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We report here the synergistic effect of graphene and diglyme electrolyte in significantly improving the sodium insertion electrochemistry of nanocrystalline anatase  $\text{TiO}_2$ .

Since its commercialization in the early 1990s, lithium ion battery technology has found widespread use in portable electronics and nowadays also in stationary energy storage applications.<sup>1</sup> Despite a continuous improvement in performance, the technology more and more approaches its limits and therefore a range of alternative concepts is currently being studied.<sup>2</sup> It is obvious that different battery types may be used for different applications, depending on whether high energy, high power or low cost are the major target, for example. Moreover, the limited abundance of lithium and other elements such as cobalt might at some later point of massive use become critical to achieve low cost batteries.<sup>3</sup> These considerations continuously trigger impetus for new research in alternative affordable electrochemical energy storage and generation technologies.<sup>4</sup>

Sodium-based batteries, therefore, are gaining renewed interest currently as possible alternative or complement to lithium-based batteries.<sup>3</sup> While the research activities on sodium-ion batteries predicated to 1970's, both sodium-air and room-temperature sodium-sulfur batteries are the latest additions – following the path in research on lithium-based batteries.<sup>5</sup> It is also noted that successful commercialization of sodium-sulfur and sodium-nickel chloride batteries shows confidence on the tremendous

## Graphene mediated improved sodium storage in nanocrystalline anatase $\text{TiO}_2$ for sodium ion batteries with ether electrolyte†

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potential for not much explored rechargeable sodium-ion/air batteries.<sup>3c,5c</sup>

The search for suitable high energy density electrode materials and electrolytes for sodium-ion batteries is at an unprecedented acceleration across the globe.<sup>3,6</sup> Different research groups successfully proposed several cathode materials for sodium-ion batteries which can be well considered as analogues of lithium-ion battery cathodes, even if there are interesting differences.<sup>3,6</sup> However, the success on the anode side is yet comparably limited.<sup>6a</sup> For example, graphite, the commercially most successful anode in lithium-ion batteries, fails to intercalate  $\text{Na}^+$  ions under normal operation. It is rather shown that  $\text{Na}^+$  ions can be intercalated in graphite by co-intercalation phenomena in an ether based electrolyte with capacities in the range of  $90\text{--}100 \text{ mA g}^{-1}$  at a current rate of  $0.1\text{C}$ .<sup>7</sup> Alternatively to carbonaceous materials, few alloys and metal oxides are explored for sodium-ion batteries.<sup>3,6a</sup> One major concern with most of these materials is their mechanical stability which is affected by drastic volume changes during sodiation/desodiation.

Titanium dioxide ( $\text{TiO}_2$ ), of late, is also found to be a promising example of anodes for sodium-ion batteries. Several advantages such as ease in processing, negligible strain, chemical stability, environmentally benign and cost effectiveness attract  $\text{TiO}_2$  for extensive investigation in sodium cells since two years.<sup>8</sup> It is reported that  $\text{TiO}_2$  electrochemically stores sodium at potentials below  $1 \text{ V vs. Na}^+/\text{Na}$ ; which is an important requirement for anodes.<sup>8a</sup> Additionally, exceptionally high cycling stability ( $>4000$  cycles) is shown by graphene coupled  $\text{TiO}_2$ .<sup>8b</sup> However, it is noticed that the initial Coulombic efficiency is relatively low in most cases (ESI,† Table S1). For example, the initial Coulombic efficiency is only approximately 30% and 39% at  $50 \text{ mA g}^{-1}$  and  $500 \text{ mA g}^{-1}$  current respectively for the graphene coupled  $\text{TiO}_2$ .<sup>8b</sup> It is also noteworthy to mention here that the sodium reactivity in  $\text{TiO}_2$  is quite dissimilar to lithium reactivity.<sup>8</sup> Apparently, many unknown subtle parameters ranging from electrolyte composition to  $\text{TiO}_2$  structures are yet to be explored to wring out the inherent strengths of  $\text{TiO}_2$ . In this communication, we report the synthesis of a nanocrystalline anatase  $\text{TiO}_2$ -graphene

