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## Redefining the roles of alkali activators for porous carbon†

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Alkali activation is a common method to prepare commercial porous carbon. In a mixed alkali activation system, the role of each individual alkali has generally been assumed to be the same as in a single alkali activation system, and the low corrosiveness of weak alkalis has mainly been emphasized. However, the intrinsic roles of the individual alkalis should be understood in detail and redefined to illuminate the activation pathways from the perspective of internal chemical reactions rather than corrosiveness. Herein, by combining *in situ* TG-MS analysis, DFT calculation and other characterizations, the activation processes were precisely tracked, and activation pathways were proposed. In the mixed alkali activation system, the strong alkali KOH served as the activation promoter, first decomposing into K<sub>2</sub>O, which then attacked the C–C bonds to form active reaction sites defined as pore seeds. The weak alkali K<sub>2</sub>CO<sub>3</sub> acted as the activation pathway modifier; CO<sub>3</sub><sup>2-</sup> preferentially etched the pore seeds over K<sub>2</sub>O due to the lower reaction barrier of CO<sub>3</sub><sup>2-</sup> interacting with the pore seeds. Consequently, the rough etching reaction of KOH was replaced and suppressed by the gentler action of CO<sub>3</sub><sup>2-</sup>, forming more micropores. When the ratio of strong to weak alkali was 1:1, the obtained CK<sub>1</sub>K<sub>2</sub>-122 exhibited the highest microporosity (82.61%) and a high specific surface area (1962.18 m<sup>2</sup> g<sup>-1</sup>). It exhibited a high specific capacitance of 296.7 F g<sup>-1</sup> and excellent cycling stability with 98.3% retention after 10 000 cycles. The supercapacitor demonstrated a high energy density of 114.4 W h kg<sup>-1</sup> at a power density of 17.5 kW kg<sup>-1</sup>, with a broad potential window of 3.5 V.

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## Introduction

Porous carbon has been extensively used in fields such as energy storage, catalysis, and adsorption and separation due to its high specific surface area (SSA), abundant pore structure, outstanding chemical stability and low cost.<sup>1–3</sup> The well-defined pore structure of porous carbon is highly desirable for excellent performance, *e.g.*, hierarchical porous carbon with a large

number of micropores and appropriate mesopores and macropores is necessary for capacitive energy storage.<sup>4–6</sup>

The structural features of porous carbon are highly dependent on the preparation strategy, and considerable efforts have been made to design and prepare porous carbon with diverse pore structures.<sup>7,8</sup> To date, chemical activation with alkalis, such as KOH, NaOH, K<sub>2</sub>CO<sub>3</sub>, KHCO<sub>3</sub> and their mixtures, remains the primary and most effective way to fabricate porous carbon.<sup>9–12</sup> Among them, the strong alkali KOH is a traditional and highly representative chemical activator that was developed early on.<sup>13–15</sup> Porous carbon prepared using KOH typically exhibits abundant pores and high specific surface area.<sup>16–18</sup> After KOH, the weak alkali K<sub>2</sub>CO<sub>3</sub>, which is used as food additive and has lower corrosiveness, was introduced as another alkaline activator to reduce or avoid the use of KOH due to the strong corrosiveness and equipment damage associated with KOH.<sup>19–22</sup> Porous carbons can also be successfully prepared using K<sub>2</sub>CO<sub>3</sub> as a single activator or as a co-activator with the strong alkali KOH.<sup>23</sup> It is worth noting that when K<sub>2</sub>CO<sub>3</sub> is used as a co-activator, the obtained porous carbons also have high specific surface areas and abundant pores comparable those achieved using to the activation effects of KOH alone.<sup>24–27</sup> For example, porous carbon derived from bamboo using a mixture KOH and K<sub>2</sub>CO<sub>3</sub> as the activator has a high specific surface area

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of  $2417 \text{ m}^2 \text{ g}^{-1}$ . In short, porous carbon can be prepared *via* the alkali activation method, and the relationships between activation conditions and pore structures have been extensively studied.

Additionally, the activation mechanisms for single-activator systems using KOH or  $\text{K}_2\text{CO}_3$  have been proposed, and the released gases during the activation process and the possible reaction processes have been investigated.<sup>28–34</sup> However, in KOH and  $\text{K}_2\text{CO}_3$  mixed alkali activation systems, the roles of KOH and  $\text{K}_2\text{CO}_3$  have been considered to be roughly the same as in the single-activator KOH or  $\text{K}_2\text{CO}_3$  systems, and  $\text{K}_2\text{CO}_3$  has mostly been considered in general terms of weak alkalinity and low corrosiveness. The intrinsic chemical roles of KOH/ $\text{K}_2\text{CO}_3$ , their combined activation effect and the real activation pathway in mixed alkali systems have not been precisely studied and revealed, and the role of  $\text{K}_2\text{CO}_3$  needs to be clarified from the perspective of chemical reactions rather than simply in terms of its corrosiveness. *In situ* tracking of the activation processes of different alkali activator systems at the chemical reaction level should be undertaken, and the results should be compared to redefine the roles of the alkalis and further clarify the chemical nature of combined strong and weak alkali activation.

Herein, commercial petroleum coke was used as the carbon precursor with pure KOH,  $\text{K}_2\text{CO}_3$ , and mixtures of KOH and  $\text{K}_2\text{CO}_3$  as the activator, and different types of porous carbons were prepared. To reveal the activation pathways and redefine the roles of the alkalis, real-time tracking and detailed comparison of the intermediate products of the activation processes were conducted. The results indicated that in the mixed activator system, KOH acted as a promoter: KOH decomposed into  $\text{K}_2\text{O}$ , which then attacked C–C bonds, resulting in the formation of numerous pore seeds. In the mixed system,  $\text{K}_2\text{CO}_3$  acted as a pathway modifier:  $\text{CO}_3^{2-}$  promoted a gentler reaction with numerous pore seeds to form porous carbon with ultra-high microporosity. By regulating the ratio of strong and weak alkalis, the optimized porous carbon CK<sub>1</sub>K<sub>2</sub>-122 exhibited the highest microporosity of 82.61%, a high specific surface area of  $1962.18 \text{ m}^2 \text{ g}^{-1}$  and excellent supercapacitive performance. This work provides new insights for the flexible design of activated carbons with tunable porous structures.

