

Supporting Information

Cation-disorder zinc blende $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P}$ compound and $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P-TiC-C}$ composite as high-performance anodes for Li-ion batteries

Guoping Liu,^{‡ a, c} Lei Zhang,^{‡ b} Yucun Zhou,^b Luke Soule,^b Yangchang Mu,^a Wenwu Li^{a,*} and Zhicong Shi^{a,*}

^a School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, PR China

^b School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

^c College of Mechanical and Automotive Engineering, Zhaoqing University, PR China

* Corresponding author

E-mail: wenwuli@gdut.edu.cn (W. Li), zhicong@gdut.edu.cn (Z. Shi)

[‡] G. Liu and L. Zhang contributed equally to this work.

First principles calculation details

First principles calculations of $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P}$ and ZnGeP_2 were conducted in the Vienna ab initio simulation package.¹ Generalized gradient approximation (GGA) function parameterized by Perdew–Burke–Ernzerhof (PBE) was applied to describe the exchange correlation potential.² The core-electrons were kept frozen in the form of a projector augmented wave function, with the valence electron configuration for P $3s^23p^3$, Ge $3s^23p^2$, and Zn $3d^{10}4s^2$. A $4 \times 4 \times 4$ Monkhorst–Pack reciprocal grid, together with a 400 eV energy cutoff, was used for sufficient energy calculations.³ Gaussian smearing with a smearing width of 0.05 eV was applied to accelerate the computation of the electronic energy near the Fermi level.

calculation details of lithium-ion diffusion coefficient (D_{Li})

D_{Li} is calculated using:

$$D_{Li} = \frac{4}{\pi} \left(\frac{IV_m}{Z_A FS} \right)^2 \left[\frac{dE(\delta)}{d\delta} / \frac{dE(t)}{d\sqrt{t}} \right]^2, \quad (t \ll L^2/D_{Li})$$

Where I is the applied current, V_M is the molar volume of $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P}$, Z_A is the charge number of the electroactive species ($Z_A = 1$ for D_{Li}), F is the Faraday constant, S is the area between the electrode and the electrolyte, δ is the moles of lithium per mole electrode (e.g., δ in the term $\text{Li}_\delta\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P}$), t is the time duration of the current pulse, and L is the characteristic length of the electrode. The value $dE(\delta)/d\delta$ is obtained by measuring the change in the equilibrium electrode potential after each current pulse. The value $dE(t)/dt^{1/2}$ is determined from the voltage response curve measured during the current pulse of the GITT test.

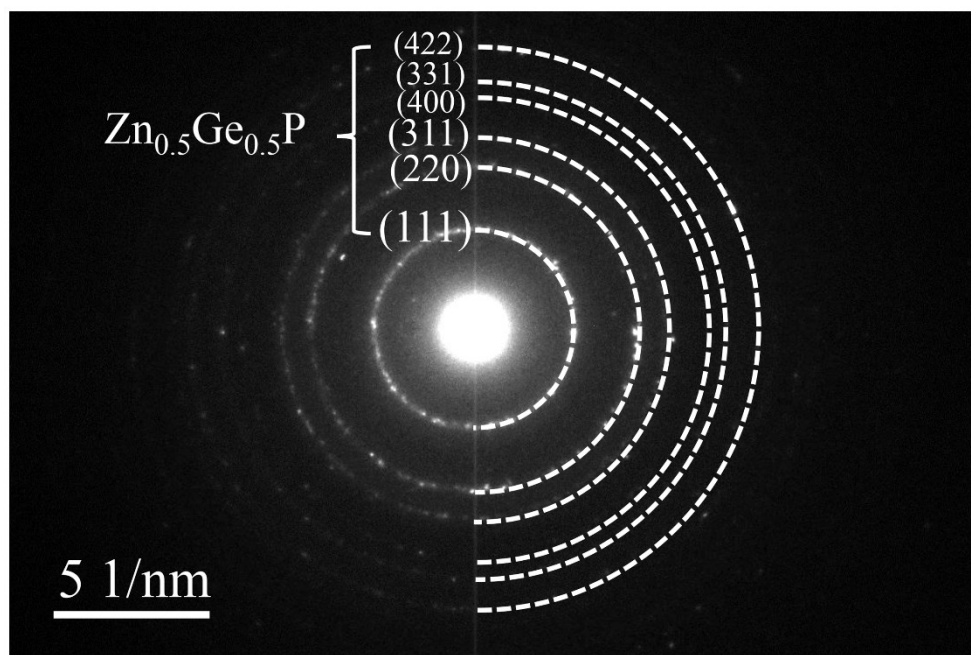


Fig. S1 Selected-area electron diffraction (SAED) pattern of the as-synthesized Zinc blende $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P}$ compound.