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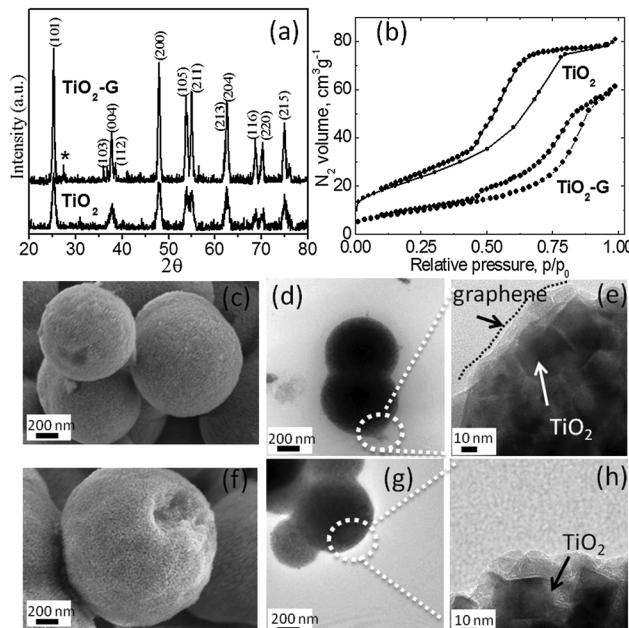


Fig. 1 (a) XRD patterns (impurity rutile phase is represented by \*), (b)  $N_2$  adsorption/desorption isotherms, SEM micrographs of (c)  $\text{TiO}_2$ -G and (f)  $\text{TiO}_2$ , TEM micrographs of (d and e)  $\text{TiO}_2$ -G and (g and h)  $\text{TiO}_2$ .

composite, and its sodium insertion electrochemistry is investigated utilizing ether and carbonate electrolytes. It is highlighted that graphene and diglyme electrolyte synergistically improve the sodium storage capacities of anatase  $\text{TiO}_2$ . Pristine  $\text{TiO}_2$  and graphene- $\text{TiO}_2$  composite are designated as  $\text{TiO}_2$  and  $\text{TiO}_2$ -G, respectively.

The materials were synthesized by a solvothermal method (details are given in the ESI†). Fig. 1a shows the X-ray diffraction (XRD) patterns of  $\text{TiO}_2$  and  $\text{TiO}_2$ -G. Both patterns can be indexed to the anatase phase with lattice parameters  $a = b = 3.7852 \text{ \AA}$ ,  $c = 9.5139 \text{ \AA}$  and space group:  $I4_1/\text{amd}$  (141) (JCPDS No. 21-1272). The crystallite size is estimated using the Scherrer equation. From the full width at half maximum (FWHM) at the (101) peak ( $\theta = 25.50^\circ$ ), the crystallite size is determined to be approximately 11 nm for  $\text{TiO}_2$  and 20 nm for  $\text{TiO}_2$ -G. The XRD pattern of  $\text{TiO}_2$ -G rules out any  $\text{TiC}$  phase. Generally, a very high temperature (greater than the annealing temperature used here) is required to form  $\text{Ti-C}$  bond.<sup>9a</sup> Therefore, graphene and  $\text{TiO}_2$  in  $\text{TiO}_2$ -G is physically mixed to form three dimensional mixed conducting networks.<sup>9b</sup> Both the materials possess spherical morphology as characterized by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). It is shown in Fig. 1(c)–(h). The spherical morphology obtained by carbohydrate mediated hydrothermal synthesis is a well-established phenomenon.<sup>9c, d</sup> Typical dimension of the  $\text{TiO}_2$  spheres are in the range of 1–2  $\mu\text{m}$ . The high resolution TEM imaging of the edge of  $\text{TiO}_2$ -G spheres shows the presence of a very thin layer of graphene covering the  $\text{TiO}_2$  nanocrystals as shown in Fig. 1e. The TEM image of pristine graphene is shown in ESI,† Fig. S1. The presence of graphene is also reflected from the Raman spectra (ESI,† Fig. S2). The typical D and G band

of graphene can be observed for  $\text{TiO}_2$ -G. Thermogravimetric analysis confirms the presence of 2.28 wt% of graphene in  $\text{TiO}_2$ -G (ESI,† Fig. S3). It is also well supported by elemental analysis confirming 2.52 wt% of carbon.  $N_2$  adsorption/desorption isotherms verify that the materials are mesoporous (Fig. 1b). The BET surface areas of  $\text{TiO}_2$  and  $\text{TiO}_2$ -G are  $80 \text{ m}^2 \text{ g}^{-1}$  and  $35 \text{ m}^2 \text{ g}^{-1}$ , respectively. The pore diameter is in the range of 2–10 nm (ESI,† Fig. S4).

