



Fast charging sodium-ion batteries based on Te-P-C composites and insights to low-frequency limits of four common equivalent impedance circuits



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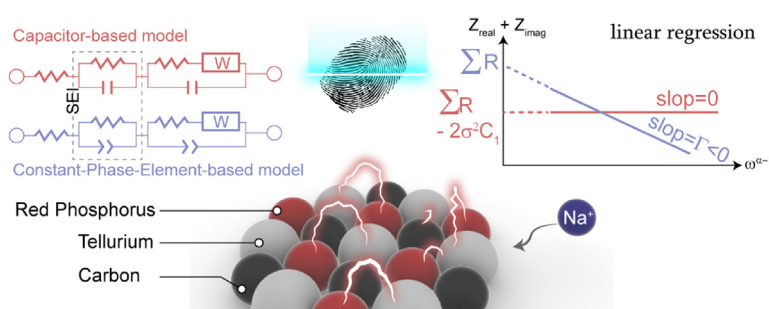
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HIGHLIGHTS

- Te does not react with red P under mechanical milling conditions.
- Te-P-C composites are worthy of fast-charging electrodes due to the conductive Te.
- Expansion formulae and low-frequency limits of EIS circuits are declared.
- Rearranging the low-frequency limits results in new linear restrictions.
- The restrictions improve the EIS fitting reliability applied on Te-P-C composites.

GRAPHICAL ABSTRACT



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ABSTRACT

Various tellurium-red phosphorus-carbon (Te-P-C) composites with different Te to P ratios were prepared via high-energy mechanical milling for application as anode materials in sodium-ion batteries. Highly conductive Te was added to increase the electrical conductivity and improve the mechanical strength of the P-C composite. The optimized Te-P-C (1:2) composite exhibited a reversible capacity of 593 mAh g⁻¹, demonstrating a capacity retention of 82% at the 100th cycle in the fast recharge test (3 A g⁻¹). This performance is related to the electrochemical impedance of each composite. Te-P-C composites are sufficiently simple, such that new constraints for the composites, provided by electrochemical impedance spectroscopy (EIS) results, can be examined. Four mathematical constraints for four frequently applied equivalent circuits at low-frequency limits were declared for batteries. The linear dependence of the sum of the real and imaginary parts of the impedance ($Z_{real} + Z_{imag}$) on the frequency was used to interpret the systems. The newly proposed restrictions significantly reduced the uncertainty of the charge-transfer resistance (R_{ct}) for the Te-P-C composites; the corrected nominal value (158 Ω to 188 Ω) of R_{ct} was more reliable than the uncorrected one (125 Ω to 560 k Ω from commercial fitting software). Therefore, it is believed that the four proposed constraints could provide a simple and convenient way (linear regression) for electrochemical engineers to control the reliability of the interpretation of EIS data in battery systems.

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Nomenclature

α	Fractal dimension of the 1st CPE
β	Fractal dimension of the 2nd CPE (SEI layer)
σ	Warburg coefficient
ω	Frequency
A_1	Nominal capacitance of the 1st CPE
A_2	Nominal capacitance of the 2nd CPE (SEI layer)
C_1	Capacitance of the 1st double layer capacitor
C_2	Capacitance of the 2nd double layer capacitor

CPE	Constant phase element
D	Diffusion coefficient
R_{ct}	Charge-transfer resistance
R_s	Series resistance
R_{SEI}	SEI resistance
SEI	Solid electrolyte interface
Z	Total impedance
Z_{real}	Real part of the total impedance
Z_{imag}	Imaginary part of the total impedance

1. Introduction

Although lithium ion batteries (LIBs) have been successfully used for decades in portable devices, the depletion and excessive cost of Li has encouraged a search for other sustainable alternatives for energy storage systems. Researchers have tried replacing Li with other abundant elements, such as Na [1], Ca [2], Mg [3], and Al [4]. Because both Li and Na are alkaline metals, sodium ion batteries (SIBs) have been developed on the basis of successful LIB implementation [5–7]. However, the ionic radius of Na^+ (106 pm) is larger than that of Li^+ (76 pm), which causes severe problems for the development of SIBs, including poor kinetic diffusion and large volume expansion [8–10]. Furthermore, the employment of Na metal raises safety concerns regarding both the violent reaction of Na metal with air/moisture and the growth of Na dendrites, which can lead to a short circuit [11]. Consequently, exploring new anode materials for SIBs is essential.

Many elements, such as Si, P, Ge, or Sn, could be utilized as anode materials for either SIBs or LIBs, owing to their high theoretical capacities [12–14]. Although Si has the highest capacity among LIB anodes ($\sim 3578 \text{ mAh g}^{-1}$), Na^+ ion cannot electrochemically intercalate to Si [15]. Hence, P with a theoretical capacity of $\sim 2594 \text{ mAh g}^{-1}$ (based on Na_3P) is the most attractive anode material for SIBs. The moderate redox potential of P at 0.4 V vs. Na/Na^+ could prevent the growth of Na dendrites and deliver high energy densities for full-cell SIBs. However, the massive volume expansion after Na^+ intercalation (491%) and remarkably low electrical conductivity ($\sim 10^{-14} \text{ S cm}^{-1}$) prohibit the commercialization of red P-based electrodes [16].

To overcome the aforementioned issues related to P, potential strategies have been considered: (i) using electrolyte additives, including fluoroethylene carbonate (FEC), to stabilize the formed SEI layers, (ii) dispersing P into various types of carbon matrices such as carbon nanotubes (CNT), which would increase electrical conductivity while suppressing volume expansion, (iii) constructing composites/alloys with P and other elements to act as mechanical buffering agents while P reacts electrochemically [17–19]. Wang et al. observed the influence of different types of carbon (e.g., CNT, C45) on the stability of P-C composites. They found that most of the P-C composite electrodes cannot endure the severe volume expansion and quickly fade within 10 cycles [20]. Because P is a highly active element, developing composites with P and other metallic elements easily generate insulating products, which deteriorate the rate performance, as expected. In 2015, Yang et al. milled red P with Fe to improve the cycling stability [21]. Despite the high conductivity of Fe, the as-prepared FeP performed as an insulator with a poor rate performance. Furthermore, because Fe cannot electrochemically form alloys with Na^+ ions, the FeP anode revealed a poor reversible capacity of $\sim 300 \text{ mAh g}^{-1}$ at 50 mA g^{-1} .

Te has received much attention as an anode material, owing to the fact that it exhibits the highest electrical conductivity among non-metallic elements (200 S cm^{-1}) [22]. In SIBs, Te can electrochemically react with Na^+ to form Na_2Te , which yields a theoretical capacity of 420 mAh g^{-1} [23]. Owing to the fact that Te is a byproduct in the copper-refining process, the price of commercial-grade Te has consistently decreased to 40–80 USD kg^{-1} , encouraging the development

of Te-related energy research [24,25].

Meanwhile, the study of the impedance in SIBs has been important for exploring essential parameters of the battery such as R_{SEI} , R_{ct} , and D, because of the direct relationship between performance and impedance. The Randles model, which includes a double-layer capacitor, Warburg element and two resistors, was the most basic circuit applied for secondary batteries [26]. The Randles circuit has two simple relationships at the low-frequency limit: (i) Z_{real} is linearly proportional to $-Z_{imag}$ with a slope of 1 in the Nyquist plot and (ii) Z_{real} is linearly proportional to $\omega^{-0.5}$ with a slope of σ in the Warburg plot. However, the existence of SEI layers requires the modification of the simple Randles model to explain practical patterns [27]. Moreover, for a variety of reasons, it is essential that CPEs replace capacitors in the Randles model to provide simulation results, such as the presence of surface roughness, distribution of reaction rates, or non-uniform current distribution after a definite time of cycling [28–30]. In secondary battery fields, the physical meaning of a CPE-based model is the existence of surface heterogeneity or distributed time constants of charge-transfer reactions; therefore, a CPE is generally considered as an imperfect capacitor [31–33]. It should be noted that without specific restrictions to the parameters, commercially available numerical software (complex nonlinear least-squares analysis (CNLS)) could give rise to large uncertainties for simulated parameters [34]. Moreover, using too flexible methods such as CNLS may cause overfitting issues, which are undesirable for quantitative studies [35]. The lack of information regarding the simple mathematical correlations often forces researchers to unavoidably apply the Randles circuit equations, resulting in the generation of inappropriate values.

In this study, we aim to make a novel composite from Te, red P, and C via the high-energy mechanical milling (HEMM) process for application as an anode material for SIBs. Because Te is a conductive metalloid, its inclusion makes it possible to prevent the formation of metal phosphide insulators and maintain high electrical conductivity. Moreover, amorphous carbon in the composite can inhibit polytelluride dissolution and alleviate volume expansion [36–38]. In addition to the cycling performance study, the electrochemical impedance is extensively investigated in both a theoretical and practical manner: (i) deriving equations describing equivalent circuits and (ii) applying the derived equations on Te-P-C composites. All the suggested equations were checked with MATLAB to ensure the application of correct algebraic derivation. Ultimately, we argue that this proposed approach will introduce a straightforward method to generate a reliable fitting and reduce the uncertainty from the fitting software.