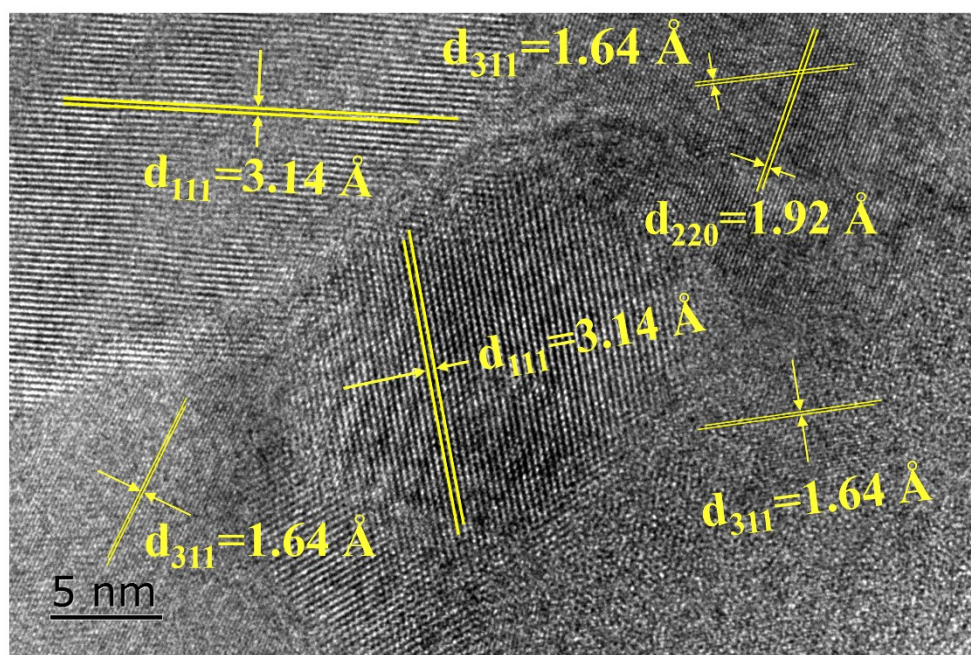


Fig. S2. HRTEM image of the synthesized Zinc blende $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P}$ with interplanar spacing identified.