The sodium storage performance of  $\text{TiO}_2$  and  $\text{TiO}_2$ -G was evaluated in cells with a sodium metal anode (ESI† for details). The electrolyte compositions were  $\text{NaPF}_6$  (0.5 M) in diglyme and  $\text{NaClO}_4$  (0.5 M) in a 1:1 w/w mixture of ethylene carbonate and dimethyl carbonate (EC/DMC). The choice of different salts in the electrolytes is based on the reported literature.<sup>8c,10</sup> It is demonstrated clearly that  $\text{NaClO}_4$  and  $\text{NaPF}_6$  are preferred conducting salts in carbonates and diglyme solvents respectively.<sup>8c,10a</sup> Physico-chemical properties of the solvents are reported elsewhere.<sup>10</sup>

Fig. 2a shows the galvanostatic charge/discharge profiles obtained from pristine  $\text{TiO}_2$  with diglyme electrolyte at a constant current density of  $33.5 \text{ mA g}^{-1}$  in the voltage range of 0.05–2.5 V. Pristine  $\text{TiO}_2$  spheres deliver a discharge capacity of  $96 \text{ mA h g}^{-1}$  in the 1st discharge cycle with an initial Coulombic efficiency of 49%. A potential plateau at much lower voltage ( $< 0.3 \text{ V}$ ) is observed in the 1st discharge curve. It is noted that the charge/discharge potential profile characteristics are identical to the reported data for anatase  $\text{TiO}_2$ .<sup>8</sup> The capacity retention of  $\text{TiO}_2$  is extremely poor showing a negligible discharge capacity of  $18 \text{ mA h g}^{-1}$  at 50th cycle (Fig. 2b).

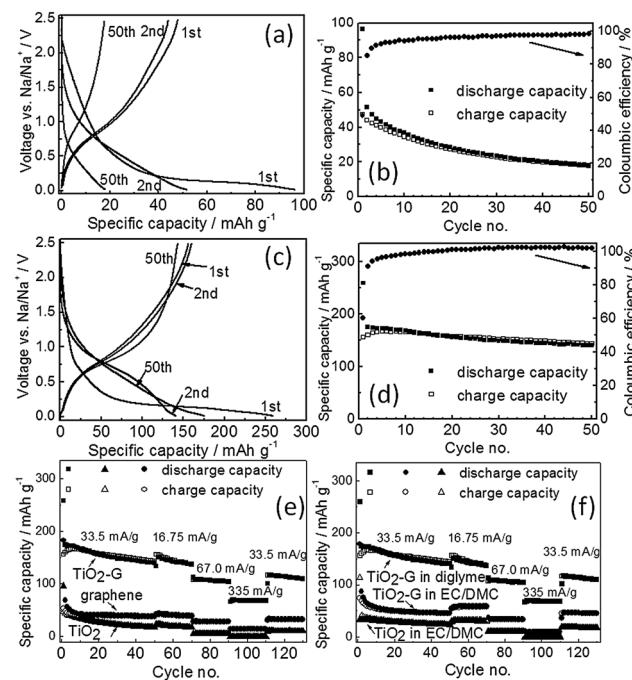


Fig. 2 Galvanostatic charge/discharge curves of (a)  $\text{TiO}_2$  and (c)  $\text{TiO}_2$ -G at a current density of  $33.5 \text{ mA g}^{-1}$  at  $25^\circ\text{C}$  in diglyme electrolyte; respective variation of capacities and Coulombic efficiencies with cycle number for (b)  $\text{TiO}_2$  and (d)  $\text{TiO}_2$ -G; variation of capacities with cycle number at different current rates for  $\text{TiO}_2$ ,  $\text{TiO}_2$ -G and graphene in diglyme electrolyte (e), and  $\text{TiO}_2$ ,  $\text{TiO}_2$ -G in carbonate electrolyte (f).