2. Experimental**2.1. Synthesis of Te-P-C composites**

A facile HEMM method was employed to prepare Te-P-C composites. A mixture of commercial Te (Merck, ~ 200 mesh, 266418) and red P (Alfa, ~ 100 mesh, 10281) was manually ground with mortar and pestle. Subsequently, an amount of acetylene black (Alfa, 45527) was added to the aforementioned mixture and left in an 80 cm^3 zirconia

container to maintain the overall carbon content at 30 wt(%). The total mass of the zirconia balls (with diameters $\frac{1}{2}$ " and $\frac{1}{4}$ "") was 20-fold that of the total mass of the raw powders. After sealing the container with all materials in an Ar-filled glove box, the milling process continued in a planetary ball mill (Pulverisette 5, Fritsch) for 24 h at a speed of 300 rpm. The as-prepared Te-P-C (1:2), Te-P-C (1:1), and Te-P-C (2:1) composites had initial Te to P molar ratios of 1:2, 1:1, and 2:1, respectively. For comparison, two di-element composites, Te-C and P-C, were prepared via the same HEMM process, in which the C content was always fixed at 30 wt(%).

2.2. Material characterization

The structure of the Te-P-C composites was characterized using X-ray diffraction (XRD, Rigaku 2200) at Smart Materials Research Center for IoT in Gachon University. The elemental distribution and morphology were investigated with high-resolution transmission electron microscopy (HRTEM, JEOL 2100) and with energy-dispersive X-ray spectroscopy (EDS) and scanning transmission electron microscopy (STEM).

2.3. Electrochemical characterization

To fabricate the working electrodes, the as-prepared composites were mixed with carbon black (Alfa, Super P, H30253) and poly(acrylic acid) (Merck, $M_v \sim 450,000$, 181285) (ratio of 70:15:15 wt/wt) in ethanol to form slurries. Cu foil was selected as the current collector and coated by the aforementioned slurries via the doctor blade method. The electrodes were dried in vacuum overnight at 70 °C. The characterization of the half-cell was performed employing a CR 2032 coin cell with Na metal as the counter electrode and glass fiber as the separator. To prepare the electrolyte, 1.22 g of NaClO_4 was dissolved in a 10 ml solution of ethylene carbonate (EC), propylene carbonate (PC), and FEC (ratio of 45:45:10 v/v). Cells were assembled in the Ar-filled glove box to prevent contact with moisture and air. The cycling performance was evaluated with an automatic battery cycling system (WonAtech, WBCS3000) in constant current mode. Further cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses were performed on a multichannel electrochemical workstation (ZIVELAB, Zive MP1).

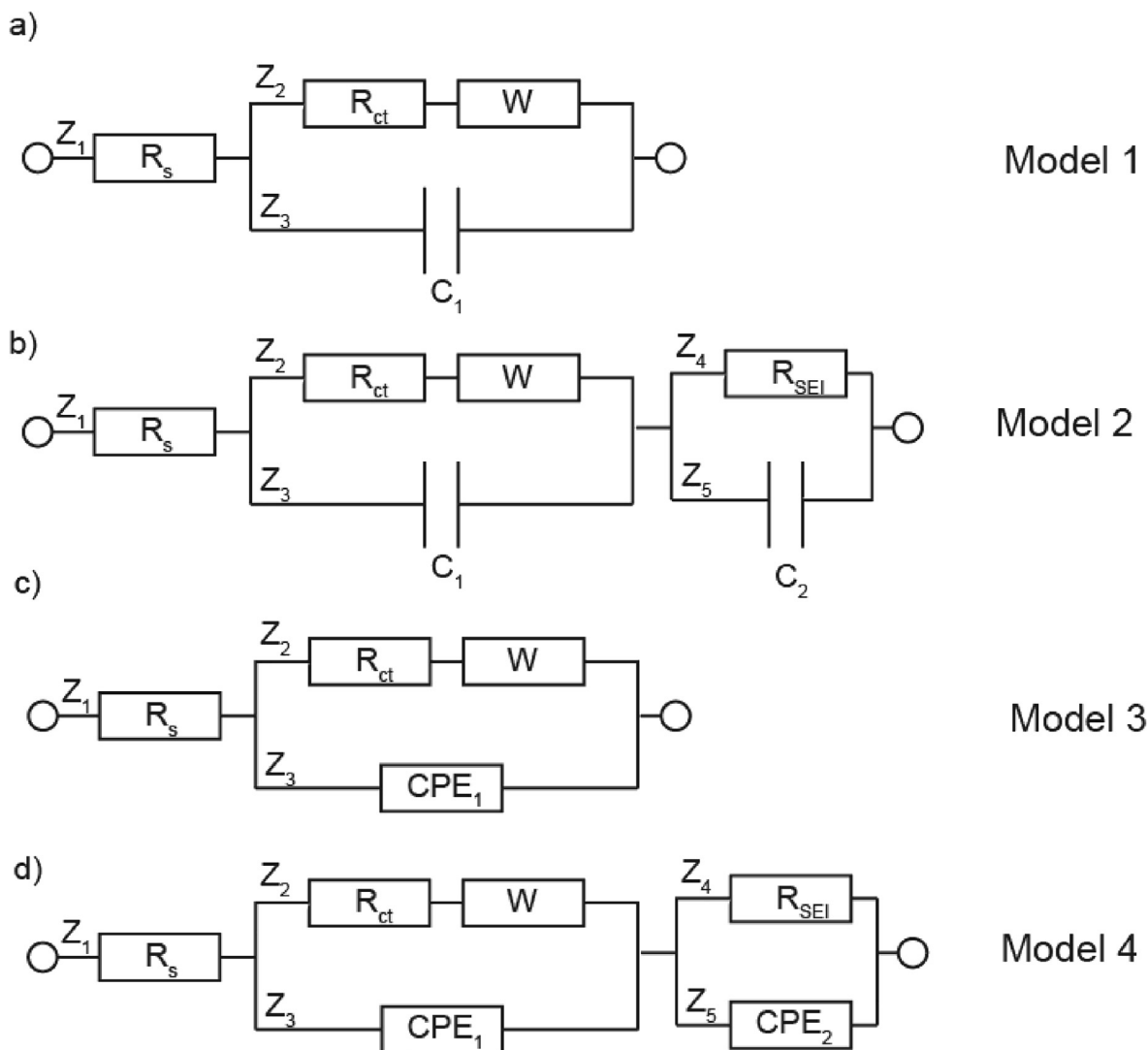


Fig. 1. Four common equivalent circuits employed for the measurement of the impedance in secondary batteries: (a) Randles circuit, Randles with (b) SEI layer circuit, (c) one-CPE circuit, and (d) two-CPE circuit.

2.4. Theoretical model and calculation

2.4.1. MATLAB calculation and exact solution for total impedance

Fig. 1 depicts the electrical circuits of four models, namely, Randles circuit (model 1), Randles circuit with SEI layer (model 2), one-CPE circuit (model 3), and two-CPE circuit (model 4). In general, the total impedance of a circuit corresponds to either Eq. 1 (model 1 and 3) or Eq. 2 (model 2 and 4):

$$Z = Z_1 + \frac{Z_2 Z_3}{Z_2 + Z_3} \quad (1)$$

$$Z = Z_1 + \frac{Z_2 Z_3}{Z_2 + Z_3} + \frac{Z_4 Z_5}{Z_4 + Z_5} \quad (2)$$

Table 1 summarizes the input parameters to calculate the exact solutions, which are the responses of the total impedances toward the applied frequencies (100 kHz to 100 mHz), with the support of MATLAB. Typically, the specific capacitances of capacitors in common batteries range from 1 to 100 $\mu\text{F cm}^{-2}$. The diffusion coefficients of Na^+ ions determined from a galvanostatic intermittent titration technique often range from 10^{-12} to $10^{-16} \text{ cm}^2 \text{ s}^{-1}$, which generates Warburg coefficients of 190–18820 $\Omega \text{ s}^{-0.5}$ at 25 $^\circ\text{C}$ [39–42] (detailed source codes for MATLAB calculation are contained in the Supplementary Information).