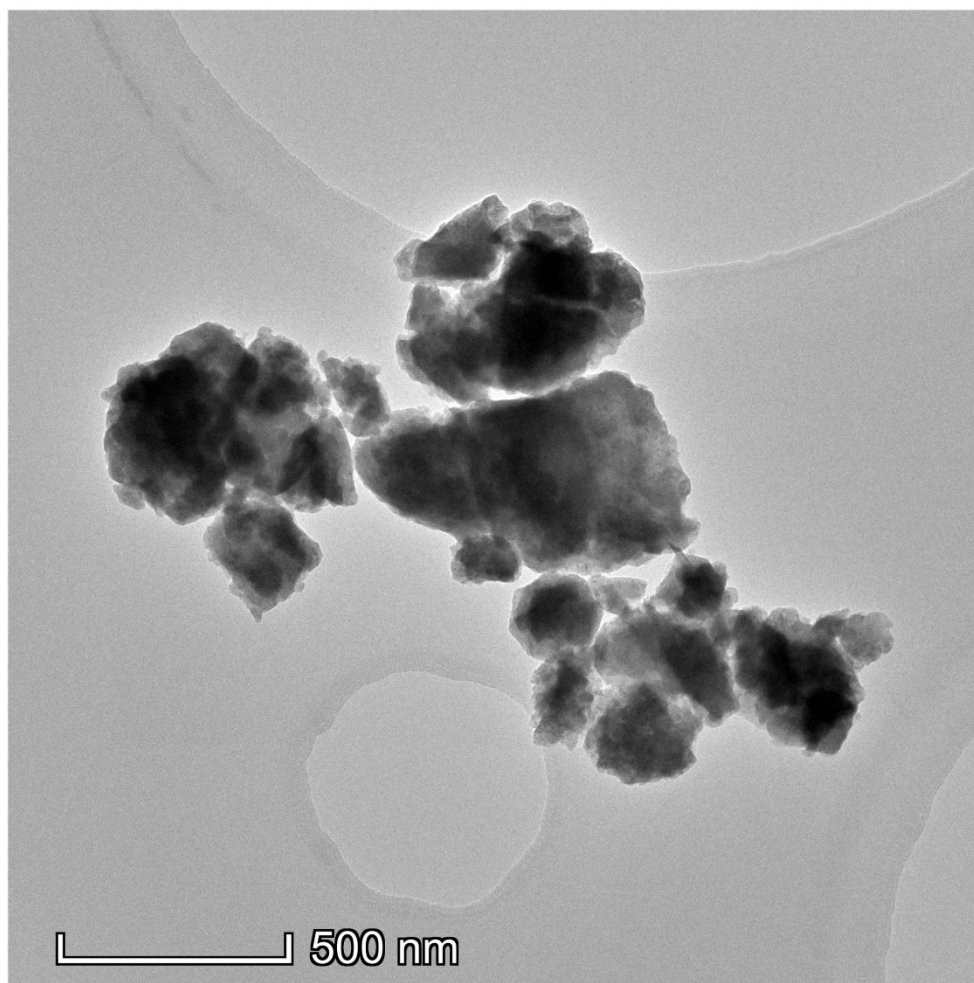


Fig. S3. Low-magnification TEM image of the synthesized Zinc blende $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P}$ compound.

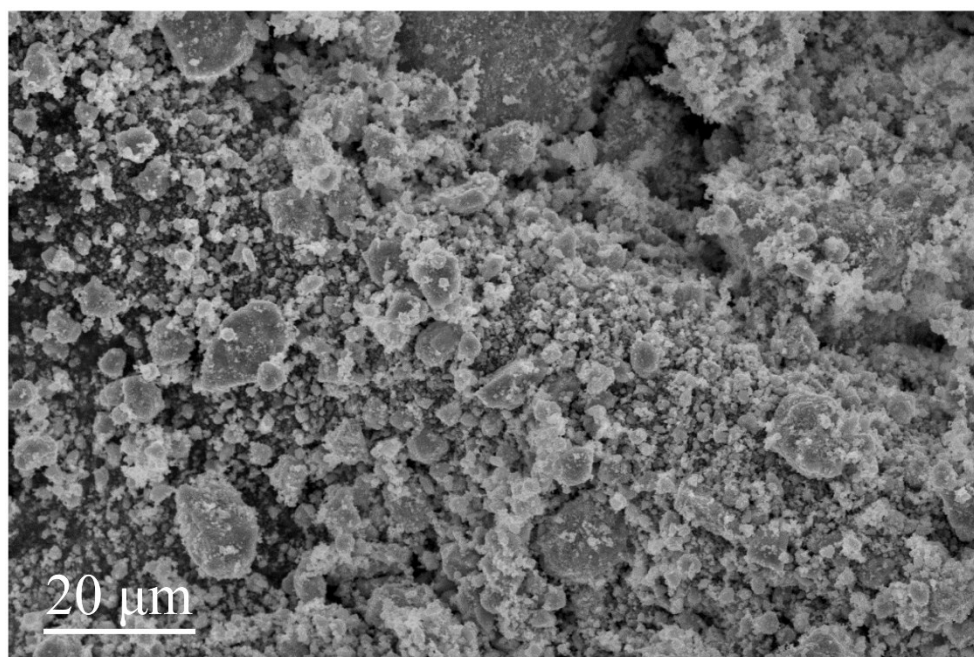


Fig. S4. Low-magnification SEM image of the synthesized Zinc blende $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P}$ compound.