The graphene– $\text{TiO}_2$  composite exhibits significantly improved capacity (Fig. 2c and d) with diglyme electrolyte although the charge/discharge potential profiles are similar to pristine  $\text{TiO}_2$ . It indicates that addition of graphene does not change the fundamental sodium insertion electrochemistry of anatase  $\text{TiO}_2$ . A high discharge capacity of  $260 \text{ mA h g}^{-1}$  is obtained in the 1st discharge cycle with a high initial Coulombic efficiency of 60% for  $\text{TiO}_2$ –G at a current density of  $33.5 \text{ mA g}^{-1}$ . Moreover, stable galvanostatic cycling is also be observed (Fig. 2d). It shows a discharge capacity of  $143 \text{ mA h g}^{-1}$  in the 50th cycle. For comparison, the individual contribution from graphene is also separately evaluated with diglyme electrolyte. Pristine graphene delivers in the 1st discharge cycle a capacity of  $183 \text{ mA h g}^{-1}$  with an initial Coulombic efficiency of 29% and stores  $40 \text{ mA h g}^{-1}$  in the 50th cycle with  $33.5 \text{ mA g}^{-1}$  (ESI,† Fig. S5). Since the graphene concentration in  $\text{TiO}_2$ –G is below 3 wt%, therefore, its contribution to the overall capacity of  $\text{TiO}_2$ –G is negligible (below  $5 \text{ mA h g}^{-1}$ ). The rate performance also shows that  $\text{TiO}_2$ –G sustains higher current rates unlike pristine  $\text{TiO}_2$  and graphene (Fig. 2e). It convincingly demonstrates the beneficial influence of graphene in eight fold enhancement (at 50th cycle,  $33.5 \text{ mA g}^{-1}$  current) of the sodium storage capacities of graphene– $\text{TiO}_2$ . A comparison of initial Coulombic efficiencies of reported  $\text{TiO}_2$  is given in ESI,† Table S1.

The electrochemical performance of  $\text{TiO}_2$  and  $\text{TiO}_2$ –G is also evaluated with carbonate (EC/DMC) electrolyte under otherwise identical conditions. All materials show inferior performance in carbonates compared to diglyme. Pristine  $\text{TiO}_2$  delivers a capacity of  $113 \text{ mA h g}^{-1}$  in the 1st discharge cycle with a Coulombic efficiency of 29% with carbonates (ESI,† Fig. S6). Similarly, a 1st discharge cycle capacity of  $192 \text{ mA h g}^{-1}$  with a Coulombic efficiency of only 18% is shown by pristine graphene (ESI,† Fig. S7). In terms of Coulombic efficiency,  $\text{TiO}_2$  and graphene shows relatively poor performance in carbonates unlike in diglyme. On the other hand, it was expected that  $\text{TiO}_2$ –G will show improvement in capacities compared to pristine  $\text{TiO}_2$  and graphene in carbonates. Surprisingly, no significant improvement is observed. The 1st discharge cycle capacity and Coulombic efficiency are  $177 \text{ mA h g}^{-1}$  and 41% respectively for  $\text{TiO}_2$ –G (ESI,† Fig. S8). Moreover, it can retain only  $45 \text{ mA h g}^{-1}$  of capacity at 50th cycle. It profoundly indicates that graphene is playing a negligible role in the sodium storage capacity of  $\text{TiO}_2$  in carbonate electrolytes unlike in diglyme.

The synergistic effect of graphene and diglyme in improving the cycling stability of  $\text{TiO}_2$  is also clearly evidenced by cyclic voltammetry (CV). Fig. 3(a) and (b) shows the CV profiles obtained from  $\text{TiO}_2$ –G and  $\text{TiO}_2$  in diglyme electrolyte at a scan rate of  $0.05 \text{ mV s}^{-1}$  at  $25^\circ\text{C}$ . Distinct differences can be observed in both cases (see also ESI,† Fig. S9). A pair of cathodic and anodic redox peaks (depicted from 2nd cycle) at  $0.72 \text{ V}$  and  $0.79 \text{ V}$  respectively is detected for  $\text{TiO}_2$ –G in diglyme (Fig. 3a), while these respective peaks are seen at  $0.51 \text{ V}$  and  $0.83 \text{ V}$  for pristine  $\text{TiO}_2$  (Fig. 3b). Typically, these peaks are located in the range of  $0.5$ – $0.9 \text{ V}$  as according to previous reports.<sup>8</sup> Again,  $\text{TiO}_2$ –G shows prominent electrochemical activity at higher scan rates (Fig. 3c), whereas pristine anatase is totally inactive (Fig. 3d). It is interesting to note that the redox peak separation is almost three times smaller in  $\text{TiO}_2$ –G than  $\text{TiO}_2$  at high scan rates (Fig. 3g). The smaller polarization in  $\text{TiO}_2$ –G ( $0.07 \text{ V}$  at  $0.05 \text{ mV s}^{-1}$

