Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Rethinking Sodium-Ion Anodes as Nucleation Layers for Anode-Free Batteries

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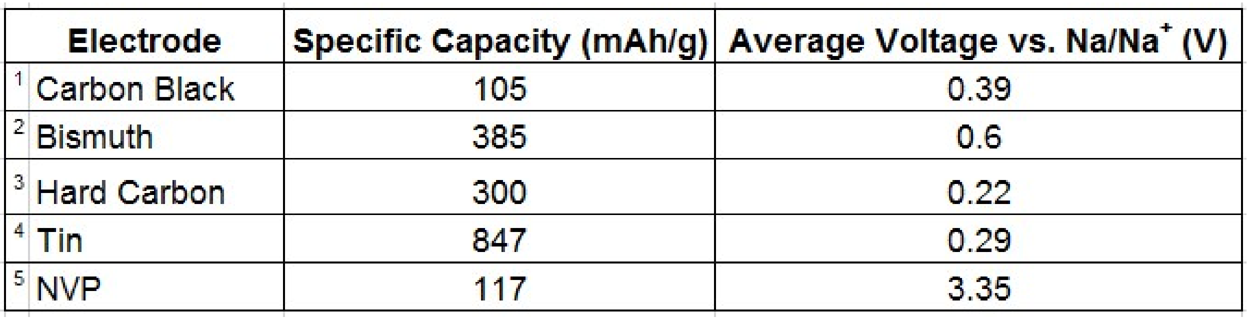
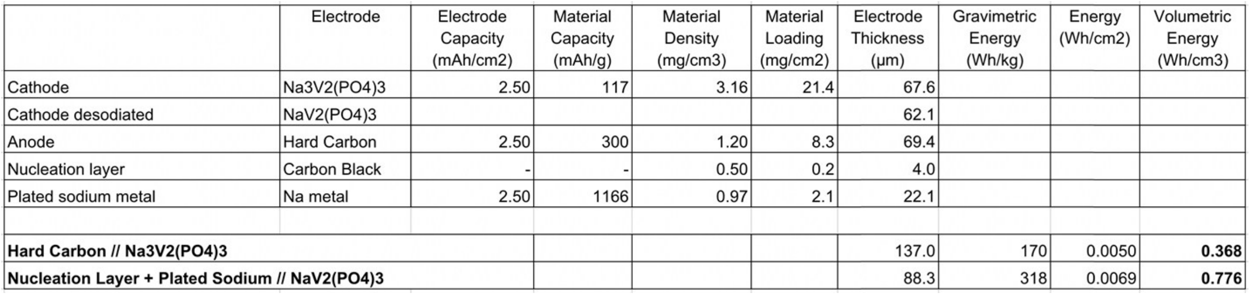
Table 1. Specific capacity and average voltage values used to calculate full-cell energy densities



Electrode	Specific Capacity (mAh/g)	Average Voltage vs. Na/Na$^+$ (V)
[1] Carbon Black	105	0.39
[2] Bismuth	385	0.6
[3] Hard Carbon	300	0.22
[4] Tin	847	0.29
[5] NVP	117	3.35

1. Carbon black specific capacity and average extraction voltage were determined from half cell testing at 0.1 A/g, as shown in Figure 2a.
2. Bismuth specific capacity was calculated with respect to the final alloy Na$_3$B. The average extraction voltage were determined from half cell testing at 0.1 A/g, as shown in Figure 3a.
3. Hard carbon specific capacity and average extraction voltage were determined from half cell testing at 0.1 A/g, as shown in Figure 2b.
4. Tin specific capacity was calculated with respect to the final alloy Na$_{15}$Sn$_4$. The average extraction voltage were determined from half cell testing at 0.1 A/g , as shown in Figure 3b.
5. NVP specific capacity was calculated with respect to the removal of two Na ions from Na$_3$V$_2$(PO$_4$)$_3$. The average insertion voltage were determined from half cell testing at 0.04 A/g.