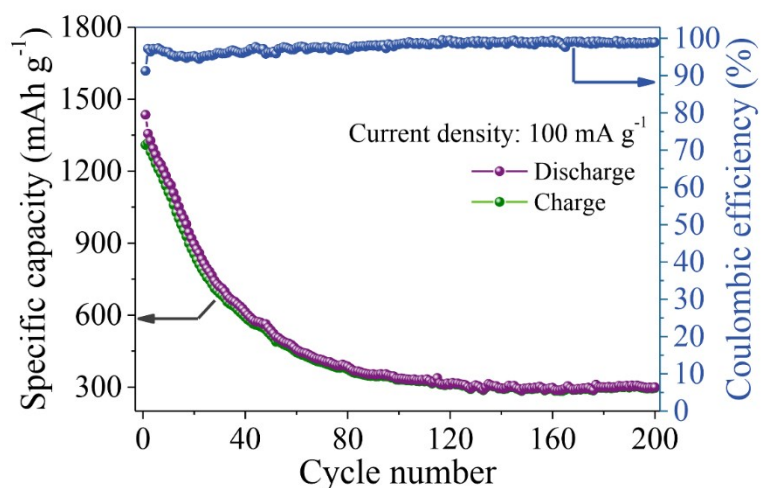


Fig. S5. Cycle performance of the as-synthesized $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P}$ electrode at 100 mA g^{-1} .

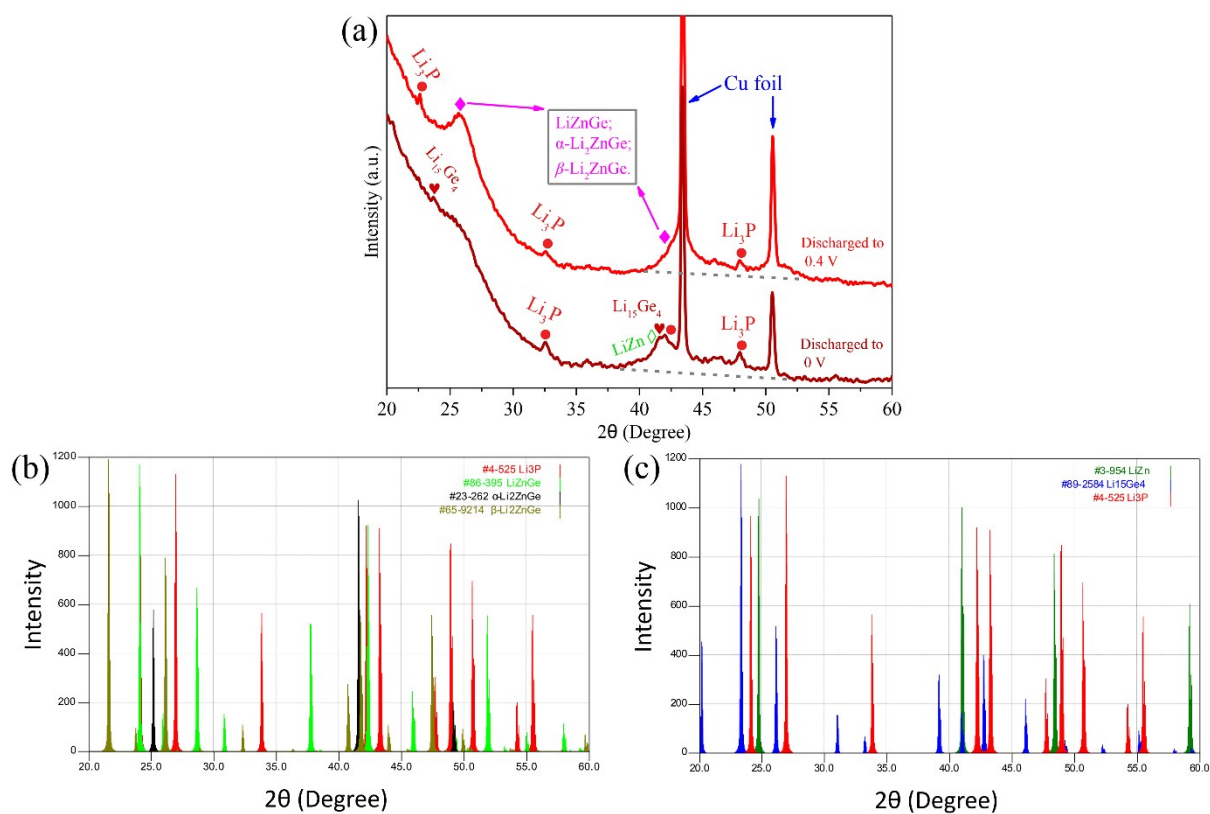


Fig. S6. (a) Magnified XRD results of discharged to 0.4 V and 0 V. (b) Standard diffraction peaks of phases at 0.4 V (Li_3P , LiZnGe , $\alpha\text{-Li}_2\text{ZnGe}$, and $\beta\text{-Li}_2\text{ZnGe}$) and (c) 0 V (LiZn , Li_3P , Li_5Ge_4).