## Results and discussion

### General understanding of preparing porous carbon

As shown in Fig. 1, alkali activation is the primary and most common method to prepare commercial porous carbon. The strong alkali KOH is a traditional and highly representative chemical activator that was developed early on. Porous carbon prepared by KOH typically features high specific surface areas and abundant pores due to the strong activation ability of KOH. After KOH, the weak alkali  $\text{K}_2\text{CO}_3$  with low corrosiveness was introduced into alkali activation systems to reduce or avoid the use of highly corrosive KOH. However, porous carbon prepared by activation with  $\text{K}_2\text{CO}_3$  alone usually exhibits low specific surface area and poor porosity due to the weak activation ability of this weak alkali. Around the same time, KOH and  $\text{K}_2\text{CO}_3$

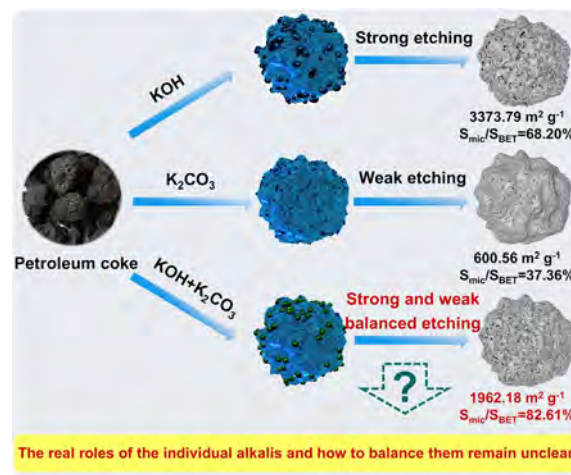


Fig. 1 General schematic illustration of the preparation of activated porous carbons using KOH,  $\text{K}_2\text{CO}_3$  and KOH +  $\text{K}_2\text{CO}_3$  activation.

mixed activation systems were developed, and their activation effects were found to be comparable to that of KOH alone. However, when  $\text{K}_2\text{CO}_3$  was introduced, only its low corrosiveness was discussed; the source of the activation results in mixed activation systems was vaguely and generally assumed to be the balanced effect of alkaline strength. The real chemical roles of the individual alkalis and the chemical nature of their combined effect are still unclear, and the view of corrosiveness or alkalinity should be promoted.

### Redefining roles of alkali for preparing porous carbon

To clarify the true chemical roles of the individual alkalis in the mixed activation system, the gases released from the different alkali systems were monitored *in situ* throughout the entire activation process using a mass spectrometer coupled to a thermogravimetry device (TG-MS); this *in situ* tracking method has also been used in other studies to investigate the pyrolysis mechanism.<sup>35,36</sup> The TG and MS curves are shown in Fig. 2 and S1.† The activation processes can be divided into three stages: (i) stage I – pore seed formation; (ii) stage II – etching of pore seeds into pores; and (iii) stage III – continuous development of pores. The definition of pore seeds will be discussed in the subsequent section. As shown in Fig. 2b, the released gases were carefully monitored and compared, and the possible chemical reaction processes are summarized in Table 1. (i) From room temperature to  $300 \text{ }^\circ\text{C}$ , in the KOH-only activation system,  $\text{H}_2\text{O}$  ( $m/z = 18$ ) and  $\text{O}^{2-}$  ( $m/z = 16$ ) were detected, and their MS curve shapes were almost the same, indicating that the  $\text{OH}^-$  initially decomposed into  $\text{H}_2\text{O}$  and  $\text{O}^{2-}$ . Meanwhile, the release of CO ( $m/z = 28$ ) was also detected, which indicated that the etching reaction had already started at this low temperature, with KOH beginning to react with the carbon petroleum coke. In contrast, in the  $\text{K}_2\text{CO}_3$ -only activation system, no CO was released at this stage.  $\text{CO}_2$  ( $m/z = 44$ ) was also detected, and the MS curve shape of  $\text{CO}_2$  was consistent with that of  $\text{O}^{2-}$ , indicating that  $\text{CO}_3^{2-}$  underwent decomposition reaction to release  $\text{CO}_2$  and  $\text{O}^{2-}$ , as shown in Table 1. In the KOH and  $\text{K}_2\text{CO}_3$  mixed activation

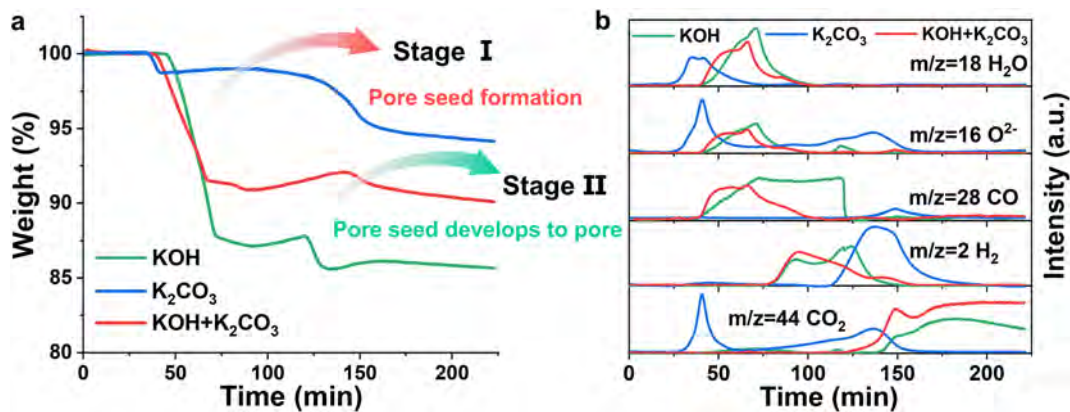


Fig. 2 Activation mechanism analysis. (a) TG profiles of KOH,  $K_2CO_3$  and KOH +  $K_2CO_3$  activation reactions. (b) MS curves of the gaseous activation products derived from the KOH,  $K_2CO_3$  and KOH +  $K_2CO_3$  activation processes tracked by TG-MS.

