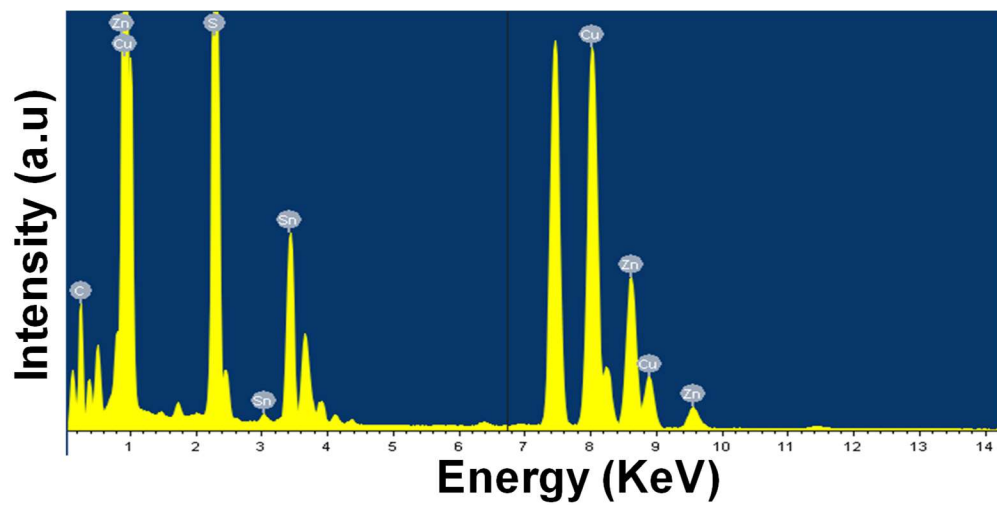


Fig. S3. EDS spectrum of Sample A

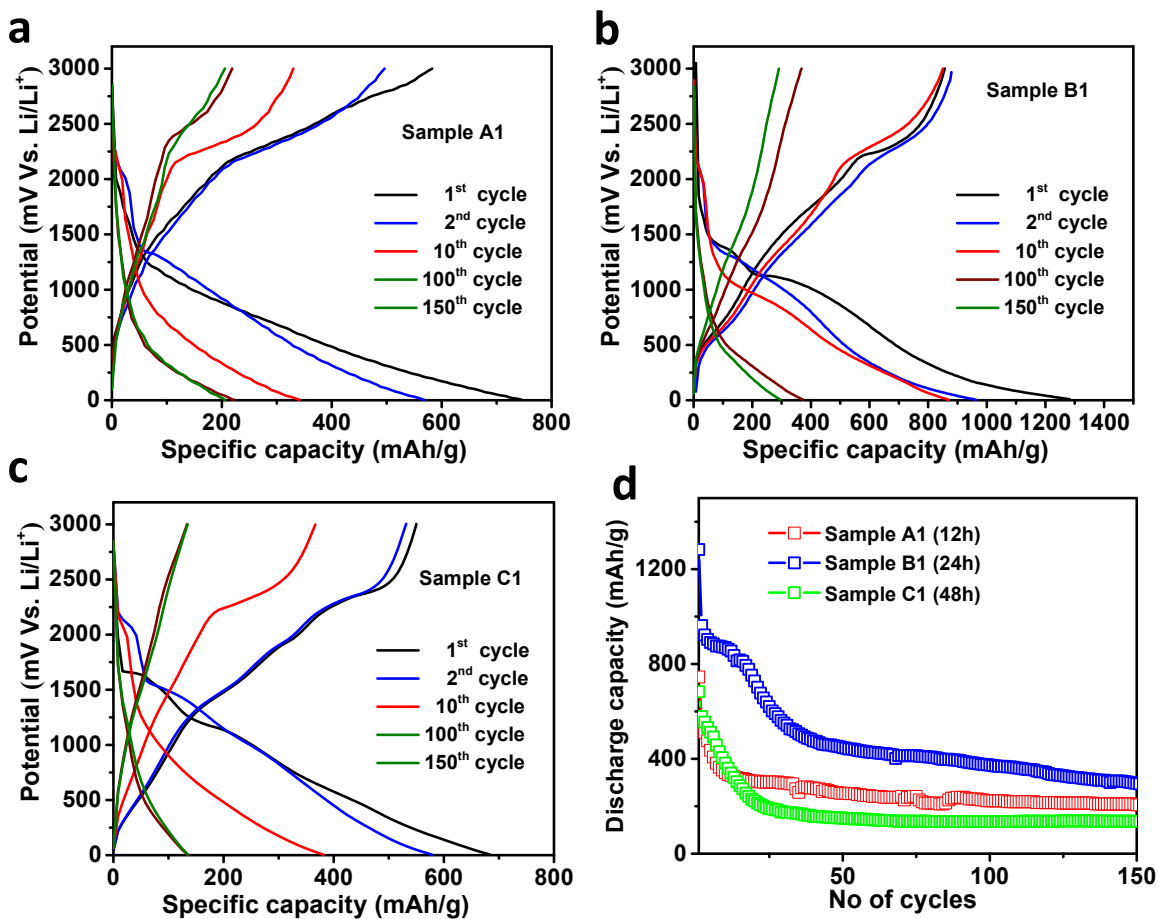


Fig. S4. Charge/discharge profile of pure CZTS growth on Mo substrate by hydrothermal method at different time intervals (a) sample A1 (12h) (b) sample