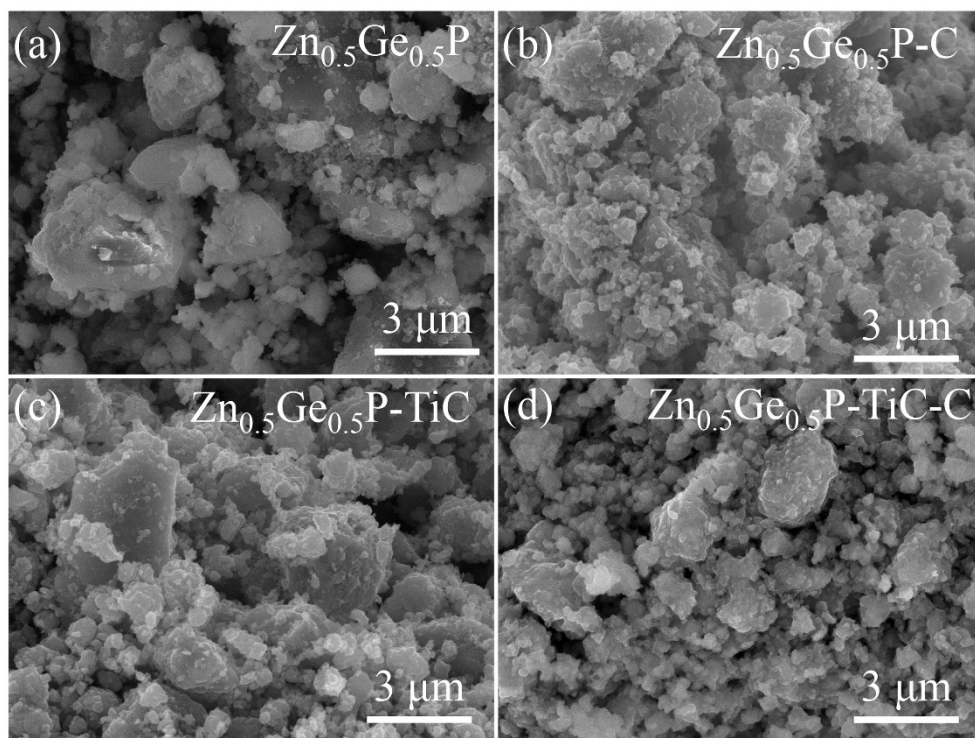


Fig. S7. SEM images of (a) the as-synthesized Zinc blende $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P}$ compound, (b) $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P-C}$ composite, (c) $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P-TiC}$ composite, and (d) $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P-TiC-C}$ composite.