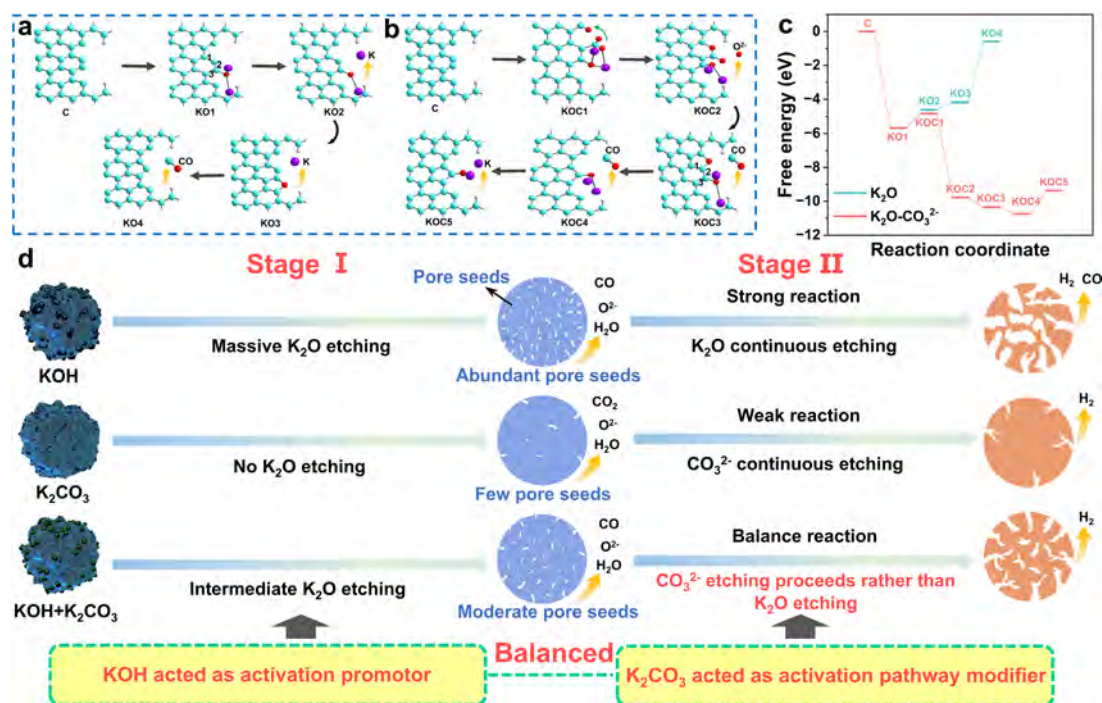
system, CO ( $m/z = 28$ ) and  $O^{2-}$  were also detected, and the temperature at which gas began to be released was the same as that of the KOH-only activation system, which also suggested that the etching reactions had already occurred in this system. At this low-temperature stage, the real pores cannot yet form. In the KOH-only activation system, CO was detected, and in the  $K_2CO_3$ -only activation system, no CO was released; thus, the release of CO ( $m/z = 28$ ) is a signal that the etching reaction has already started between KOH and petroleum coke. This early etching reaction cannot produce actual pores and porous carbon but can generate active reaction sites for the subsequent formation of a large number of real pores; thus, these active reaction sites were defined as pore seeds. This can explain why most reported porous carbons and our carbons discussed in the following text obtained using activation involving KOH have a large specific surface area and abundant pore structure, whereas the porous carbons activated by  $K_2CO_3$  alone usually have a smaller specific surface area.<sup>9,11,16,19,24,26</sup> Therefore, the strong alkali KOH acted as an activation promoter. It can decompose into  $K_2O$ , which can attack C–C bonds to release CO (Table 1) and form pore seeds for subsequent development into pores. Compared with activation using  $K_2CO_3$  alone, in the mixed activation system, no  $CO_2$  was released, which indicated that the decomposition of  $K_2CO_3$  was inhibited. Compared with KOH-only activation, the peaks of the  $H_2O$ ,  $O^{2-}$  and CO molecules released in the mixed activation system shifted forward, and shape of the MS curve of CO was almost the same as that of  $O^{2-}$  from this low temperature to 750 °C; however, this curve shape was obviously different from that in KOH-only activation. These results indicated that in the mixed activation system, the activation pathway was different than that in the KOH-only activation system, even though the released gas components were the same. Considering that the decomposition of  $K_2CO_3$  was prevented, and the release trends of CO and  $O^{2-}$  were consistent in the mixed activation system, we propose that the  $CO_3^{2-}$  that was prevented from decomposing, can react with the carbon atoms from the pore seeds preferentially instead of  $K_2O$  to release CO and  $O^{2-}$ , as shown in Table 1. The reason that  $CO_3^{2-}$  can react with the pore seeds preferentially over  $K_2O$  is

due to the lower reaction barrier for the combination of  $CO_3^{2-}$  with carbon free radicals; this lower reaction barrier will be analyzed in detail later in the text. Therefore, the weak alkali  $K_2CO_3$  acted as an activation pathway modifier; the strong etching reaction of KOH was suppressed, and  $CO_3^{2-}$  promoted a gentler reaction with the pore seeds to form porous carbon with ultra-high microporosity. (ii) As the temperature rose from 300 °C to 700 °C, in the KOH activation system,  $K_2O$  continuously and strongly attacked C–C bonds to produce carbon free radicals and could participate in a strong activation reaction with carbon free radicals, releasing CO ( $m/z = 28$ ). Additionally, KOH can directly react with carbon free radicals, releasing  $H_2$  ( $m/z = 2$ ). The pore seeds developed explosively to form larger pores rather than ultra-micropores. In the mixed KOH and  $K_2CO_3$  systems, the strong etching reaction of KOH was continuously suppressed due to the lower barrier for the reaction of  $CO_3^{2-}$  and carbon free radicals, and the pore seeds developed gently to form numerous ultra-micropores. In the pure  $K_2CO_3$  system, in addition to the continuous decomposition of  $CO_3^{2-}$  to produce  $CO_2$ , only a small amount of  $K_2O$  attacks C–C bonds to form a small number of pores. (iii) During the prolonged heating at 700 °C, the mixed KOH and  $K_2CO_3$  system released a large amount of  $CO_2$  due to the decomposition of  $K_2CO_3$ . However, in the KOH-only system, the amount of  $CO_2$  released is lower due to the violent decomposition reaction at the early stage.

To further reveal the reason why  $CO_3^{2-}$  preferentially reacts with the pore seeds over  $K_2O$ , thereby altering the activation pathway, we constructed molecular models of the  $K_2O$  etching reactions both with and without the  $CO_3^{2-}$  structure, and DFT calculations of the entire activation process were also carried out. The reaction of the activators with the petroleum coke will occur first on the surface/pores of the coke, and petroleum coke contains abundant aromatic structures. Therefore, a surface/pore model was constructed using a single aromatic structure in our calculation. Fig. 3a presents the detailed calculation of the reaction pathways without the involvement of  $CO_3^{2-}$  in the activation. First, the oxygen atom of  $K_2O$  attacks the C atom to form the C–O–K2 complex (KO1). Due to electron transfer and

Table 1 Relative reaction equations of KOH, K<sub>2</sub>CO<sub>3</sub> and KOH + K<sub>2</sub>CO<sub>3</sub> at different activation temperatures