B1 (24h) (c) sample C1 (48h) and (d) corresponding cyclic performance.

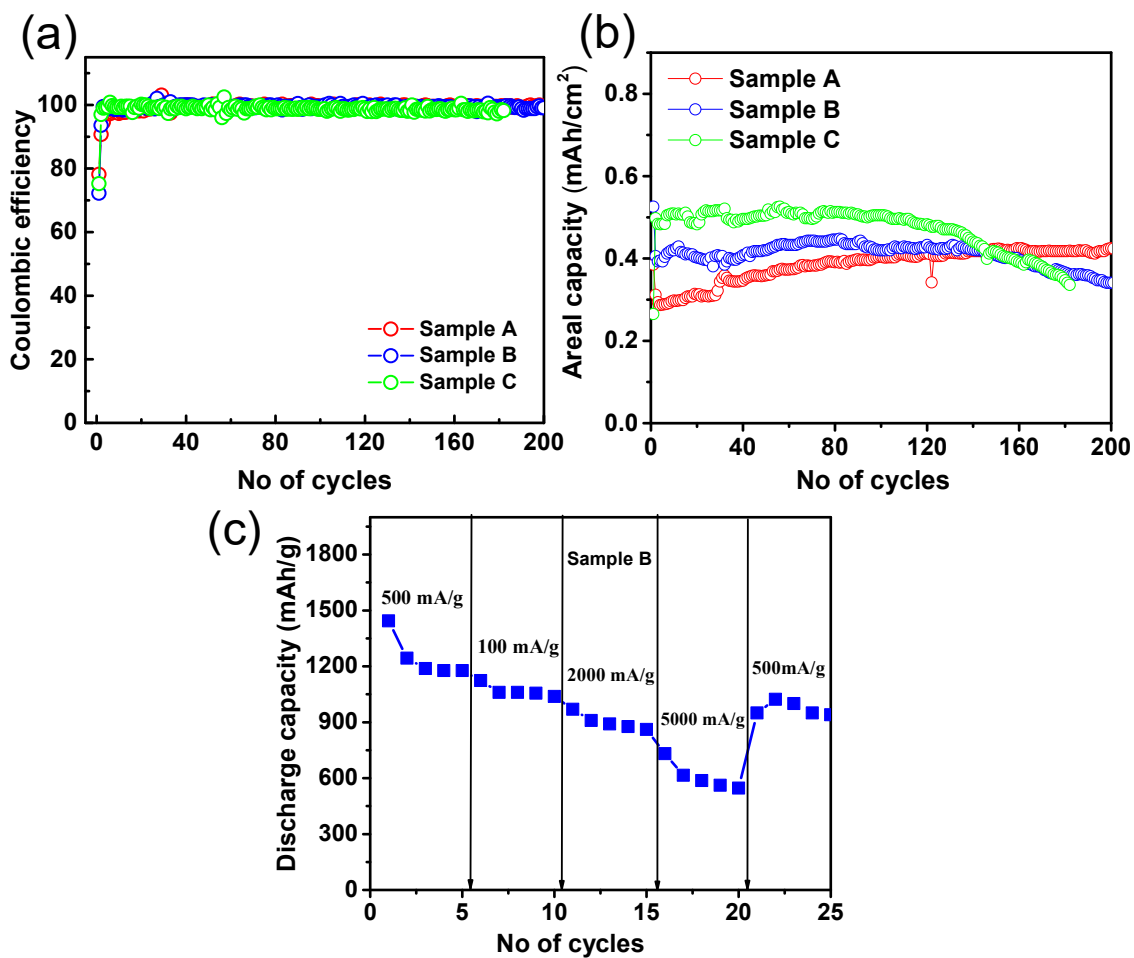


Fig. S5. (a) Coulombic efficiency (b) Areal capacity of Sample A, B and C and (c) Discharge capacity of Sample B

Calculation of volumetric capacity.