Eq. 3, 4, and 5 describe the mathematical behaviors of the total impedance as a function of frequency for model 1 (refer to the nomenclature and proofs of the equations in the Supplementary Information):

$$Z_{\text{mod1}} = (Z_{\text{real}})_{\text{mod1}} + (Z_{\text{imag}})_{\text{mod1}} \times i \quad (3)$$

$$(Z_{\text{real}})_{\text{mod1}} = R_s + \frac{R_{\text{ct}} + \sigma\omega^{-0.5}}{(1 + C_1\sigma\omega^{0.5})^2 + (R_{\text{ct}} + \sigma\omega^{-0.5})^2 C_1^2 \omega^2} \quad (4)$$

$$(Z_{\text{imag}})_{\text{mod1}} = -\frac{R_{\text{ct}}^2 C_1 \omega + 2R_{\text{ct}} C_1 \sigma \omega^{0.5} + 2C_1 \sigma^2 + \sigma \omega^{-0.5}}{(1 + C_1\sigma\omega^{0.5})^2 + (R_{\text{ct}} + \sigma\omega^{-0.5})^2 C_1^2 \omega^2} \quad (5)$$

Clearly, model 2 is a simple expansion of model 1. Therefore, the total impedance for model 2 can be calculated as follows:

$$Z_{\text{mod2}} = Z_{\text{mod1}} + \frac{R_{\text{SEI}}}{1 + R_{\text{SEI}} C_2 \omega i} = Z_{\text{mod1}} + \frac{R_{\text{SEI}} - R_{\text{SEI}}^2 C_2 \omega i}{1 + (R_{\text{SEI}} C_2 \omega)^2} \quad (6)$$

$$(Z_{\text{real}})_{\text{mod2}} = (Z_{\text{real}})_{\text{mod1}} + \frac{R_{\text{SEI}}}{1 + (R_{\text{SEI}} C_2 \omega)^2} \quad (7)$$

$$(Z_{\text{imag}})_{\text{mod2}} = (Z_{\text{imag}})_{\text{mod1}} - \frac{R_{\text{SEI}}^2 C_2 \omega}{1 + (R_{\text{SEI}} C_2 \omega)^2} \quad (8)$$

Meanwhile, the existences of α and β within CPEs lead to complicated exact solutions for the total impedances of models 3 and 4, as shown in Eq. 9–12:

$$(Z_{\text{real}})_{\text{mod3}} = R_s + \frac{R_{\text{ct}} + \sigma\omega^{-0.5} + (2\sigma^2\omega^{-1} + 2R_{\text{ct}}\sigma\omega^{-0.5} + R_{\text{ct}}^2)\omega^\alpha A_1 \cos\frac{\alpha\pi}{2}}{|\psi|^2} \quad (9)$$

$$(Z_{\text{imag}})_{\text{mod3}} = -\frac{\sigma\omega^{-0.5} + (2\sigma^2\omega^{-1} + 2R_{\text{ct}}\sigma\omega^{-0.5} + R_{\text{ct}}^2)\omega^\alpha A_1 \sin\frac{\alpha\pi}{2}}{|\psi|^2} \quad (10)$$

$$(Z_{\text{real}})_{\text{mod4}} = (Z_{\text{real}})_{\text{mod3}} + \frac{R_{\text{SEI}}(1 + R_{\text{SEI}} A_2 \omega^\beta \cos\frac{\beta\pi}{2})}{(1 + R_{\text{SEI}} A_2 \omega^\beta \cos\frac{\beta\pi}{2})^2 + (R_{\text{SEI}} A_2 \omega^\beta \sin\frac{\beta\pi}{2})^2} \quad (11)$$

$$(Z_{\text{imag}})_{\text{mod4}} = (Z_{\text{imag}})_{\text{mod3}} - \frac{R_{\text{SEI}}^2 A_2 \omega^\beta \sin\frac{\beta\pi}{2}}{(1 + R_{\text{SEI}} A_2 \omega^\beta \cos\frac{\beta\pi}{2})^2 + (R_{\text{SEI}} A_2 \omega^\beta \sin\frac{\beta\pi}{2})^2} \quad (12)$$

where $\psi = 1 + (R_{\text{ct}} + \sigma\omega^{-0.5}(1 - i))A_1\omega^{\alpha/2}$ and the low-frequency

limit of $|\psi|^2$ is 1.

2.4.2. Low-frequency limit approximation

When ω approaches zero, both the real and imaginary parts of the total impedance in the Randles circuit (model 1) are linearly proportional to $\omega^{-0.5}$. The aforementioned approximation resulted from the assumption that R_{ct} is not too large such that the current would mainly pass the capacitors and skip the Warburg element. Meanwhile, any term related to a positive exponent of ω was neglected to obtain the low-frequency limit [26]. By applying similar assumptions to Eq. 7, 8, 9, 10, 11, and 12, the low-frequency limits of models 2, 3, and 4 can be summarized as shown in Table 2.

Based on Table 2, the following relationships could be obtained when ω approaches zero:

$$(Z_{\text{real}} + Z_{\text{imag}})_{\text{mod1}} = R_s + R_{\text{ct}} - 2C_1\sigma^2 \quad (13)$$

$$(Z_{\text{real}} + Z_{\text{imag}})_{\text{mod2}} = R_s + R_{\text{ct}} + R_{\text{SEI}} - 2C_1\sigma^2 \quad (14)$$

$$(Z_{\text{real}} + Z_{\text{imag}})_{\text{mod3}} = R_s + R_{\text{ct}} + \Gamma\omega^{\alpha-1} \quad (15)$$

$$(Z_{\text{real}} + Z_{\text{imag}})_{\text{mod4}} = R_s + R_{\text{ct}} + R_{\text{SEI}} + \Gamma\omega^{\alpha-1} \quad (16)$$

$$\Gamma = -2A_1\sigma^2 \left(\sin\frac{\alpha\pi}{2} - \cos\frac{\alpha\pi}{2} \right).$$

3. Results and discussion

3.1. Characterization and electrochemical performance of Te-P-C composites

The XRD patterns of the as-prepared Te-P-C composites with various Te to P molar ratios are shown in Fig. 2. All the Te-P-C composites exhibited strong diffraction peaks at $2\theta = 27.6^\circ, 38.3^\circ, 40.4^\circ$, and 43.3° , which correspond to the (1 0 1), (1 0 2), (1 1 0), and (1 1 1) planes of hexagonal Te (PDF#36–1452), respectively. Without the residual peaks of impurities, the XRD patterns suggested that Te reacted with neither P nor C during the applied HEMM process; thus, all the Te-P-C composites were concluded to have simple mixtures consisting of individual Te, P, and C. It is noted that P in the composites was completely amorphous because all the Te-P-C composites did not have diffraction peaks related to the black phosphorus (COD#4307698) (Fig. 2), which was also consistent with the work of R. Wang et al. [20].

To explore the crystallographic and morphological characteristics of the composite, transmission electron microscopy (TEM) equipped with energy dispersive X-ray spectroscopy was utilized. Fig. 3 shows the morphology of the Te-P-C (1:2) composite. In Fig. 3a, the bright TEM image reveals that the Te-P-C (1:2) composite contained few-nanometer Te crystals dispersed in amorphous C and red P. The HRTEM image in Fig. 3b clearly shows two interplanar spacings of (1 0 1) plane (0.32 nm) and (1 1 1) plane (0.21 nm) of the Te phase. Elemental Te, P,

Table 1

Input parameters to compare the exact solution and derived low-frequency limits for the four equivalent circuit models.

	Model 1	Model 2	Model 3	Model 4
R_s , [Ω]	10	10	10	10
R_{ct} , [Ω]	100	100	100	100
R_{SEI} , [Ω]	–	50	–	50
σ , [$\Omega \text{ s}^{-1/2}$]	2000	2000	2000	2000
C_1 , [F]	10×10^{-6}	10×10^{-6}	–	–
C_2 , [F]	–	2×10^{-6}	–	–
A_1 , [$\text{s}^{0.7} \Omega^{-1}$]	–	–	10×10^{-6}	10×10^{-6}
α	–	–	0.7	0.7
A_2 , [$\text{s}^{0.8} \Omega^{-1}$]	–	–	–	2×10^{-6}
β	–	–	–	0.8
ω , [Hz]	10^5 to 10^{-1}	10^5 to 10^{-1}	10^5 to 10^{-1}	10^5 to 10^{-1}

Table 2

Total impedance of the four common equivalent circuits at the low-frequency limit.

Model	Low-frequency limit	
	Z_{real}	$-Z_{\text{imag}}$
1	$R_s + R_{ct} + \sigma\omega^{-0.5}$	$2C_1\sigma^2 + \sigma\omega^{-0.5}$
2	$R_s + R_{ct} + \sigma\omega^{-0.5} + R_{SEI}$	$2C_1\sigma^2 + \sigma\omega^{-0.5}$
3	$R_s + R_{ct} + \sigma\omega^{-0.5} + 2A_1\sigma^2\omega^{\alpha-1}\cos\frac{\alpha\pi}{2}$	$\sigma\omega^{-0.5} + 2A_1\sigma^2\omega^{\alpha-1}\sin\frac{\alpha\pi}{2}$
4	$R_s + R_{ct} + \sigma\omega^{-0.5} + 2A_1\sigma^2\omega^{\alpha-1}\cos\frac{\alpha\pi}{2} + R_{SEI}$	$\sigma\omega^{-0.5} + 2A_1\sigma^2\omega^{\alpha-1}\sin\frac{\alpha\pi}{2}$

and C were well dispersed in the composite, which was confirmed by the elemental mapping image, as shown in Fig. 3c. Because Te and P had different working potentials, the uniform dispersion of the elements within the composite can play an important role as a buffer matrix to absorb the stress during the sodiation/desodiation processes.