Stage	System		
	KOH	K <sub>2</sub> CO <sub>3</sub>	KOH + K <sub>2</sub> CO <sub>3</sub>
Stage I 25–300 °C	2OH <sup>-</sup> → H <sub>2</sub> O + O <sup>2-</sup> KOH → K <sub>2</sub> O + H <sub>2</sub> O C – C → <sup>K<sub>2</sub>O</sup> C' (abundant pore seeds) K <sub>2</sub> O + C' → 2K + CO (strong)	CO <sub>3</sub> <sup>2-</sup> → CO <sub>2</sub> + O <sup>2-</sup> H <sub>2</sub> O (bound) → H <sub>2</sub> O (g) K <sup>+</sup> intercalation compounds	2OH <sup>-</sup> → H <sub>2</sub> O + O <sup>2-</sup> KOH → K <sub>2</sub> O + H <sub>2</sub> O C – C → <sup>K<sub>2</sub>O</sup> C' (moderate pore seeds) C' + CO <sub>3</sub> <sup>2-</sup> → 2CO + O <sup>2-</sup> (gentle and abundant)
Stage II 300–700 °C	K <sub>2</sub> O + C' → 2K + CO (strong)  6KOH + 2C' → 2K + 3H <sub>2</sub> + 2K <sub>2</sub> CO <sub>3</sub> (strong and abundant)	CO <sub>3</sub> <sup>2-</sup> → CO <sub>2</sub> + O <sup>2-</sup>  K <sub>2</sub> CO <sub>3</sub> → K <sub>2</sub> O + CO <sub>2</sub>  C – C → <sup>K<sub>2</sub>O</sup> C' (few pore seeds) K <sup>+</sup> catalysis	C' + CO <sub>3</sub> <sup>2-</sup> → 2CO + O <sup>2-</sup> (gentle and abundant) 6KOH + 2C' → 2K + 3H <sub>2</sub> + 2K <sub>2</sub> CO <sub>3</sub> (strong but poor) K <sup>+</sup> catalysis
Stage III 700 °C maintenance	K <sub>2</sub> CO <sub>3</sub> → K <sub>2</sub> O + CO <sub>2</sub>	C' + CO <sub>3</sub> <sup>2-</sup> → 2CO + O <sup>2-</sup> (gentle but very poor)	K <sub>2</sub> CO <sub>3</sub> → K <sub>2</sub> O + CO <sub>2</sub>

Fig. 3 (a) Activation reactions for K<sub>2</sub>O model. (b) Activation reactions for the K<sub>2</sub>O–CO<sub>3</sub><sup>2-</sup> model. (c) Free energy profiles for the activation reactions of the K<sub>2</sub>O and K<sub>2</sub>O–CO<sub>3</sub><sup>2-</sup> models. (d) Schematic illustration of the real roles of the alkalis and the redefined activation pathway.

the close interaction of the electronegative O, the K–O bond is broken, and the ring closing reaction occurs to provide KO2 and KO3, respectively. As shown in Fig. 3c, this reaction requires more energy, resulting in a more vigorous etching reaction. Subsequently, the O atoms attack the aromatic group C to form pores, and a CO molecule is released. When CO<sub>3</sub><sup>2-</sup> is involved in the activation process, the reaction pathway and energy change tremendously. As shown in Fig. 3b, the ester group O on CO<sub>3</sub><sup>2-</sup> first attacks the carbon atom adjacent to K<sub>2</sub>O and forms a bond with K. Due to the high electronegativity of O, one O atom on CO<sub>3</sub><sup>2-</sup> could transfer to the secondary aromatic ring to form a C–O bond, and the remaining –CO<sub>2</sub> group forms a C–C bond

with the aromatic ring to give the complex KOC1. The carbon atom in the –O–C=O group in the KOC1 further reacts with the O atom, which the carbon atom in this group undergoes a cyclization reaction with the O on the secondary ring, and a carbonyl oxygen (O<sup>2-</sup>) is released to form the KOC2 complex. This step significantly reduces the energy required for etching. The O atom on the secondary aromatic ring carbon then undergoes a cyclization reaction with the C atom adjacent to K<sub>2</sub>O, and a CO molecule is released to form the complex KOC3. The O atom further attacks the adjacent carbon atom, another CO molecule is released, and the structure is changed from a six-membered ring to a five-membered ring to form the

complex KOC4. Finally, breakage of the K–O bond and escape of another CO molecule occur to form KOC5. As can be seen from the free energy profiles in Fig. 3c, the activation path of  $K_2O$  is simple, but it requires high energy and the activation reaction is violent. In the activation involving  $K_2CO_3$ , the barrier for the reaction of  $CO_3^{2-}$  and the carbon free radical is much lower than that of  $K_2O$  and the carbon free radical, which is beneficial for gentle activation reactions, and the activation path was changed due to the introduction of  $K_2CO_3$ . The key factor in this change in the reaction path is that the adjacent carbon atom of  $K_2O$  in KOC3 is favorable for forming a five-membered ring with O, weakening the C–C bond. As depicted in Fig. S2 and S3,<sup>†</sup> comparing the strengths of bond 1, bond 2 and bond 3 in KO1 and KOC3, it is found that bond 1 and bond 2 of KOC3 exhibit weak bond energy. Therefore, it is more likely to be attacked by O to form a CO molecule.

In summary, Fig. 3d schematically illustrates the real roles of the alkalis in the KOH and  $K_2CO_3$  mixed activation system. The strong alkali KOH acts as the activation promoter; it first decomposes into  $K_2O$ , which can attack the C–C bond to form a large number of pore seeds. The pore seeds then develop into pores through subsequent etching reactions, but the development pathway differs for the different alkali activation systems. The weak alkali  $K_2CO_3$  acted as an activation pathway modifier in the mixed alkali activation system. Compared to  $K_2O$ ,  $CO_3^{2-}$  requires a lower reaction barrier to bind with carbon free radicals, and thus  $CO_3^{2-}$  will preferentially react with carbon atoms in the pore seeds. Therefore, in the mixed alkali activation system, the strong etching reaction of KOH can be suppressed, and the reaction pathway changes from strong explosive etching by KOH to gentle etching by  $CO_3^{2-}$ . The roles of KOH and  $K_2CO_3$  in the mixed alkali activation system were redefined, and the vague concept of weak alkaline balanced activation was clarified from the perspective of the internal chemical reactions instead of simply in terms of corrosiveness and alkaline strength. The proposed activation mechanism will provide a foundation for regulating the pore structure in alkali activation.