The thickness of the CZTS@C films was measured to be 1.7, 2.4 and 3.2 μm for all electrodes with different mass loading of 0.35, 0.53 and 0.8 mg cm^{-2} .

Therefore, the density (ρ) of the electrode is:

$$\text{Electrode-1} \quad \rho_1 = \frac{0.35 \text{ mg cm}^{-2}}{1.75 \mu\text{m}} = 2.00 \text{ g cm}^{-3}$$

$$\text{Electrode-2} \quad \rho_2 = \frac{0.53 \text{ mg cm}^{-2}}{2.4 \mu\text{m}} = 2.20 \text{ g cm}^{-3}$$

$$\text{Electrode-3} \quad \rho_3 = \frac{0.8 \text{ mg cm}^{-2}}{3.2 \mu\text{m}} = 2.50 \text{ g cm}^{-3}$$

The gravimetric capacity (C_g) of present electrode is measured to be 1214, 784 and 520 mAh/g as reported in Figure. 4. The volumetric capacity (C_v) is calculated:

$$\text{Electrode-1} \quad C_v = C_g * \rho = 1214 * 2.05 = 2488 \text{ mAh cm}^{-3}$$

$$\text{Electrode-2} \quad C_v = C_g * \rho = 784 * 2.20 = 1724 \text{ mAh cm}^{-3}$$

$$\text{Electrode-3} \quad C_v = C_g * \rho = 520 * 2.5 = 1300 \text{ mAh cm}^{-3}$$

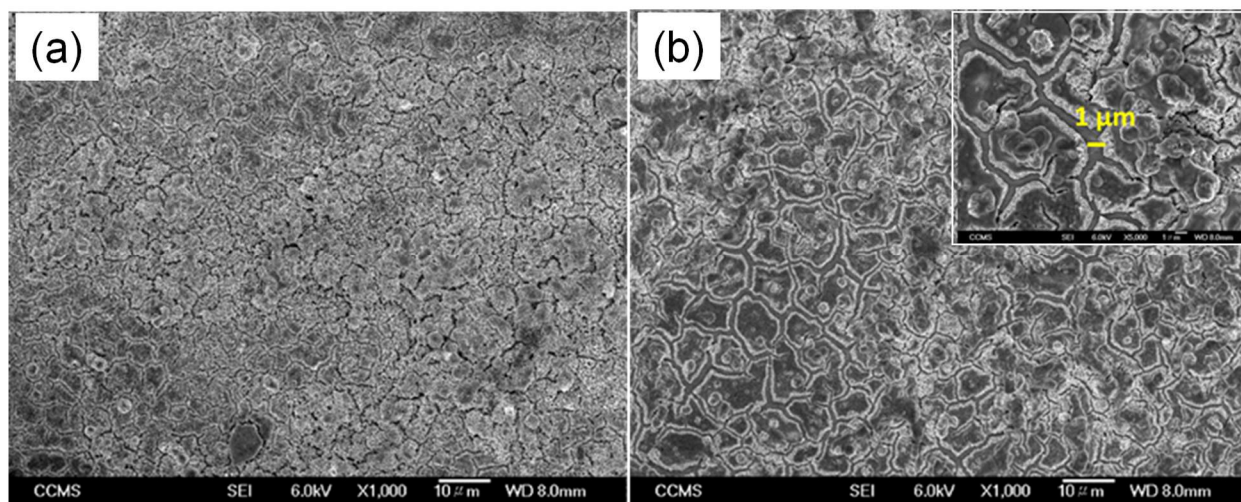


Fig. S6. SEM images of sample A1 (a) after 10th and (b) after 100th cycle (Inset: High magnification scale 1 μm)