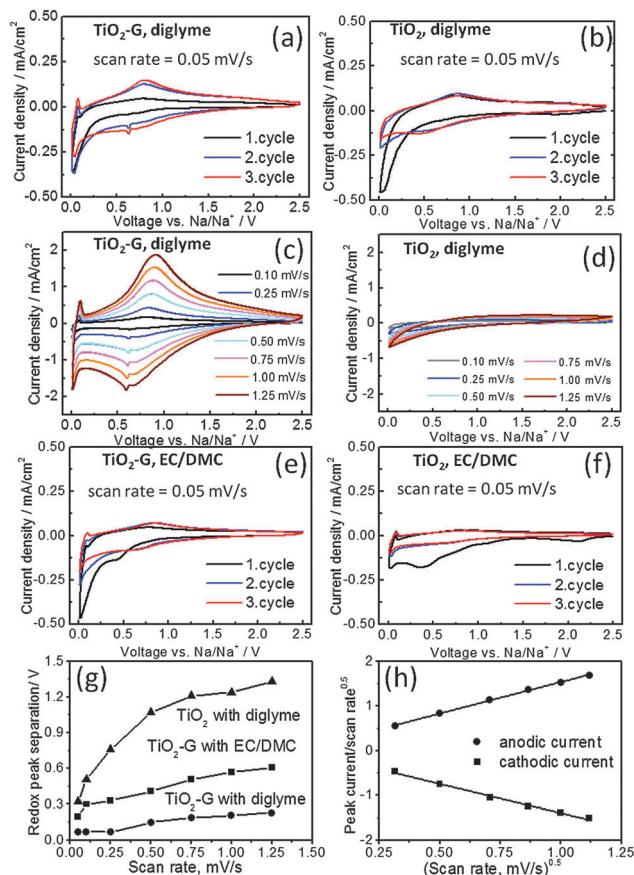


Fig. 3 Cyclic voltammetry curves of (a and c)  $\text{TiO}_2$ –G and (b and d)  $\text{TiO}_2$  in diglyme electrolyte; (e)  $\text{TiO}_2$ –G and (f)  $\text{TiO}_2$  in carbonate electrolyte; (g) respective variation of redox peak separation with scan rate; (h) variation of redox peak currents versus scan rates according to equation  $I = k_1\gamma + k_2\gamma^{0.5}$  for  $\text{TiO}_2$ –G (see text for detail).

and  $0.2 \text{ V}$  at  $1.25 \text{ mV s}^{-1}$ ) compared to  $\text{TiO}_2$  ( $0.32 \text{ V}$  at  $0.05 \text{ mV s}^{-1}$  and  $>0.5 \text{ V}$  at  $1.25 \text{ mV s}^{-1}$ ) and stability at higher scan rates both strongly suggests that graphene significantly facilitates  $\text{Na}^+$  insertion kinetics in  $\text{TiO}_2$ . An additional cathodic peak at  $0.63 \text{ V}$  is also observed for  $\text{TiO}_2$ –G (Fig. 3a). CV profile of graphene in diglyme prominently shows a cathodic peak at  $0.52 \text{ V}$  and anodic peak at  $0.83 \text{ V}$  (ESI,† Fig. S10a). Therefore, the additional peak is attributed to the  $\text{Na}^+$  insertion in graphene/carbon black. The anodic peak is expected to be overlapping with the anodic  $\text{TiO}_2$  peak. The CV results are further corroborated by the differential capacity plots obtained from the galvanostatic cycling experiments. For example, the anodic and cathodic peaks are prominently seen and they are perfectly overlapping in the voltage range of  $0.6$ – $1 \text{ V}$  in  $\text{TiO}_2$ –G (ESI,† Fig. S11a). However, these peaks are weakly observed in  $\text{TiO}_2$  (ESI,† Fig. S11b). The cathodic and anodic peaks at  $0.57 \text{ V}$  and  $0.8 \text{ V}$  respectively can also be observed for graphene (ESI,† Fig. S11c).