### Regulating pore structures and characterization of carbon

Based on the aforementioned perspective that the strong alkali KOH served as an activation promoter to produce pore seeds for the formation of abundant pores and the weak alkali  $K_2CO_3$  acted as an activation pathway modifier to suppress the strong etching reaction of KOH and thus form more smaller micropores, we regulated the pore structure by adjusting the content of alkalis as described in the Experimental section. A porous carbon with ultra-high microporosity, large specific surface area and hierarchical pores was obtained for excellent capacitive energy storage by using a moderate ratio of strong to weak alkali. Fig. 4 presents the characterizations of the porous carbons prepared using several typical alkaline ratios. As shown in Fig. 4a, as the amount of  $K_2CO_3$  was gradually decreased, the characteristic (002) peak at approximately  $26^\circ$  showed a decreasing trend;<sup>37</sup> this peak nearly disappeared when KOH alone was used as the activator, indicating that the graphite microcrystalline structure of carbon had been completely

corroded and destroyed by KOH, which led to poor electrical conductivity.<sup>38</sup> The Raman spectra are shown in Fig. 4b; the G band peak intensity gradually decreased, and the defects increased with decreasing  $K_2CO_3$ . Thus, it is necessary to regulate the alkali content to control the etching degree and pathway to prepare porous carbon with the needed defects, microcrystalline structure and active sites.

The specific surface area and pore size distribution are very important for capacitive energy storage performance. Generally, the pore size should be slightly larger than the electrolyte ion.<sup>39</sup> The specific surface area, pore size distribution, structural parameters and relevant data are shown in Fig. 4c, d and Table S1.<sup>†</sup> The isotherms of  $CK_1K_2-1x(4-x)$  ( $x = 0, 1, 2, 3, 4$ ) were all type I; the adsorption and desorption curves were almost overlapped without obvious hysteresis loops, which verified that the petroleum-coke-derived porous carbon was dominated by micropores. From Table S1,<sup>†</sup> it can be seen that the specific surface area and pore volume showed a gradual decreasing trend with increasing the amount of potassium  $K_2CO_3$ . The micropore percentages of  $CK_1K_2-1x(4-x)$  ( $x = 0, 1, 2, 3, 4$ ) were 37.36%, 40.97%, 82.61%, 75.19% and 68.20%, respectively;  $CK_1K_2-122$  has the largest microporosity and second-highest specific surface area of  $1962.18 \text{ m}^2 \text{ g}^{-1}$  ( $CK_1K_2-104$ :  $600.56 \text{ m}^2 \text{ g}^{-1}$ ;  $CK_1K_2-113$ :  $880.33 \text{ m}^2 \text{ g}^{-1}$ ;  $CK_1K_2-131$ :  $1928.45 \text{ m}^2 \text{ g}^{-1}$ ;  $CK_1K_2-140$ :  $3373.79 \text{ m}^2 \text{ g}^{-1}$ ). Different alkali ratios can lead to different pore size distributions; the pore size distributions are shown in Fig. 4d. In the KOH-only activation system, the pore seeds developed into 0.55 nm and 1.27 nm pores. Due to the strong etching reaction of KOH, the pore seeds tended to develop into larger micropores in the KOH-only activation system; compared with the other alkali ratio systems, the proportion of larger micropores (1.27 nm) in this system was higher. As the amount of  $K_2CO_3$  was gradually increased, the strong etching reaction of KOH was inhibited, and the 1.27 nm micropores were first reduced first to 1.22 nm, then to 1.17 nm and finally disappeared. The microporosity of 0.55 nm gradually increased, and the microporosity of  $CK_1K_2-122$  reached the maximum. This is attributed to the fact that  $K_2CO_3$  acted as an activation pathway modifier that appropriately inhibited the strong etching reaction of KOH. In addition, in the  $K_2CO_3$ -only activation system, the few pore seeds could not develop into abundant pores. The temperature can affect the formation of pores; the specific surface area and pore size distribution of porous carbon obtained at different activation temperatures ranging from 600 °C to 800 °C are also shown in Fig. S4, S5 and Table S2.<sup>†</sup> It can be observed that as the activation temperature increased, the proportion of micropores increased, while the specific surface area and pore volume first increased and then decreased. It is worth noting that the size distribution of the micropores was always dominated at about 0.55 nm for the different activation temperatures and alkali ratios. The micropore pore size is perfectly matched to the solvated ion size,<sup>40</sup> and the most effective ion adsorption is achieved by maximizing the available space (Fig. S6<sup>†</sup>), so excellent specific capacitance and energy density would be realized.  $CK_1K_2-122$  has greatest microporosity and second-highest specific surface area, demonstrating that the moderate amount of KOH acted as an

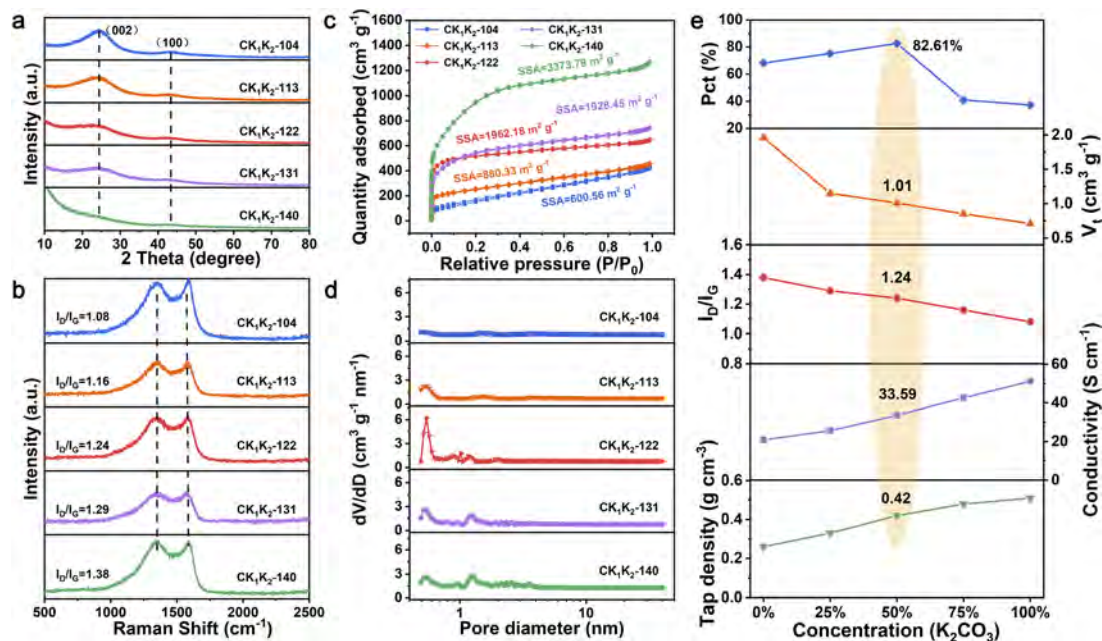


Fig. 4 (a) XRD patterns and (b) Raman spectra of  $\text{CK}_1\text{K}_2-1x(4-x)$  ( $x = 0, 1, 2, 3, 4$ ).  $\text{N}_2$  adsorption–desorption isotherms of (c)  $\text{CK}_1\text{K}_2-1x(4-x)$  ( $x = 0, 1, 2, 3, 4$ ). Pore size distribution of (d)  $\text{CK}_1\text{K}_2-1x(4-x)$  ( $x = 0, 1, 2, 3, 4$ ). (e) Summary of the structure parameters of  $\text{CK}_1\text{K}_2-1x(4-x)$  ( $x = 0, 1, 2, 3, 4$ ).