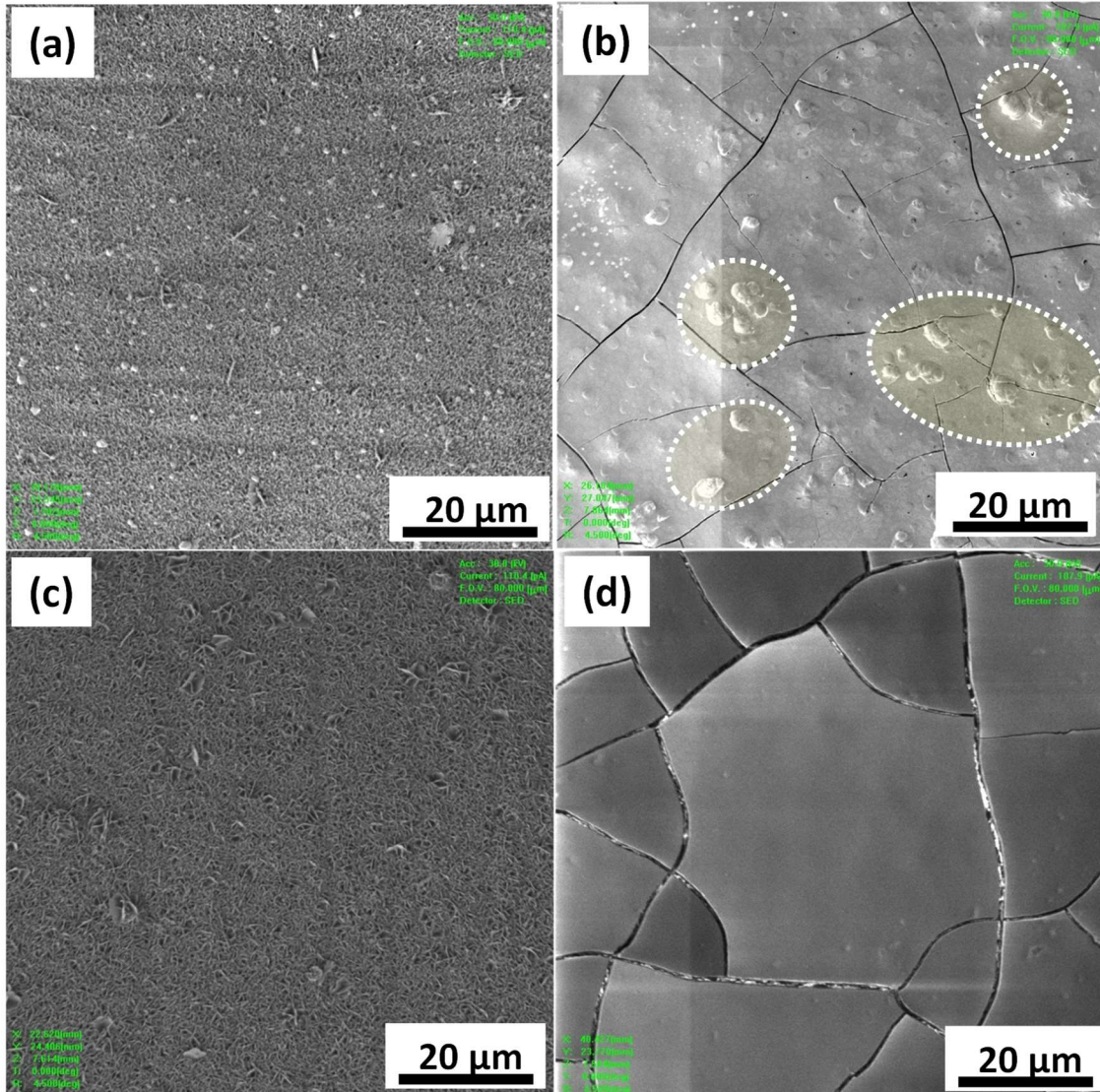


Fig. S7. (a-b) before and after cycling sample B1 and (c-d) before and after cycling sample B