Table 2. Volumetric energy density calculations for a cell with a loading of 2.5 mAh/cm^2



	Electrode	Electrode Capacity (mAh/cm2)	Material Capacity (mAh/g)	Material Density (mg/cm3)	Material Loading (mg/cm2)	Electrode Thickness (µm)	Gravimetric Energy (Wh/kg)	Energy (Wh/cm2)	Volumetric Energy (Wh/cm3)
Cathode	Na3V2(PO4)3	2.50	117	3.16	21.4	67.6			
Cathode desodiated	NaV2(PO4)3					62.1			
Anode	Hard Carbon	2.50	300	1.20	8.3	69.4			
Nucleation layer	Carbon Black	-	-	0.50	0.2	4.0			
Plated sodium metal	Na metal	2.50	1166	0.97	2.1	22.1			
Hard Carbon // Na3V2(PO4)3						137.0	170	0.0050	**0.368**
Nucleation Layer + Plated Sodium // NaV2(PO4)3						88.3	318	0.0069	**0.776**

For simplicity, only the active materials are considered. Current collectors, binders, separators, packaging, and electrode porosity are not considered. The hard carbon//NVP gravimetric energy density is taken from Ref. 20 and the hard carbon density is taken from Ref. 4.

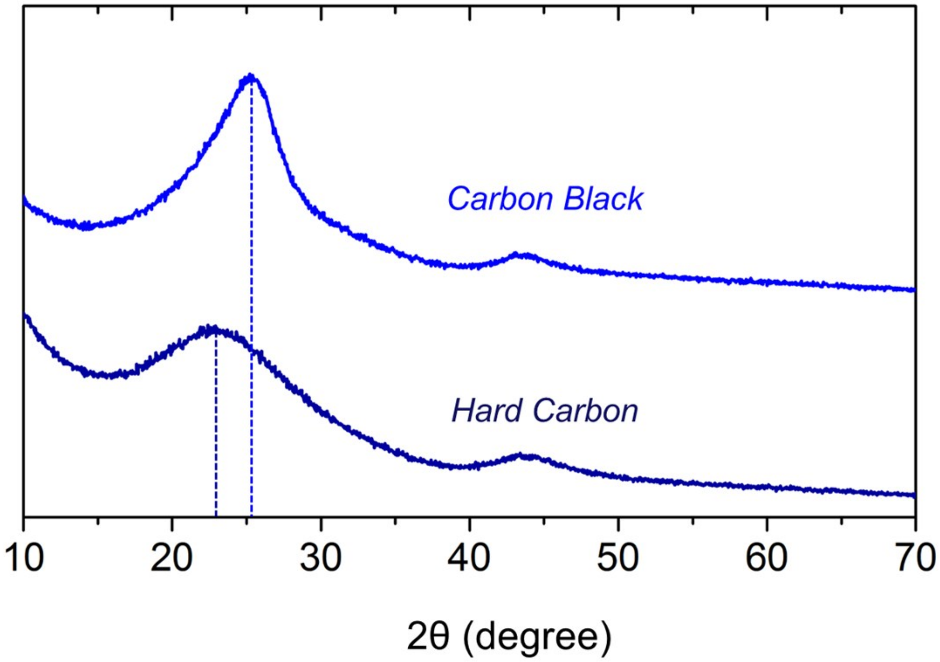


Figure S1. X-ray diffraction patterns for carbon black (TIMCAL Super C45) and synthesized hard carbon. The lower angle 002 peak (highlighted with the dashed line) observed for hard carbon indicates a larger interlayer spacing between graphene sheets in the hard carbon than the carbon black.