activation promoter to produce pore seeds for forming abundant pores, and the appropriate content of  $\text{K}_2\text{CO}_3$  acted as an activation pathway modifier to suppress the strong etching reaction of KOH and thus form more smaller micropores. A sufficiently large micropore ratio and an ultra-high specific surface area are beneficial for adsorbing more electrolyte ions, so we believe that regulating the pore formation processes of stage I and stage II is essential to achieve porous carbon exhibiting high performance capacitor storage. In summary, an optimized porous carbon possessing the highest microporosity ratio, moderate pore volume and tap density and combining reasonable defects and conductivity can be prepared by carefully adjusting the alkali activator ratio and pathway (Fig. 4e and S7†).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to characterize and analyze the micromorphology and graphite microcrystalline changes of the different samples. From Fig. S8,† it can be seen that the porous carbon gradually became fragmented with increasing KOH concentration;<sup>41</sup> the block size of  $\text{CK}_1\text{K}_2-122$  is intermediate. The TEM images are shown in Fig. S9.† Graphite microcrystallites are present in the  $\text{CK}_1\text{K}_2-104$  sample, which may result from the catalytic effect of potassium;  $\text{K}_2\text{CO}_3$  can be reduced into potassium vapor, and metal K can catalyze graphitization.<sup>42</sup> The  $\text{CK}_1\text{K}_2-140$  did not have an ordered structure due to the strong etching of KOH. The  $\text{CK}_1\text{K}_2-122$  also exhibited some microcrystallites, indicating that  $\text{K}_2\text{CO}_3$  inhibited the strong etching activation of KOH. The existence of microcrystallites is favorable for improving the conductivity.<sup>43–45</sup> The presence of the elements C, O and N was determined for  $\text{CK}_1\text{K}_2-122$  using energy dispersive spectroscopy (Fig. S10†). The uniform distribution of

the elements O and N indicated that there were a large number of nitrogenous oxygen-containing functional groups in the porous carbon. The distribution of surface functional groups is conducive to the improvement of capacitance.

### Electrochemical performance of porous carbon

The electrochemical performance of the  $\text{CK}_1\text{K}_2-1x(4-x)$  ( $x = 0, 2, 4$ ) was evaluated using a three-electrode system. The CV curves from  $-1$  to  $0$  V are illustrated in Fig. 5a. Compared with  $\text{CK}_1\text{K}_2-104$  and  $\text{CK}_1\text{K}_2-140$ ,  $\text{CK}_1\text{K}_2-122$  displayed the greatest integrated area and a quasi-rectangular shape at  $20$   $\text{mV s}^{-1}$ , indicating that it had the largest double-layer specific capacitance. The CV curves exhibited rectangle-like shapes at scan rates from  $5$  to  $100$   $\text{mV s}^{-1}$ , indicating excellent capacitive behavior and high reversibility (Fig. S11†). In addition, the GCD curve of  $\text{CK}_1\text{K}_2-122$  in Fig. S12† exhibits an approximately symmetrical triangle, demonstrating good coulombic efficiency and the absence of a significant voltage drop.<sup>46</sup>  $\text{CK}_1\text{K}_2-122$  has a specific capacitance of  $296.7$   $\text{F g}^{-1}$ , which is about 1.5 times higher than that of  $\text{CK}_1\text{K}_2-104$  ( $197.8$   $\text{F g}^{-1}$ ) and  $\text{CK}_1\text{K}_2-140$  ( $197.3$   $\text{F g}^{-1}$ ) (Fig. 5b and S13†). The reason for this is that  $\text{CK}_1\text{K}_2-122$  has the highest percentage of microporous pores, a high specific surface area, hierarchical pores, a reasonable pore size distribution, and good electrical conductivity. Electrochemical impedance tests were carried out, and the results are shown in Table S3.† The charge transfer resistance ( $R_{ct}$ ) and equivalent series resistance ( $R_s$ ) of  $\text{CK}_1\text{K}_2-122$  are slightly larger than those of  $\text{CK}_1\text{K}_2-104$  (Fig. S14†), because more graphite microcrystals were produced in  $\text{CK}_1\text{K}_2-104$  when  $\text{K}_2\text{CO}_3$  alone was used as the activator. The slope of  $\text{CK}_1\text{K}_2-122$  in the low-frequency region is almost parallel to the y-axis, which