On the other hand, negligible electrochemical activity is observed in carbonate electrolyte for pristine  $\text{TiO}_2$  (Fig. 3f) and graphene (ESI,† Fig. S10b), while a certain level of activity (cathodic peak at  $0.66 \text{ V}$  and anodic peak at  $0.85 \text{ V}$ ) is seen in  $\text{TiO}_2$ –G (Fig. 3e). A broad peak around  $0.4 \text{ V}$  is also observed in 1st cathodic sweep for both  $\text{TiO}_2$  and  $\text{TiO}_2$ –G unlike seen



in diglyme. *Ex situ* SEM images (ESI,† Fig. S12) obtained from the discharge products of  $\text{TiO}_2\text{-G}$  in diglyme and carbonate electrolytes show that a thick polymeric layer is spread over the microspheres in carbonates while the original spherical structure is retained in diglyme. This layer is probably due to the decomposition of carbonates (8a, c). Interestingly,  $\text{TiO}_2\text{-G}$  can also sustain high scan rates in carbonates, although the polarization is higher than in the case of diglyme (Fig. 3g and ESI,† Fig. S13). The polarization in carbonates is almost six times higher than diglyme in  $\text{TiO}_2\text{-G}$ . Interestingly, a contrast in electrochemical activity of graphene in diglyme and carbonates can also be figured out (ESI,† Fig. S10 and S14). While certain redox peaks are prominently observed in diglyme, these are totally absent in carbonates. This effect might be simply due to the co-intercalation phenomena which has been demonstrated in the case of graphite.<sup>7</sup> It suggests that the beneficial effects of graphene are dependent on the nature of electrolytes. It is also noteworthy to mention here that despite having a lower surface area and larger crystallite size of  $\text{TiO}_2\text{-G}$  ( $35 \text{ m}^2 \text{ g}^{-1}$ , 20 nm) than  $\text{TiO}_2$  ( $80 \text{ m}^2 \text{ g}^{-1}$ , 11 nm),  $\text{TiO}_2\text{-G}$  shows better electrochemical stability and sodium storage capacities.<sup>11</sup> The coating of  $\text{TiO}_2$  by graphene might also reduce side reactions and hence will benefit higher coulombic efficiency values. Therefore, considering all these observations, it can be concluded that graphene synergistically couples with diglyme to significantly improve the sodium insertion electrochemistry of  $\text{TiO}_2$ .

To better understand the sodium storage behavior in  $\text{TiO}_2\text{-G}$ , the functional dependence of current response ( $I$ ) at peak potentials (obtained from Fig. 3c) is plotted against scan rates ( $\gamma$ ) according to the following equation:  $I = k_1\gamma + k_2\gamma^{0.5}$ ,  $k_1$  and  $k_2$  are constants (see Fig. 3h). It combines two separate mechanisms of ion storage, namely surface capacitive effects and diffusion-controlled insertion processes.<sup>12</sup> A straight line is observed as shown in Fig. 3h. This indicates that  $\text{Na}^+$  is stored in  $\text{TiO}_2\text{-G}$  both by capacitive and diffusion controlled processes. Additionally, the current response is also plotted against scan rates as per equation  $I = a\gamma^b$  (Fig. S15, ESI†).<sup>8b,10</sup> The obtained  $b$ -value of 0.968 and 0.945 for cathodic and anodic peaks respectively suggests that the kinetics is dominated by capacitive process than diffusion controlled process. Further studies are required to clearly understand the storage phenomenon.<sup>13</sup>

In summary, graphene mediated improvement in sodium storage capacities and cycling stability of anatase  $\text{TiO}_2$  is convincingly demonstrated in diglyme electrolyte. A high initial Coulombic efficiency of 60% is obtained in graphene– $\text{TiO}_2$  composite. Moreover, it is seen that graphene strongly reduces the polarization. The present work suggests that synergy of conductive additives and electrolyte plays pivotal role in improving the performance of sodium-ion batteries.

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