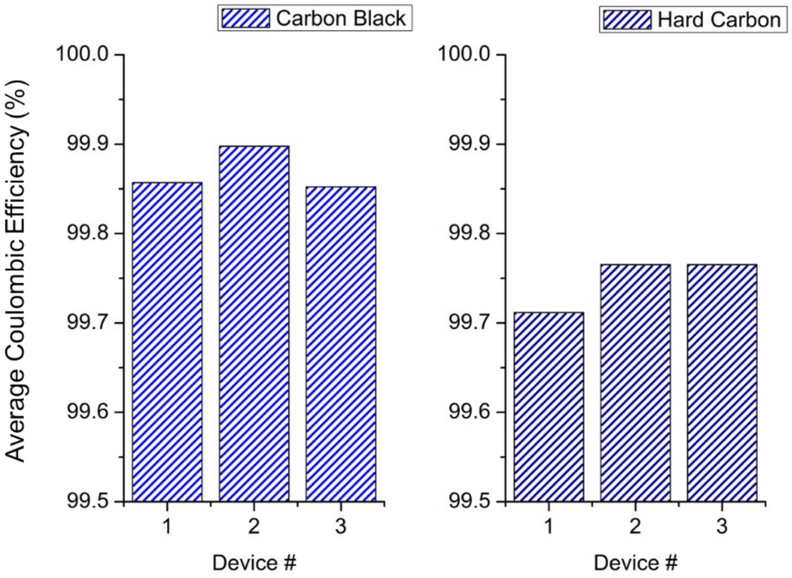


Figure S2. Average Coulombic efficiency over 50 cycles of plating and stripping of 0.5 mAh/cm^2 of sodium metal at a current of 0.5 mA/cm^2 for three carbon black devices (left) and three hard carbon devices (right). To minimize variation due to electrolyte or glovebox conditions, fresh electrolyte was always prepared prior to assembling cells, and batches of comparative cells were always made together (rather than making carbon black cells one day and hard carbon cells another day).