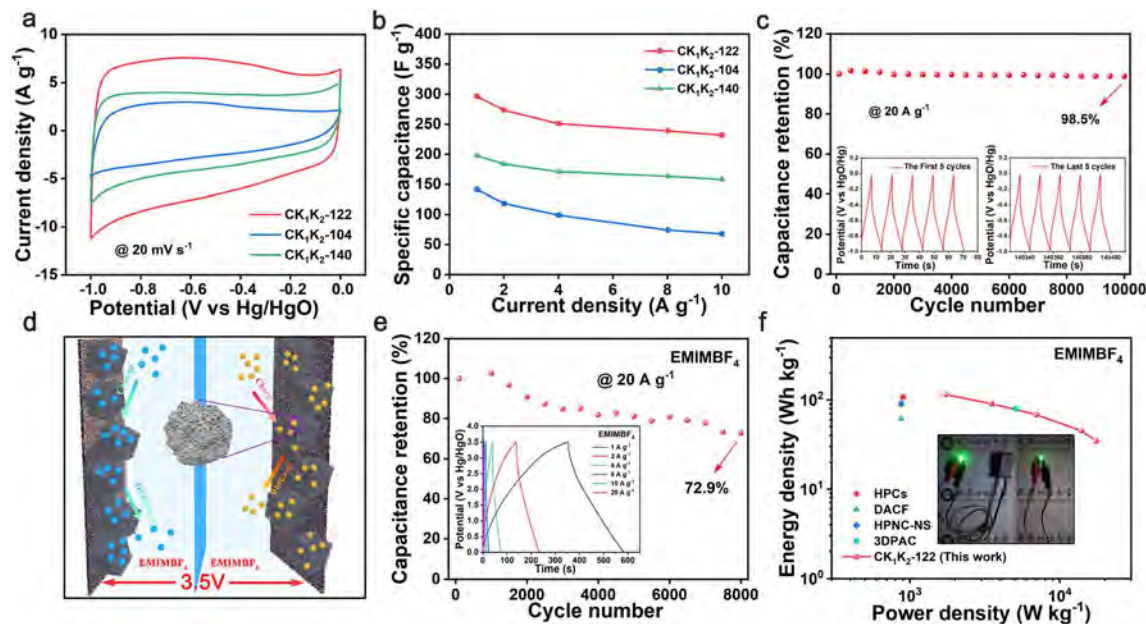


Fig. 5 Electrochemical properties: (a) CV curves of  $\text{CK}_1\text{K}_2-1x(4-x)$  ( $x = 0, 2, 4$ ) at  $20 \text{ mV s}^{-1}$ . (b) Specific capacitance at different current densities. (c) Cycling stability of  $\text{CK}_1\text{K}_2-122$  at  $20 \text{ A g}^{-1}$  (inset is GCD curves for first and last five cycles). Electrochemical performance of supercapacitor utilizing  $\text{EMIMBF}_4$  as the electrolyte: (d) schematic diagram of the supercapacitor. (e) Cycling stability at  $20 \text{ A g}^{-1}$  (inset is GCD curves for different current densities from  $1-20 \text{ A g}^{-1}$ ). (f) Ragone plots (inset is LED lights illuminated using supercapacitors as the power source).

represents optimal fast transport characteristics. The cycling stability was tested at  $20 \text{ A g}^{-1}$ , and the capacitance retention was 98.5% after 10 000 cycles (Fig. 5c). This was attributed to the uniquely high microporosity, which mitigated the structural damage caused by volume shrinkage during the charging and discharging process.<sup>47</sup> The  $b$  value of  $\text{CK}_1\text{K}_2-122$  was calculated to be 0.903 (Fig. S15<sup>†</sup>), revealing the capacitive-dominated characteristics, as a  $b$  value close to 1 indicates electrochemical behavior dominated by surface pseudocapacitance control.<sup>48</sup> As shown in Fig. S16,<sup>†</sup> the surface capacity control process accounts for 71%, 78%, 83%, 89% and 92% at 5, 10, 20, 50 and  $100 \text{ mV s}^{-1}$ , respectively.

To further assess the electrochemical performance of the petroleum coke porous carbon  $\text{CK}_1\text{K}_2-122$ , a symmetrical supercapacitor was assembled using  $\text{CK}_1\text{K}_2-122$  as the electrode and KOH as the electrolyte. Subsequent electrochemical tests were performed over a potential window of 0–1 V, as shown in Fig. S17.<sup>†</sup> The CV tests were conducted at scan rates from 10 to  $100 \text{ mV s}^{-1}$  (Fig. S18<sup>†</sup>) and showed rectangle-like shapes, and the GCD images showed symmetrical isosceles triangles; both these results indicated bilayer properties (Fig. S19<sup>†</sup>). The  $\text{CK}_1\text{K}_2-122$  SCs showed a specific capacitance of  $105.5 \text{ F g}^{-1}$ . After increasing the current 10 times, the capacity retention was 74%; the  $\text{CK}_1\text{K}_2-122$  SCs displayed an excellent rate performance, as shown in Fig. S20.<sup>†</sup> The EIS diagrams exhibited a pronounced semicircle and a straight line nearly parallel to the  $y$ -axis (Fig. S21<sup>†</sup>). The equivalent series resistance ( $R_s$ ) is  $1.04 \Omega$ , as displayed in Table S4,<sup>†</sup> which demonstrates the presence of a small charge transfer resistance and near-ideal capacitor behavior. It was determined that the supercapacitor achieved an energy density of  $14.7 \text{ W h kg}^{-1}$  at a power density of  $500 \text{ W kg}^{-1}$

when KOH is used as the electrolyte (Fig. S22<sup>†</sup>). The cycling stability of the aqueous supercapacitor was further evaluated at a current density of  $20 \text{ A g}^{-1}$ , and a capacitance retention of 86.3% was observed after 10 000 cycles (Fig. S23<sup>†</sup>).

To improve the practical applicability of the carbon materials, the organic system  $\text{EMIMBF}_4$  was used as the electrolyte to increase the voltage window to improve the energy density of supercapacitors. The model is depicted in Fig. 5d, and the GCD performance of the supercapacitor was evaluated using a potential window of 3.5 V. A capacitance retention of 72.9% was achieved after 8000 charge/discharge cycles at  $20 \text{ A g}^{-1}$  (Fig. 5e). The Ragone plot of the device clearly shows that the energy density reaches a maximum of  $114.4 \text{ W h kg}^{-1}$  at  $1749 \text{ W kg}^{-1}$  and  $34.5 \text{ W h kg}^{-1}$  at  $17.5 \text{ kW kg}^{-1}$  (Fig. 5f). To verify its performance in practical applications, it was used to power an LED light, which remained lit for 13 min until it was extinguished (inset and S24<sup>†</sup>). The energy density and power density compare favourably with those of other carbon-based materials (see Table S5<sup>†</sup> for details), such as HPCs ( $900 \text{ W kg}^{-1}$ ,  $107 \text{ W h kg}^{-1}$ ),<sup>49</sup> N, S-C ( $50 \text{ W kg}^{-1}$ ,  $9.75 \text{ W h kg}^{-1}$ ),<sup>50</sup> HPNC-NS ( $875 \text{ W kg}^{-1}$ ,  $102 \text{ W h kg}^{-1}$ ),<sup>51</sup> and 3DPAC ( $5100 \text{ W kg}^{-1}$ ,  $79.4 \text{ W h kg}^{-1}$ ),<sup>52</sup> among others. This high energy density and cycling stability demonstrate the potential of petroleum coke porous carbon materials in energy storage devices.

## Conclusions

Various porous carbons were prepared using commercial petroleum coke as a carbon precursor and KOH,  $\text{K}_2\text{CO}_3$ , or mixtures of KOH and  $\text{K}_2\text{CO}_3$  as an alkaline activator. Small molecules were monitored using *in situ* TG-MS to propose

possible activation processes. The internal chemical reaction and pathway were further understood using DFT calculations and molecular simulations of the activation process. The strong alkali KOH acts as an activation initiator; it first decomposes into  $K_2O$  to attack C–C bonds to form a large number of pore seeds. This is important for preparing porous carbon with a large number of pores and high specific surface area. The weak alkali  $K_2CO_3$  acts as a modifier of the activation pathway;  $CO_3^{2-}$  reacts with the carbon atom of the pore seeds more preferentially than  $K_2O$  owing to the lower reaction energy barrier. This can suppress the strong etching reaction between  $K_2O$  and the pore seeds to form porous carbon with high microporosity. By optimizing the ratio of strong and weak alkalis, the porous carbon  $CK_1K_2-122$  was obtained; it exhibited an ultra-high microporosity of 82.61%, a high specific surface area of  $1962.18 \text{ m}^2 \text{ g}^{-1}$  and a hierarchical pore structure. It also showed a high specific capacitance of  $296.7 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$  and retained 98.5% of the initial capacity after 10 000 cycles. The symmetric supercapacitor displayed an energy density of  $114.4 \text{ W h kg}^{-1}$  at a power density of  $1749 \text{ W kg}^{-1}$ . After 8000 cycles at a current density of  $20 \text{ A g}^{-1}$ , the capacity retention was 72.9%. This work offers a new perspective on the rational design of porous carbon materials for energy storage.