Galvanostatic cycling tests were performed for the Te-P-C composites with various Te contents at a current density of 100 mAh g^{-1} from 0.001 to 2 V vs. Na/Na⁺. For comparison, the di-element composites (Te-C and P-C) were tested as well under the same galvanostatic conditions, which is summarized in Table 3. Fig. 4a shows the potential profile of the Te-P-C composites for the 1st cycle. Generally, all the observed composites had low initial coulombic efficiencies (ICE), below

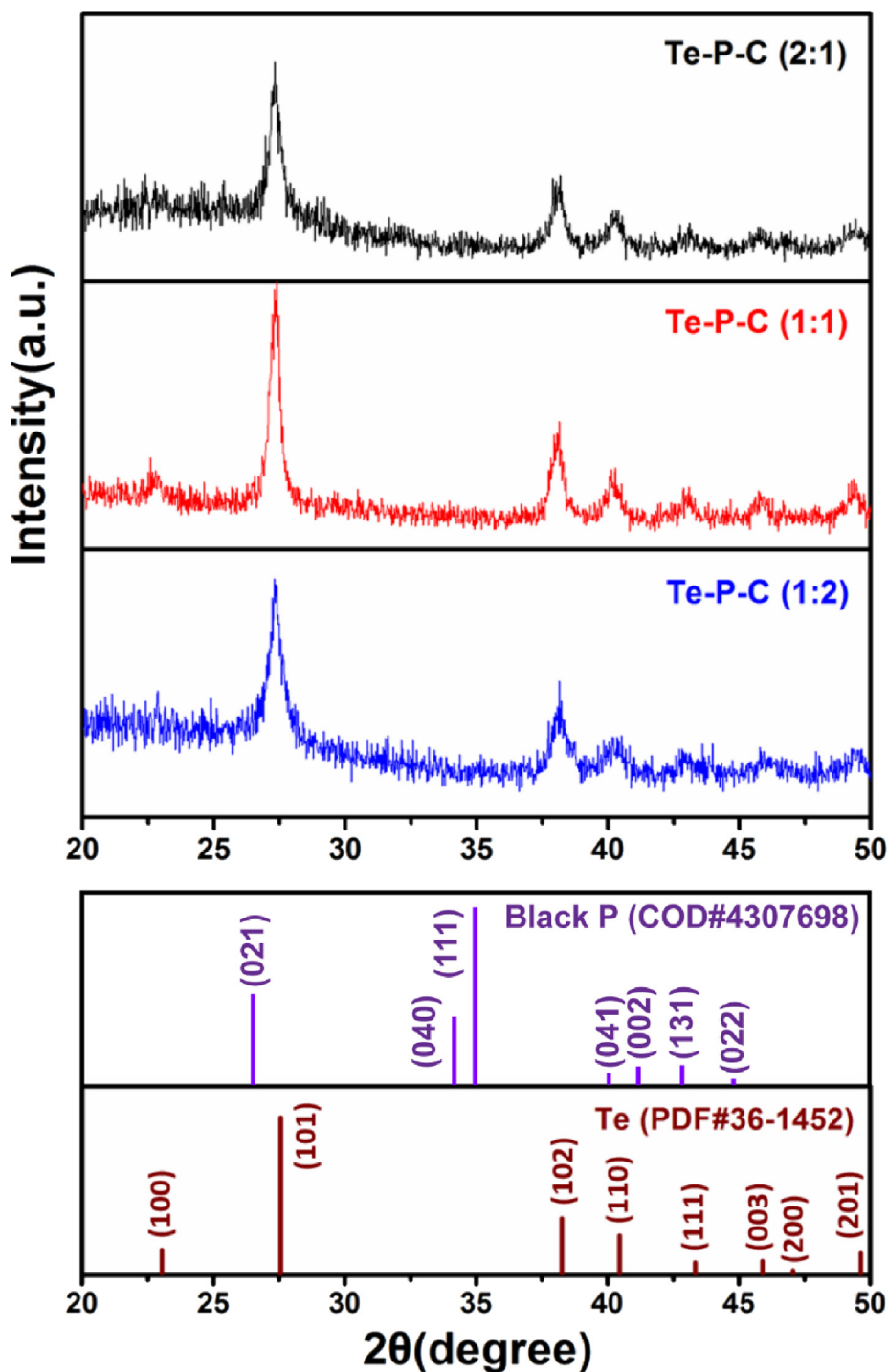


Fig. 2. XRD patterns of as-prepared Te-P-C composites at various Te to P molar ratios (2:1, 1:1, and 1:2).

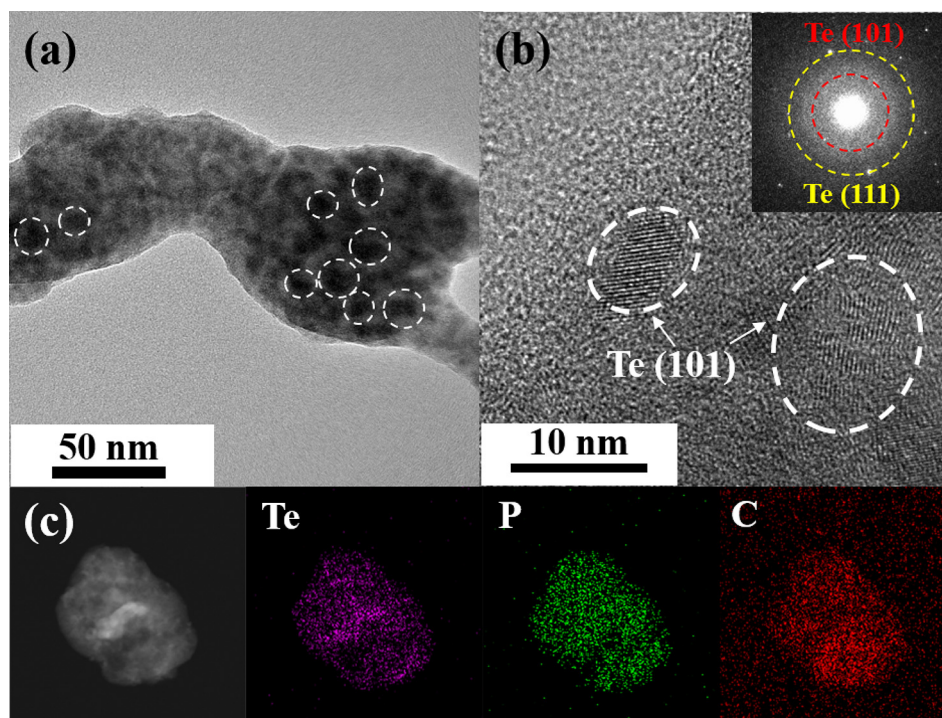


Fig. 3. Morphological characterization of Te-P-C (1:2) composite: (a) TEM image, (b) HRTEM image with SAED pattern, (c) STEM image with elemental maps of Te, P, and C.

Table 3

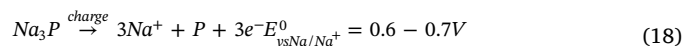
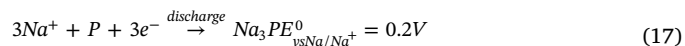
Comparison of the electrochemical performances of the Te-C, P-C, and Te-P-C composites.

Sample	Initial specific capacity		Initial coulombic efficiency(%)	Capacity retention at 200th cycle(%)
	Discharging (mAh g ⁻¹)	Charging (mAh g ⁻¹)		
P-C	1076	819	76	–
Te-P-C (1:2)	878	659	75	67
Te-P-C (1:1)	595	359	60	71
Te-P-C (2:1)	462	303	65	87
Te-C	404	223	55	–

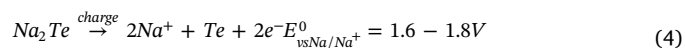
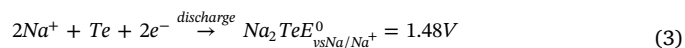
80%. The low ICE values could result from the irreversible reaction of the SEI formation and electrolyte decomposition. Specifically, the ICE value (55%) of the Te-C composite was the lowest among the composites, as shown in Table 3, whereas the P-C composite exhibited the highest ICE value (76%). The large amount of Te content led to the low values of ICE—approximately 60% for Te-P-C (1:1) and 65% for Te-P-C (2:1). Meanwhile, the P-rich composite (Te-P-C (1:2)) had an initial charge capacity of 659 mAh g⁻¹ with an ICE value of 75%, the highest among the Te-P-C composites. However, P-moderate and P-less composites, including Te-P-C (1:1) and Te-P-C (2:1), delivered initial capacities of only 359 mAh g⁻¹ and 303 mAh g⁻¹, respectively. Because the theoretical capacity of P (2594 mAh g⁻¹) is much higher than that of Te (420 mAh g⁻¹), the P-rich composite demonstrated a higher charging capacity than those of P-moderate or P-poor composites during the initial cycles.