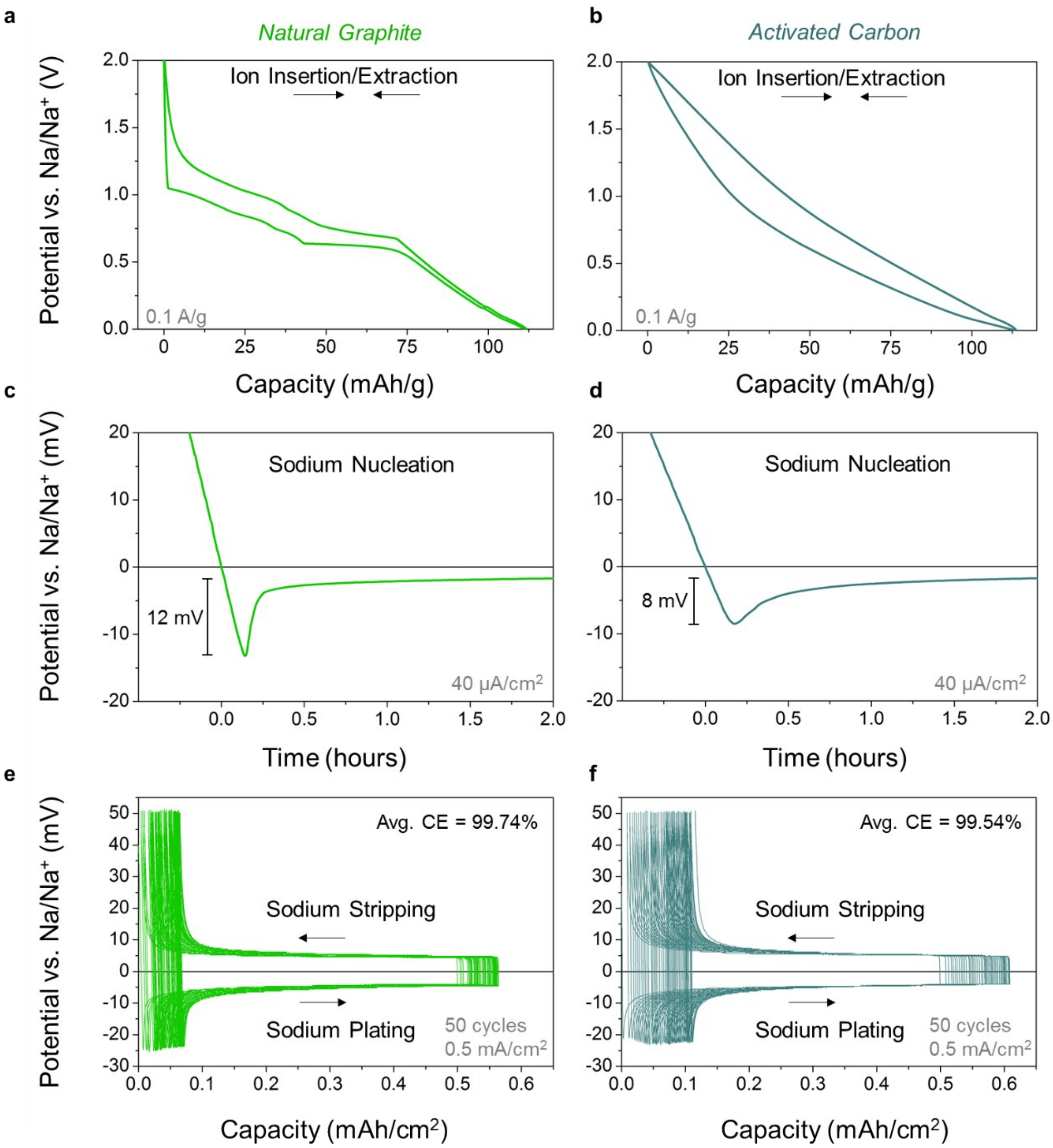


Figure S3. (a,b) Electrochemical voltage profiles of the third cycle for sodium ion insertion/extraction at 0.1 A/g for natural graphite (left) and activated carbon (right) electrodes. (c,d) Sodium metal nucleation profiles at 40 μA/cm^2 on sodiated electrodes. (e,f) Slippage profiles for sodium metal plating and stripping over 50 cycles at 0.5 mA/cm^2 on sodiated electrodes. For the natural graphite electrode, the process by which sodium ions insertion occurs is through the co-intercalation of sodium ions and diglyme molecules as detailed in Ref 18.