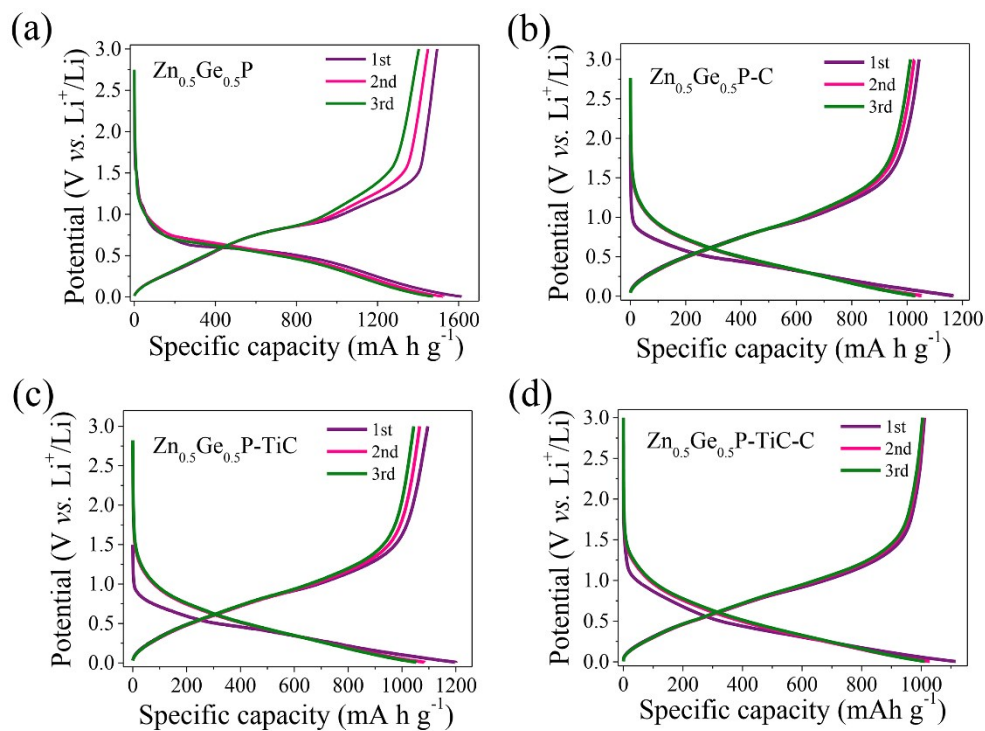


Fig. S8. Initial three discharge-charge profiles of (a) Zinc blende $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P}$ compound, (b) $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P-C}$ composite, (c) $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P-TiC}$ composite, and (d) $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P-TiC-C}$ composite electrodes at a current density of 100 mA g^{-1} .

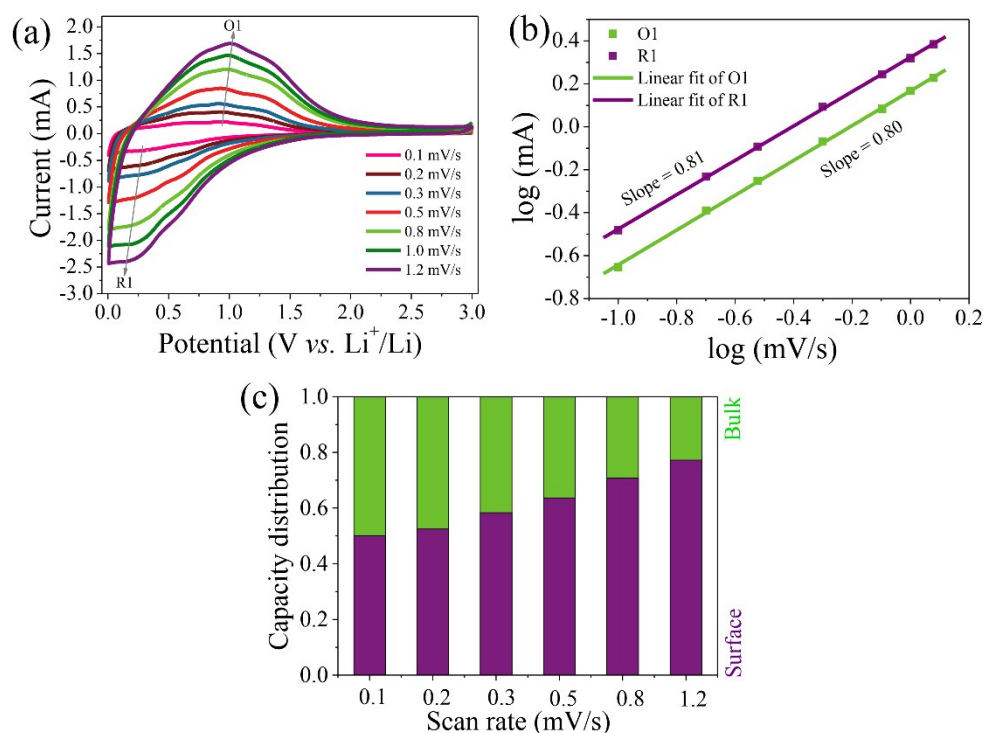


Fig. S9. (a) CV curves at different scan rates of the $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{P-TiC-C}$ electrode. (b) Relationship between logarithm cathodic and anodic peak current and logarithm scan rates. (c) Normalized contribution ratio of capacitive contribution diffusion contribution at different scan rates.

References

1. G. Kresse and J. Furthmüller, *Physical Review B*, 1996, 54, 11169-11186.
2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865.
3. J. D. Pack and H. J. Monkhorst, *Physical Review B*, 1977, 16, 1748.