Differential capacity plots (DCPs) were analyzed for the Te-P-C and di-element composites to investigate the reaction mechanisms between the electrochemically active components (Te and P) and Na⁺ ions. First, the DCPs of the reference composites, Te-C and P-C, were explored to facilitate the assignment of the sodiation potential of either Te or P, as shown in Fig. 4b and 4c. In the P-C composite (Fig. 4b), the 1st cathodic peak at 0.09 V could be related to the sodiation of red P. The peak at 0.09 V was shifted to 0.2 V in the following cycles as reported

[15]:



Two anodic peaks at 0.6 V and 0.7 V could be assigned to the multiple desodiation of Na₃P. The DCP of Te-C composite in Fig. 5b declares the sodiation/desodiation potential of Te. Compared with the previous work of Zhang and He [22,43], the 1st cathodic peak at 1.35 V represented the reduction in Te with the formation of an SEI layer. In the next cycles, the redox pairs at approximately 1.48 V and 1.8 V could be assigned to the electrochemical conversion reaction between Te and Na₂Te/Na₂Te₂:



Upon examination of the Te-P-C composite electrodes, all the Te-P-C composites clearly showed two distinguished redox potential groups as illustrated in Fig. 4d, 4e, and 4f, namely, P at low potential (below 0.9 V) and Te at high potential (above 1.35 V). In the case of the Te-P-C (2:1) composite electrode, the high intensity of the 1st cathodic peak near 1.35 V indicated the formation of a large SEI layer that occurred because of the high Te content in the Te-P-C composites. With the decrease in Te content, the peak intensity at 1.35 V decreased, as depicted in Fig. 4e and 4f. Therefore, Te-P-C (1:2) electrode is thought to demonstrate the highest ICE value, owing to the reduction in the formation of the SEI layer. Moreover, the constantly overlapped plots in the subsequent cycles illustrate that the highest stability and reversibility of all the composites at the initial cycles is represented by Te-P-C.

The cycling performance of the prepared Te-P-C composites at 100 mA g⁻¹ is shown in Fig. 5a. Although the increase in Te content decreased the overall reversible capacity, the capacity retentions were drastically improved. The Te-P-C (1:1) and Te-P-C (2:1) composites demonstrated charge capacities of 255 mAh g⁻¹ and 263 mAh g⁻¹,

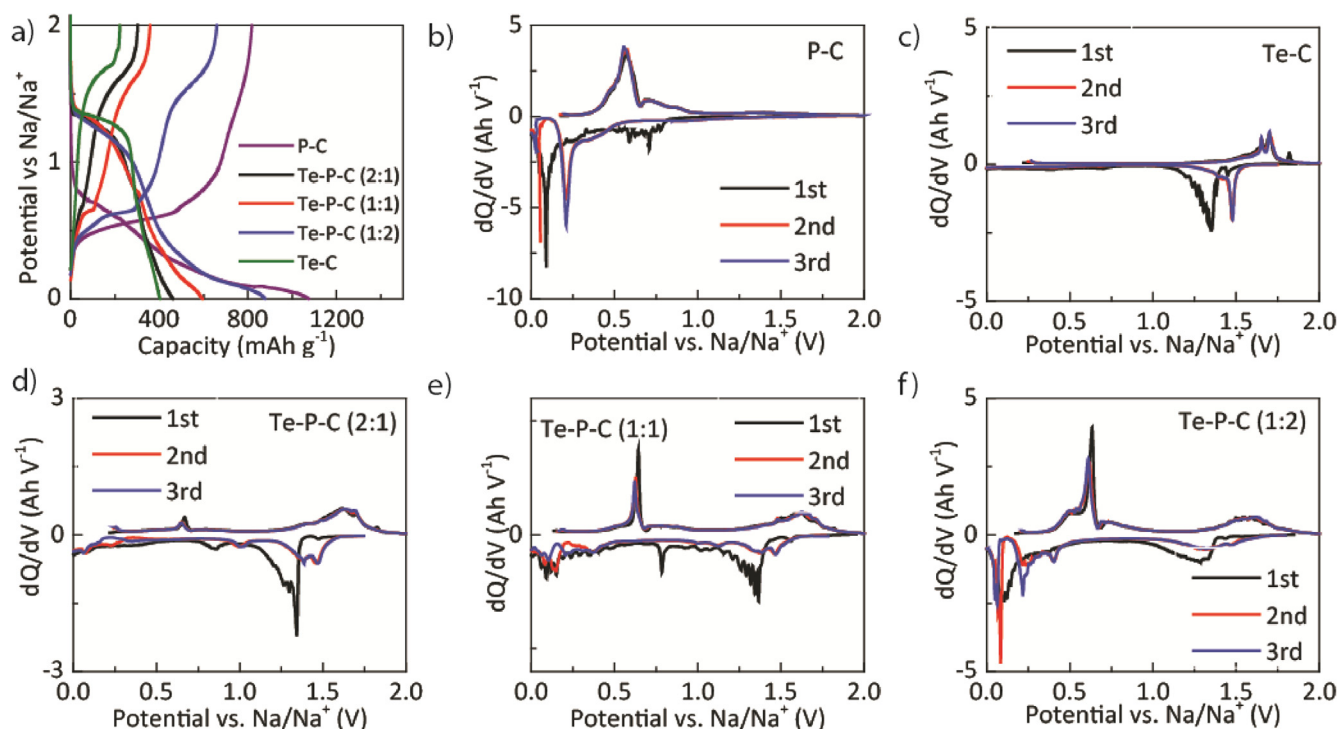


Fig. 4. (a) Initial potential profiles of P-C, Te-C, and Te-P-C composites with various Te to P molar ratios (2:1, 1:1, and 1:2) at 0.1 A g⁻¹; differential capacity plots of (b) P-C, (c) Te-C, (d) Te-P-C (2:1), (e) Te-P-C (1:1), and (f) Te-P-C (1:2).

respectively, after 200 cycles, which were equivalent to capacity retentions of 71% and 87%, respectively. However, as discussed earlier, because of the high capacity contribution of P in the composite, Te-P-C (1:2) exhibited the highest reversible capacity among the Te-P-C

composites, demonstrating a charging capacity of 659 mAh g⁻¹ at the 1st cycle and 441 mAh g⁻¹ at the 200th cycle, which corresponds to a capacity retention of 67%. Furthermore, the presence of Te likely efficiently enhances the mechanical strength of the composite, owing to its

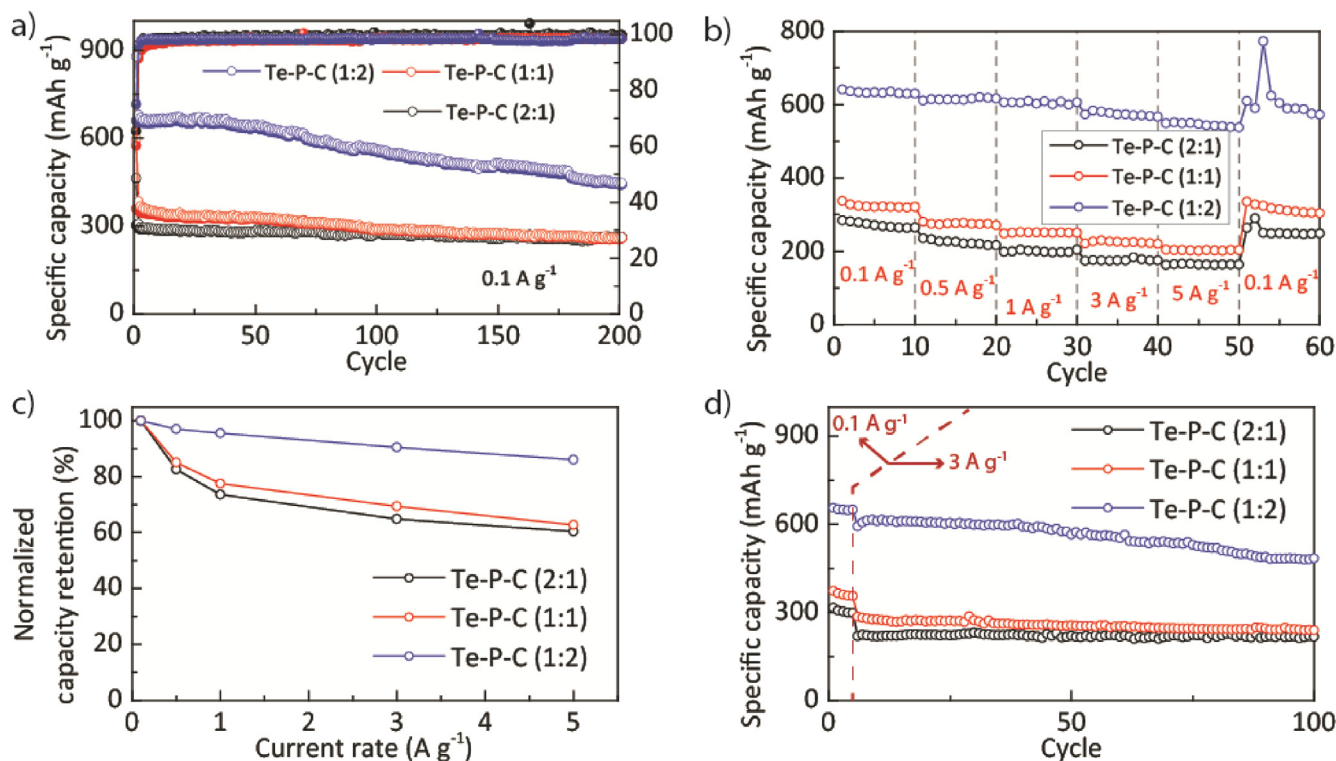


Fig. 5. (a) Effect of Te:P ratios on the cycling performance of Te-P-C composites from 0.001 to 2.0 V at 0.1 A g⁻¹; (b) rate performance of Te-P-C composites at various current densities; (c) normalized capacity retentions of Te-P-C composites in the rate capability test, and (d) fast charging test of Te-P-C composites at 3 A g⁻¹.

crystalline nature when the other element (red P) reacts with Na^+ ions. Based on the aforementioned discussion, the most optimal electrode could be Te-P-C (1:2), containing the highest specific capacity among the Te-P-C composite electrodes, even though its capacity retention is moderate compared with the others. Finally, the coulombic efficiency of all the Te-P-C composites reached $\sim 99\%$ within the first 10 cycles, demonstrating the high reversibility of Te-P-C composites upon cycling.