## Experimental section

### Materials and reagents

Potassium carbonate ( $K_2CO_3$ , AR,  $\geq 99.0\%$ ), potassium hydroxide (KOH, AR,  $\geq 99.0\%$ ), concentrated hydrochloric acid (HCl, 37%), ethyl alcohol ( $CH_3CH_2OH$ , AR,  $\geq 99.7\%$ ), and 1-ethyl-3-methylimidazolium tetrafluoroborate ( $C_6H_{11}BF_4N_2$ , EMIMBF<sub>4</sub>) were bought from Aladdin Industrial Inc., Shanghai, China. All the chemicals were analytical reagents and were utilized directly without further purification. Petroleum coke was purchased from Shandong Lianhua New Material Co. The distilled water (DI) was prepared in the laboratory.

### Synthesis of porous carbon $CK_1K_2-1x(4-x)$ ( $x = 0, 1, 2, 3, 4$ )

The petroleum coke was pretreated before the experiment. It was broken up using a pulverizer, ball-milled (400 rpm, 2 h) and sieved (70 °C, 12 h) for the next step. The petroleum coke powder was ground and mixed with KOH and  $K_2CO_3$  in a mass ratio of 1 : 2 : 2. The mixed samples were activated in a tube furnace under an  $N_2$  atmosphere with a rate of  $100 \text{ mL min}^{-1}$  at 700 °C for 5 h. After cooling to room temperature, the sample was washed with 1 M HCl at 80 °C for 5 h to remove excess  $K_2CO_3$  and KOH. It was then ultrasonically rinsed to neutrality with deionized water, filtered and freeze-dried for 12 h. The resulting material was labeled as  $CK_1K_2-122$ . The C stands for petroleum coke, and  $K_1$  and  $K_2$  stand for KOH and  $K_2CO_3$ . For comparison, other mass ratios of petroleum coke, KOH and  $K_2CO_3$  (1 : 0 : 4, 1 : 1 : 3, 1 : 3 : 1 and 1 : 4 : 0) were used, and the resulting samples were labeled as  $CK_1K_2-104$ ,  $CK_1K_2-113$ ,  $CK_1K_2-131$  and  $CK_1K_2-140$ , respectively. The different temperatures used to prepare  $CK_1K_2-122$  were 600 °C, 650 °C, 700 °C, 750 °C and 800 °C, and the samples were demoted as  $CK_1K_2-$

600,  $CK_1K_2-650$ ,  $CK_1K_2-700$ ,  $CK_1K_2-750$  and  $CK_1K_2-800$ , respectively.

### Materials characterization

To study the crystal structure and composition of the materials, their X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer instrument from 5°–90° at a scanning rate of 5 s per step. The X-ray photoelectron spectrum (XPS) was obtained using an X-ray photoelectron spectrometer (XPS, Escalab 210 system, Germany) to analyze the elemental composition of the samples. Scanning electron microscopy (SEM; Carl Zeiss-Ultra Plus, Germany) and transmission electron microscopy (TEM; FEI Tecnai G<sup>2</sup>F20, USA) were performed to investigate the morphological characteristics and the nanostructure of the materials. The Brunauer–Emmett–Teller (BET) specific surface areas and pore size distribution of the material were determined using  $N_2$  adsorption–desorption (Micromeritics ASAP 2020, USA). Thermogravimetric-mass analysis was performed using a Rigaku Thermo Mass Photo (TG-MS) with a skimmer type mass spectrometer (MS/EI). The measurements were conducted in the range 30–700 °C at  $5 \text{ °C min}^{-1}$ . In addition, this measurement was carried out at 700 °C for 1 h. The whole experiment was carried out under an argon gas atmosphere.

### Computational details

All calculations were carried out based on density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP) with exchange–correlation functional of the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) method. A grid of  $1 \times 1 \times 1$  Monkhorst–Pack  $k$ -points was used for the structural relaxation. A vacuum layer of 15 Å was adopted in the direction perpendicular to the monolayer surface to avoid interactions between periodic slabs. The energy cutoff was set to 450 eV. The free energy changes were calculated according to the following equation:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$$

where  $\Delta E$ ,  $\Delta E_{ZPE}$ , and  $\Delta S$  are the differences in the total energy, zero point energy, and entropy between the product and reactants, respectively. Here, we considered only the ground states of species at a temperature of 0 K. Thus, the contribution from the entropy term is zero.

### Electrochemical measurements

The electrochemical properties of the material, including cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) were all tested using an electrochemical workstation (CHI760E, Chenhua, Shanghai, China) with a three-electrode system composed of the active materials as the working electrode, a saturated calomel electrode as the reference electrode, and  $1 \times 1 \text{ cm}^2$  Pt as the counter electrode in 6 M KOH electrolyte. The cycle stability evaluation was performed using a LAND CT2001A device from Wuhan, China. The  $CK_1K_2-122$  electrode was obtained by mixing the active material, acetylene black and PTFE (6 wt%) in

a mass ratio of 8 : 1 : 1 until a homogenous slurry was formed. The slurry was made into carbon flakes of about 1.5 mg and dried. The carbon flakes were coated onto nickel foam (1 cm × 1 cm) and pressed at 10–20 MPa to form a thin slice. Then, the performance of the three-electrode system was tested using a CHI760E instrument.

## Data availability

All data have been provided in the main text and ESI.† We do not have additional data to provide.

## Author contributions

Yonghui Zhang, Xin Xu and Qingxuan Geng: conceptualization, methodology, formal analysis, writing – original draft. Qingwei Li: conceptualization, writing – review & editing. Xiuli Li: methodology. Yixuan Wang: validation, visualization. Zihuan Tang: validation, visualization. Biao Gao: conceptualization, supervision. Xuming Zhang: conceptualization, supervision. Paul K. Chu: conceptualization, administration. Kaifu Huo: conceptualization, writing – review & editing, supervision, project administration.

## Conflicts of interest

The authors declare no competing financial interest.

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