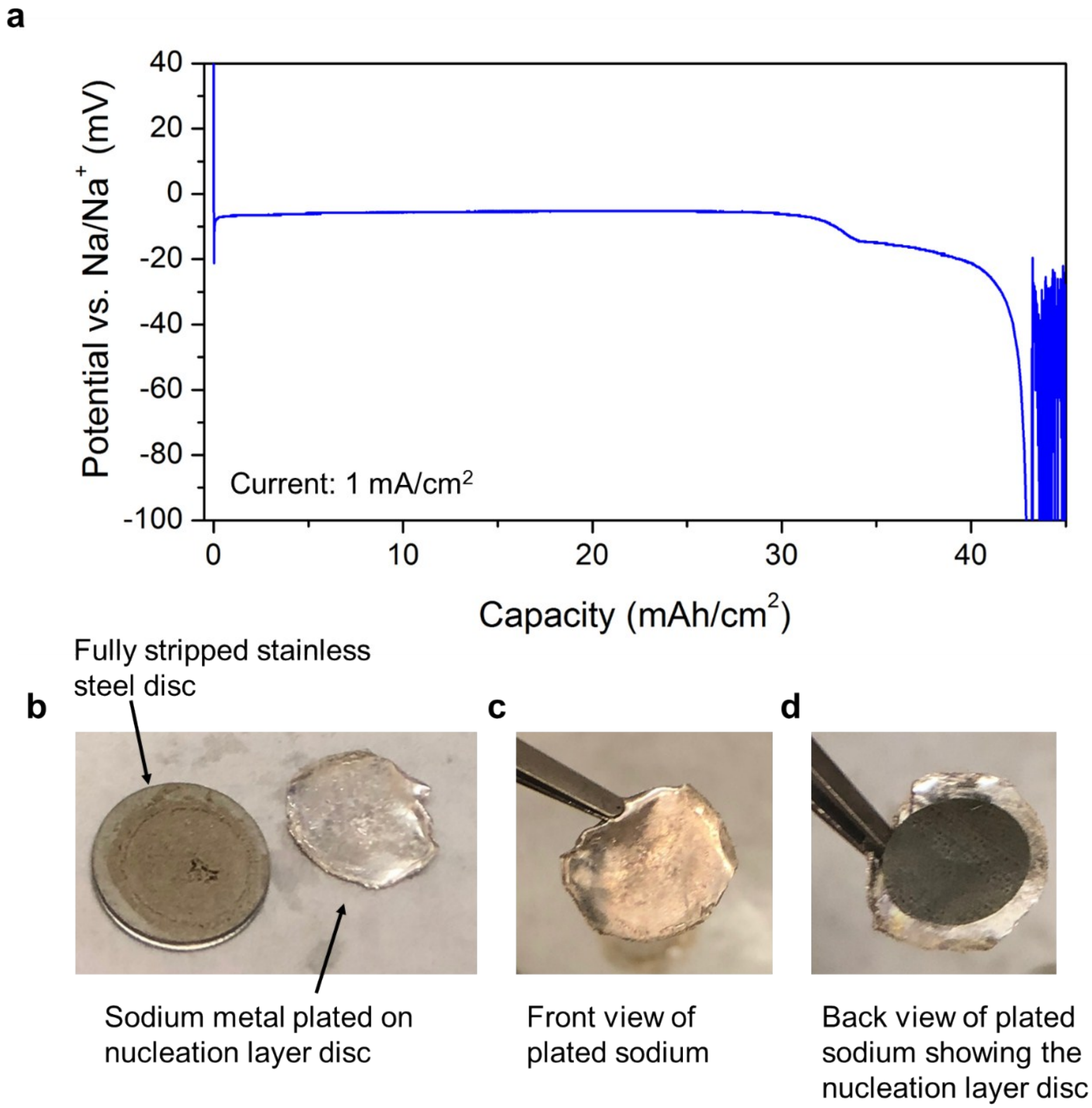


Figure S4. Plating on carbon black nucleation layer in a half-cell configuration until exhaustion of the sodium metal counter/reference electrode. Voltage profile shows stable plating over ~30 mAh/cm^2 of operation. Images show the full removal of all the sodium metal from the stainless steel disc and the deposition of sodium metal on the nucleation layer disc.