The rate capability and normalized charge capacity retention of the Te-P-C composites were investigated for fast recharge analyses, with the results presented in Fig. 5b and 5c. All Te-P-C electrodes are expected to show notable rate performance as Te improves the electrical conductivity of the composites. Fig. 5b shows that the P-rich electrode, Te-P-C (1:2), still demonstrates the highest reversible capacity at all current densities owing to the large capacity contribution of red P, exhibiting charging capacities of 615, 605, 574, and 545 mAh g^{-1} at the current densities of 0.5, 1, 3, and 5 A g^{-1} , respectively. When the current density returned to 0.1 A g^{-1} from 5 A g^{-1} , the charging capacity was 611 mAh g^{-1} , representing 97% of the initial charging capacity. Meanwhile, at the high current density of 5 A g^{-1} , Te-P-C (1:1) and Te-P-C (2:1) electrodes exhibited charging capacities of 200 mAh g^{-1} and 160 mAh g^{-1} , respectively, which revealed capacity retentions of 60%–63%, as shown in Fig. 5c. It is noted that the Te-P-C (1:2) electrode shows the best rate capacity retention, where it exhibited a rate capacity retention of $\sim 86\%$ at 5 A g^{-1} , suggesting that Te-P-C (1:2) has the highest conductivity compared with the other Te-P-C

composites. Although the amount of Te in the composite decreased, Te-P-C (1:2) electrode generated a smaller and more stable SEI layer, as mentioned in the DCP discussion, leading to improved electrochemical performance.

The fast-charging test was carried out using a low current density of 0.1 A g^{-1} as an electrochemical activation for five cycles before the application of a high current density of 3 A g^{-1} to the composites (Fig. 5d). Although the capacity suddenly dropped owing to the change in the current density, all the Te-P-C composites showed stable performance. After increasing the current density to 3 A g^{-1} , Te-P-C (1:2) still exhibited the highest charging capacity of 593 mAh g^{-1} and maintained 82% of the capacity at the 100th cycle, whereas the Te-P-C (1:1) and Te-P-C (2:1) electrodes delivered charging capacities of 239 mAh g^{-1} and 216 mAh g^{-1} , corresponding to capacity retentions of 84% and 99%, respectively, at the 100th cycle. The results suggested that all the prepared Te-P-C composites exhibit notable cycling performance, even in fast charging mode.

3.2. Theoretical behaviors of four equivalent circuits for EIS results

Fig. 6 illustrates specific steps to construct, verify, and apply a constraint from the EIS study. Expanding all the math expressions of the circuit's components generates an exact solution for the total impedance of the circuit. The low-frequency limit is the behavior of the exact solution near zero frequency. Rearranging the real and the imaginary

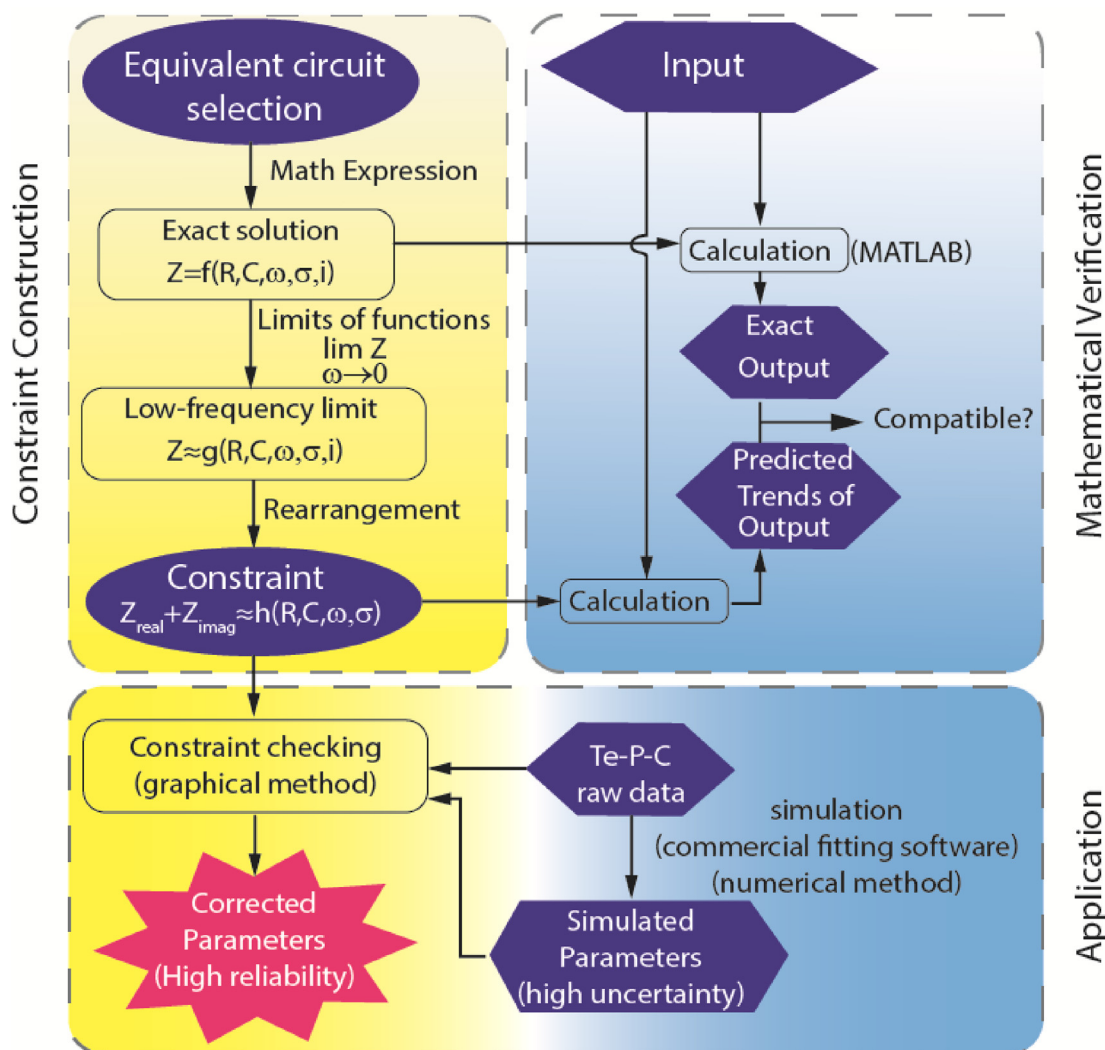


Fig. 6. Illustration of the EIS study from the theoretical constraint construction and verification to the application of the constraints on the actual Te-P-C composites.

parts of the low-frequency limit yields a constraint for the selected model. As the constraint construction requires some approximation to take the limit, it is essential to verify the restrictions mathematically. Applying the input (Table 1) for all the variables in the exact solution generates an exact output without any manual approximation. Furthermore, the constraint will provide some simple predictions on the trend of the exact output. The restriction is ready if the predicted trends match the exact output at the low-frequency region. The verified constraints (graphical method) will then support the commercial fitting software (numerical method) to correct the simulated parameters and produce a highly reliable EIS analysis.

Table 2 suggests the behaviors of the four models at the low-frequency range (low-frequency limits). Regardless of the existence of SEI layers, Z_{real} was linearly proportional to $\omega^{-0.5}$ and exhibited a common slope σ in the Randles-based models (models 1 and 2). Therefore, in the capacitor-based models, the graph of Z_{real} vs. $\omega^{-0.5}$ would give a slope of σ , which could determine the value of the diffusion coefficient (D). However, models 3 and 4 were deviated from the linear relationships when the CPEs were changed to the capacitors. Therefore, it can be concluded that when CPE-based models are more preferred than capacitor-based models, the values of D derived from the relationship between Z_{real} and $\omega^{-0.5}$ would be less reliable in models 3 and 4.