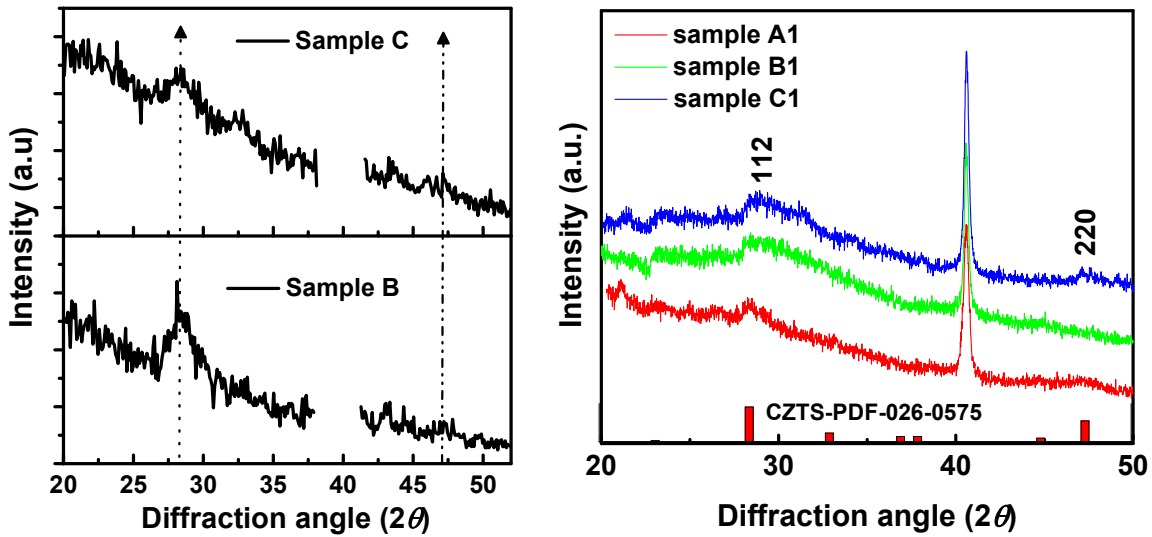


Fig. S8. Ex-situ XRD for all carbon coated CZTS after 100 cycles.

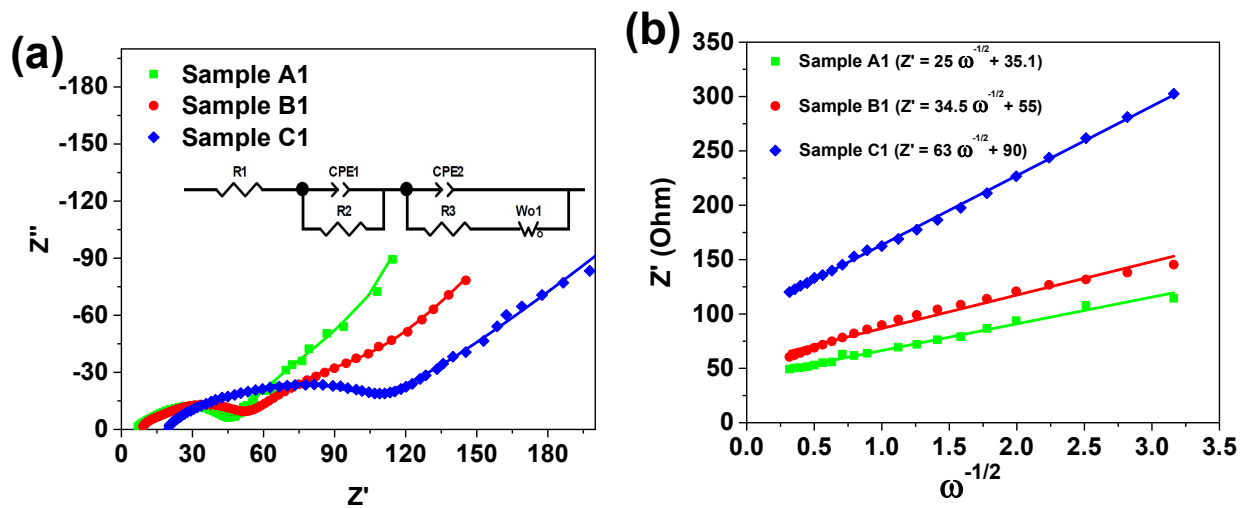


Fig. S9. (a) Nyquist plots of sample A1, B1 and C1 after 100 cycles, and (b) their corresponding linear fitting between Z'_{re} and $\omega^{-1/2}$ in the low frequency region.

Table S1. Carbon content measured from elemental analysis (EA)

Sample name	Carbon amount from EA (wt. %)
CZTS@C samples	4.4

Table S2. EIS of pure CZTS and carbon coated CZTS samples after 100 cycles

Sample name With code	R ₁ (Ohm)	R ₂ (Ohm)	R ₃ (Ohm)
Sample A1	7.4	35	43
Sample B1	6.3	40	51.2
Sample C1	9	42	121
Sample A	6.5	6.7	30.7
Sample B	7	6	31
Sample C	7.4	7	31.7