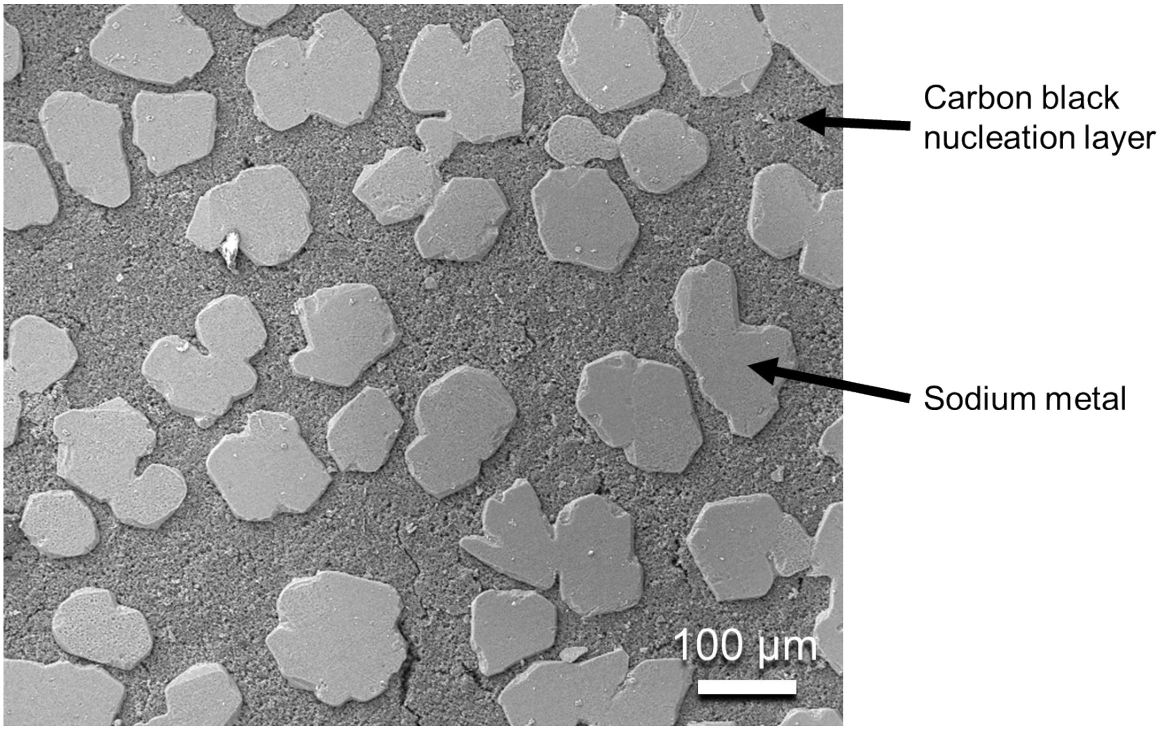
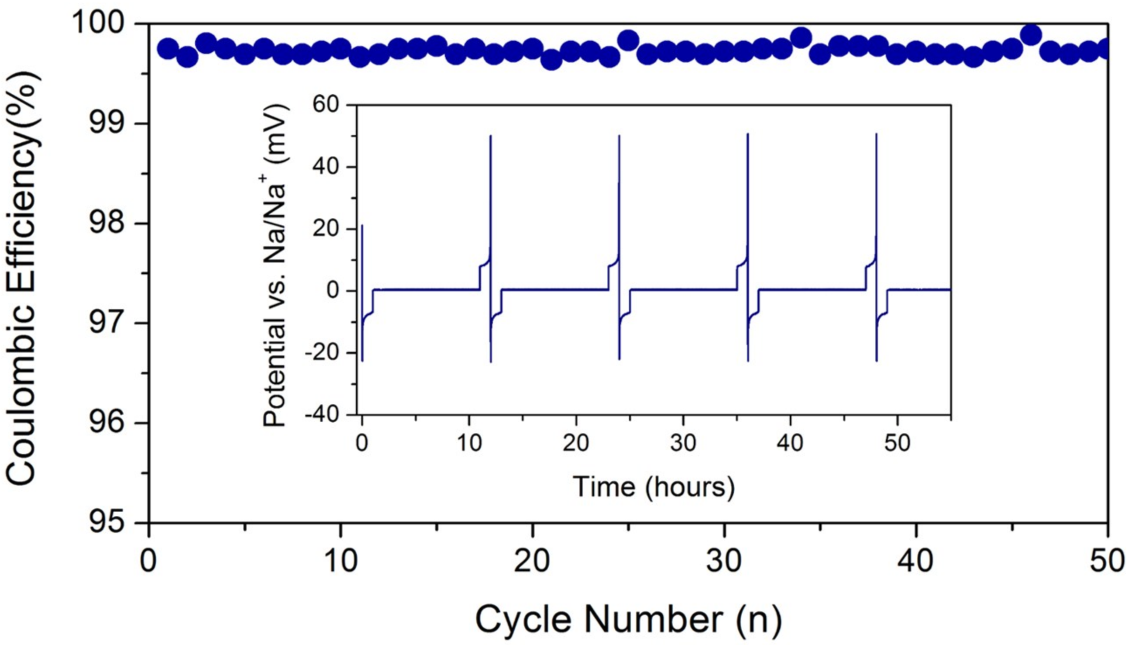


Figure S5. Scanning electron microscope image of sodium metal (0.5 mAh/cm^2) plated on a carbon black nucleation layer, showing the islands of sodium metal that appear to grow on the surface of the carbon black nucleation layer.