Owing to the significant differences in the mathematical behavior of the models, distinguishing CPE-based models from capacitor-based models is essential. Presenting a graph of $(Z_{\text{real}} + Z_{\text{imag}})$ vs. $\omega^{\alpha-1}$ could be a facile way to distinguish and identify the models. Eq. 13 and 14 for models 1 and 2 suggest that $(Z_{\text{real}} + Z_{\text{imag}})$ depend on neither ω nor $\omega^{\alpha-1}$. The presence of an SEI layer resistance would increase the $(Z_{\text{real}} + Z_{\text{imag}})$ impedance line with R_{SEI} , if C_1 and σ do not change. On the contrary, Eq. 15 and 16 for models 3 and 4 illustrate that $(Z_{\text{real}} + Z_{\text{imag}})$ is linearly proportional to $\omega^{\alpha-1}$ and has a slope of Γ . Because Γ is always negative for all α varying from 0.5 to 1.0, $(Z_{\text{real}} + Z_{\text{imag}})$ is a linearly decreasing function for $\omega^{\alpha-1}$ in CPE-based models. Moreover, the aforementioned lines in CPE-based models have y-intercepts at either $(R_s + R_{\text{ct}})$ or $(R_s + R_{\text{ct}} + R_{\text{SEI}})$, which is one of the most important parameters to be extracted in most studies. Therefore, there is a strict constraint at low ω . With a known α , the total resistance of pure resistors ($R_s + R_{\text{ct}} + R_{\text{SEI}}$) is the y-intercept of the trendline at

the low-frequency point in the graph of $(Z_{\text{real}} + Z_{\text{imag}})$ vs. $\omega^{\alpha-1}$. Fig. 7 summarizes the constraints of the four models at low ω , where a simple linear regression can be the key to explore the models.

To verify the low-frequency limit approximation, the exact output of input data (Table 1) was extracted from MATLAB and compared with the predicted output trends (Eq. 13, 14, 15, and 16). Fig. 8a shows that $(Z_{\text{real}} + Z_{\text{imag}})$ at a low-frequency region approached 28.5 Ω in model 1, which was only 5% difference compared with that of the prediction data from Eq. 13 ($R_s + R_{\text{ct}} - 2C_1\sigma = 30 \Omega$). The existence of the SEI layer vertically shifted the trend line 50.0 Ω , which was also consistent with the prediction data from Eq. 14. In Fig. 8b, the trend line of model 3 was a linearly decreasing function for $\omega^{\alpha-1}$ with a slope of -32.0 , which is highly consistent with Eq. 15 (predicted Γ was -35.0). Furthermore, the y-intercept of the trend line in model 3 (102.4 Ω) was only 6.9% smaller than the prediction data of Eq. 15 ($R_s + R_{\text{ct}} = 110.0 \Omega$). Similarly, the presence of the SEI layer also vertically shifted the trend line 49.9 Ω , which was similar to the input R_{SEI} value, regardless of β . These results demonstrated that the approximation was sufficient to predict the behaviors of the discussed models. Further reduction of the minimum value of ω is believed to decrease the difference between the exact solution and low-frequency limit approximation. In sum, all equations (Eq. 13, 14, 15, and 16) are simple. Therefore, they could provide a fast and convenient graphical method (Fig. 7) to test the simulated parameters or minimize the errors from numerical methods (e.g., commercial software).

3.3. Applying low-frequency limit approximation to Te-P-C composites

Fig. 9 shows the pristine EIS results of various Te-P-C composites at the 50th cycle. In general, commercial EIS fitting software has employed geometric methods to estimate the initial values of pure resistors, where the x-intercepts of semi-circles in the Nyquist plot correspond with R_s , R_{SEI} , and R_{ct} . [34] As the total impedance of a circuit in Fig. 1 consists of 5 to 9 independent variables (Eq. 4–13), the regression can be easily overfitted [35]. Although the difference between the simulated data and practical patterns (Figure S1) were very small, Table 4 shows that the uncertainty of R_{ct} , which were self-estimated by the fitting software, were very large for all the Te-P-C composites.

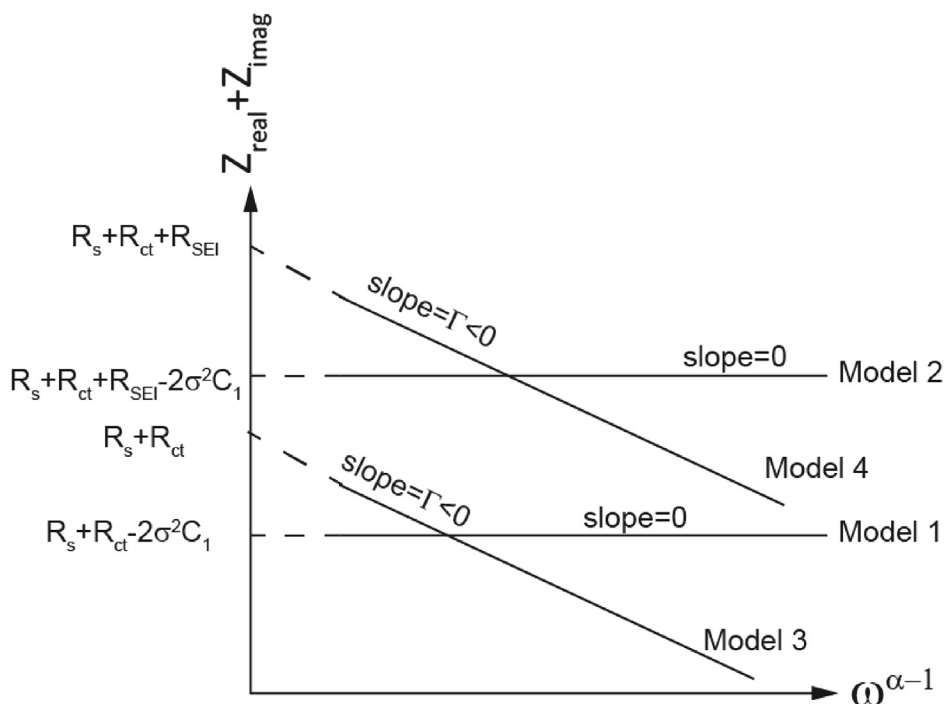


Fig. 7. Summary of the constraints of the four equivalent circuit models at low frequencies in the graph of $(Z_{\text{real}} + Z_{\text{imag}})$ with respect to $\omega^{\alpha-1}$.

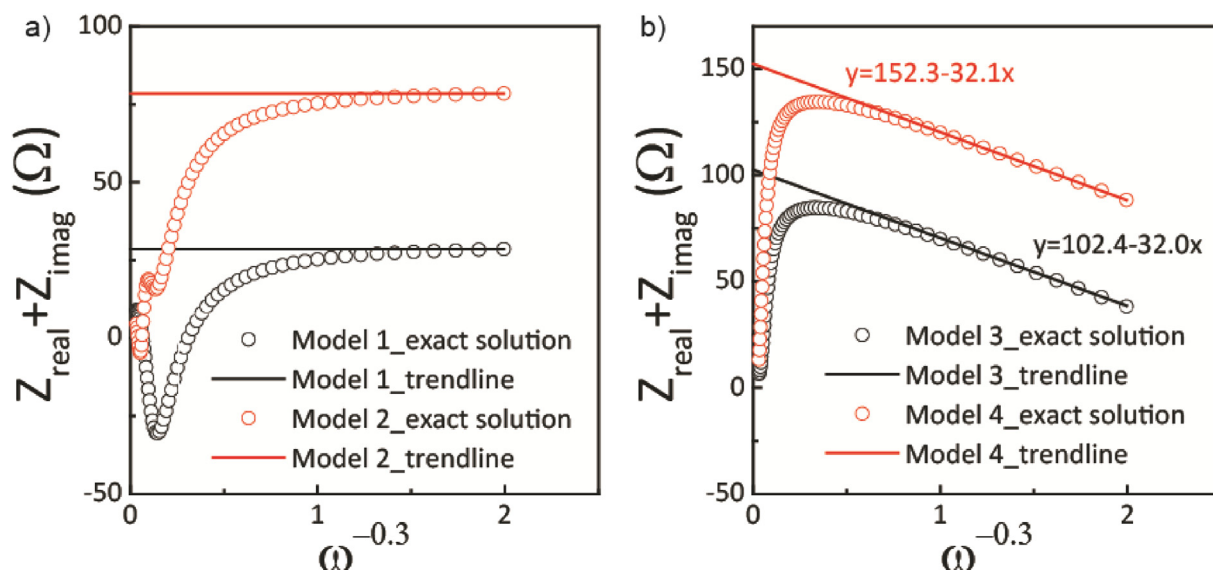


Fig. 8. Mathematical verifications of the four constraints: ($Z_{\text{real}} + Z_{\text{imag}}$) (exact output) and its trend lines at low frequencies for (a) models 1 and 2 and (b) models 3 and 4, which were directly calculated from the input data without any approximation.

Moreover, the nominal, simulated value of R_{ct} for Te-P-C (2:1) sample (560 kΩ) was too large to be adopted. Such a large R_{ct} value could not exhibit a good rate performance as seen in Fig. 5b.

As the value of ($Z_{\text{real}} + Z_{\text{imag}}$) decreased linearly with respect to $\omega^{-0.1}$ (Fig. 9b), Eq. 16 was employed to correct the R_{ct} value of the Te-P-C (1:2) composite. By taking the y-intercept of the trend line at low ω in Fig. 9b, Eq. 16 suggested that the total resistance of ($R_s + R_{\text{ct}} + R_{\text{SEI}}$) for Te-P-C (1:2) was 255.1 Ω. Because the uncertainties of R_s (0.5 Ω) and R_{SEI} (23.5 Ω) were sufficiently small, the R_{ct} value of the Te-P-C (1:2) composite was recalculated to 158.5 Ω. The ($Z_{\text{real}} + Z_{\text{imag}}$) value of other composites also decreased linearly with respect to $\omega^{-0.1}$ (Fig. 9c and 9d). Therefore, repeating the aforementioned procedure deliberately corrected R_{ct} for other composites (Table 4). The R_{ct} values of the Te-P-C composites were nearly identical (~170 Ω), as expected, as the composites were simple mixtures consisting of Te, P, and C at the nanoscale level. The EIS results were highly consistent with the rate performance as well. The Te-P-C (1:2) composite showed the best rate performance, because it had the lowest R_{SEI} value (92.4 Ω) among the composites (Table 4).

In sum, in previous study, we suggested the minimization of “residual of $|Z|$ ” as a primary criterion in EIS fitting [44]. In that case, a simulated pattern seemed to be compatible to a practical EIS pattern when the “residual of $|Z|$ ” remained below 10% [45]. From this study, however, even though the “residual of $|Z|$ ” was only 4% (Figure S1), the as-simulated parameters could not satisfy the Te-P-C performance elucidation. Therefore, we recommend the four constraints (Fig. 7) as primary criteria in addition to the “residual of $|Z|$ ” criterion for EIS fitting.

4. Conclusion

In summary, Te-P-C composites were successfully prepared from Te, red P, and C via a facile HEMM route and explored as advanced anode materials for sodium ion cells. The HEMM process did not facilitate the formation of any new insulating products between Te and P, ensuring the high conductivity of the composites. Because of the effective dispersion of the elements and various working potentials, Te-P-C composite could absorb the mechanical stress during sodiation/desodiation, improving cycling performance. The high conductivity of elemental Te facilitated the superior rate performance of the Te-P-C composites. However, the high Te content also accelerated the formation of SEI layers, which caused a low initial coulombic efficiency and, ultimately,

served to decrease the electrical conductivity of the system. To obtain the relationship between electrochemical performance and impedance, the mathematical behaviors of four common equivalent circuits in the EIS (Randles, Randles with SEI, one-CPE, and two-CPE circuits) were compared at the low-frequency limit. The key to identifying and refining the four models was the linear relationships between ($Z_{\text{real}} + Z_{\text{imag}}$) and $\omega^{-0.1}$. The new constraints provided a simple, convenient way for electrochemical engineers to reduce errors from the traditional numerical fittings and may be a premise for a new EIS interpretation algorithm. Finally, owing to the reduced SEI layer formation, Te-P-C (1:2) exhibited superior rate and fast charging performance.

CRediT authorship contribution statement

Thuan Ngoc Vo: Methodology, Investigation, Formal analysis, Software, Visualization, Writing - original draft. **Doo Soo Kim:** Methodology, Investigation, Validation, Writing - original draft. **Yoo Seok Mun:** Resources, Investigation. **Hyun Jong Lee:** Conceptualization, Investigation. **Suk-kyun Ahn:** Supervision, Funding acquisition, Conceptualization. **Il Tae Kim:** Supervision, Funding acquisition, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2020.125703>.

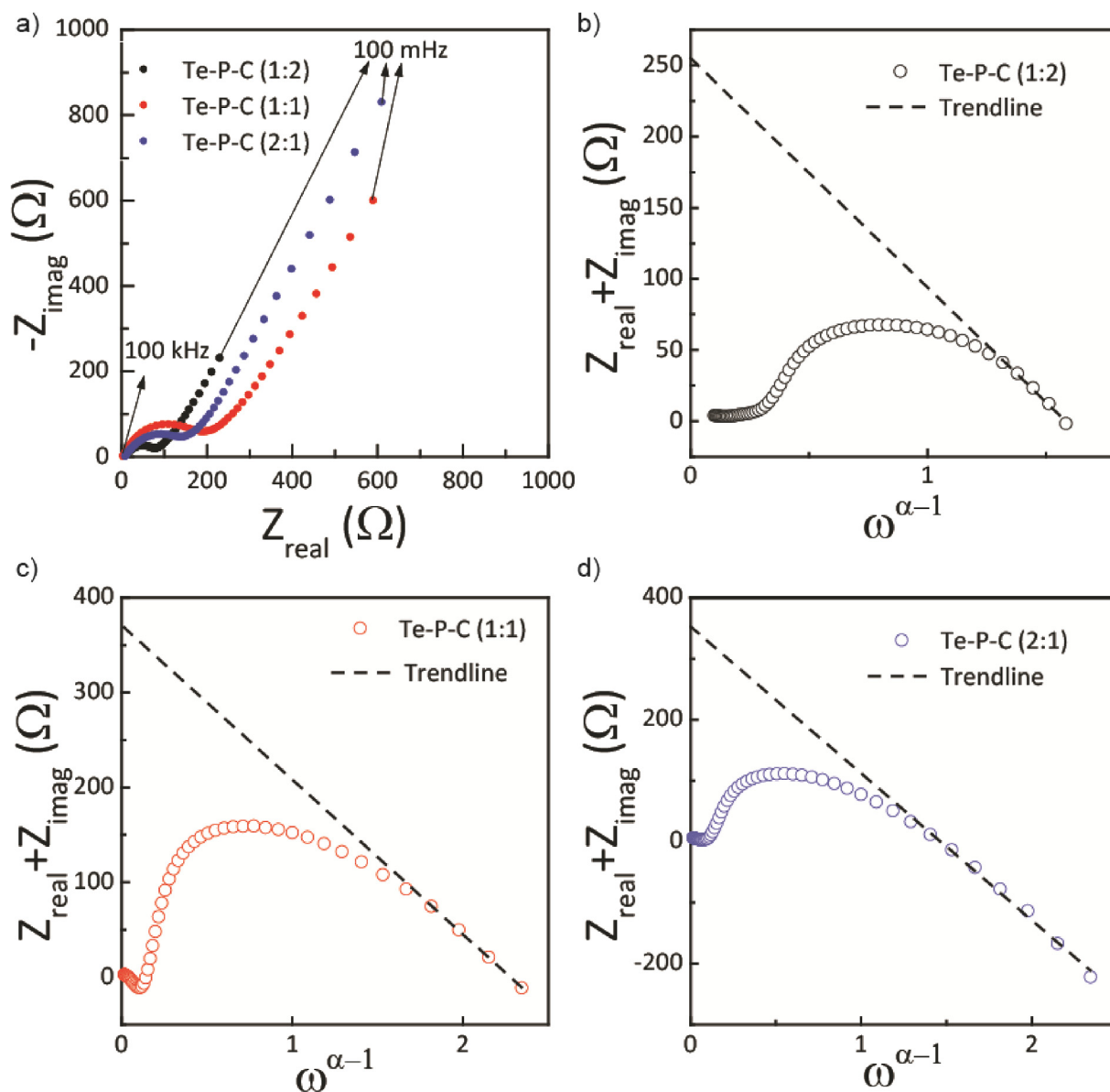


Fig. 9. (a) Nyquist plots of the various Te-P-C composite electrodes at the 50th cycle. ($Z_{real} + Z_{imag}$) plots with respect to $\omega^{\alpha-1}$ of various composite electrodes at the 50th cycle: (b) Te-P-C (1:2), (c) Te-P-C (1:1), and (d) Te-P-C (2:1).

Table 4

Simulated parameters obtained from the numerical method and corrected parameters predicted from the low-frequency constraints.

Sample	Simulated parameters via numerical method				Corrected Parameters	
	$R_s[\Omega]$	$R_{SEI}[\Omega]$	$R_{ct}[\Omega]$	α	$R_s + R_{SEI} + R_{ct}[\Omega]$	$R_{ct}[\Omega]$
Te-P-C (1:2)	4.2 ± 0.5	92.4 ± 23.5	$124.6 \pm 4.7 \times 10^3$	0.80	255.1	158.5
Te-P-C (1:1)	3.6 ± 0.4	201.9 ± 25.4	$583.3 \pm 5.5 \times 10^9$	0.63	370.9	165.4
Te-P-C (2:1)	7.2 ± 0.5	157.3 ± 16.3	$5.6 \times 10^4 \pm 6.2 \times 10^5$	0.63	352.8	188.3

Simulated parameters were collected with ZMAN2.4 while the corrected values of ($R_s + R_{SEI} + R_{ct}$) were manually extracted from ($Z_{real} + Z_{imag}$) plots; the predicted value of R_{ct} is the difference between ($R_s + R_{SEI} + R_{ct}$)_{corrected} and ($R_s + R_{SEI}$)_{simulated}.

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