Current: 1 mA/cm^2
Capacity: 1 mAh/cm^2
Rest Period: 10 hours

Figure S6. 50 cycles of plating and stripping on a carbon black nucleation layer in a half-cell configuration using a 10 hour rest between each plating and stripping step to test the resting stability of the plated sodium metal. The inset shows the voltage profile for 4+ of these cycles. The average Coulombic efficiency of 99.73% over these 50 cycles indicates that minimal sodium is lost during the 10 hour resting period.

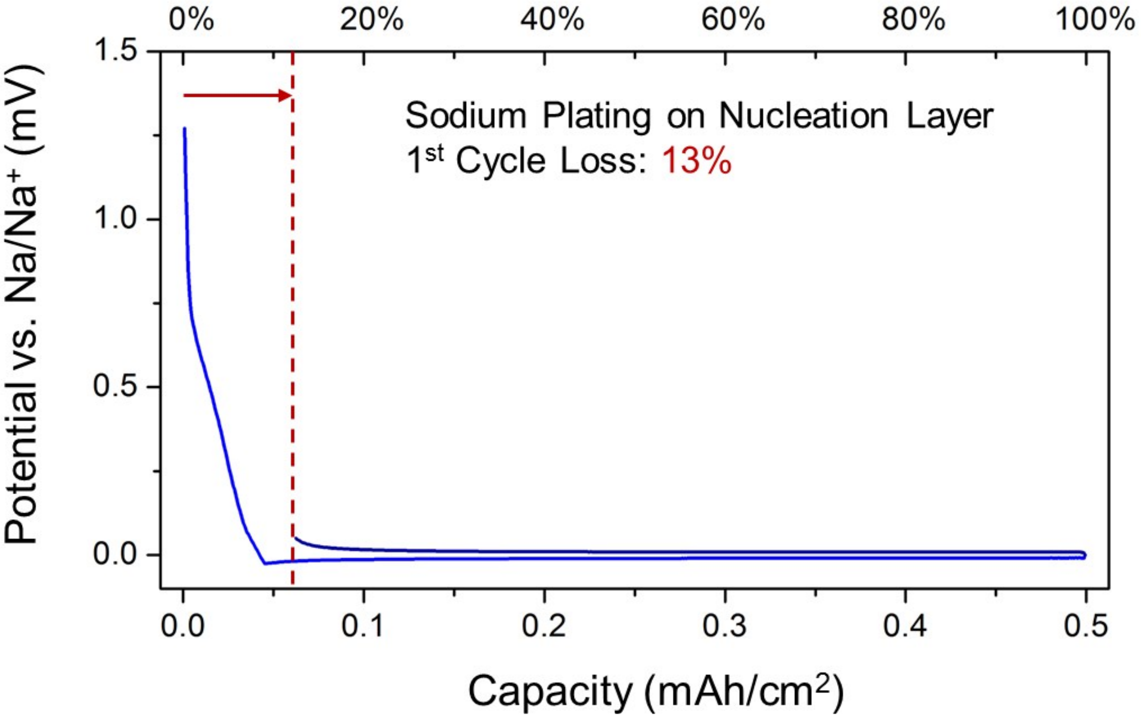


Figure S7. First-cycle voltage profiles for sodium metal plating on a 0.25 mg/cm^2 carbon black electrode at 0.5 mA/cm^2 for a capacity of 0.5 mAh/cm^2.

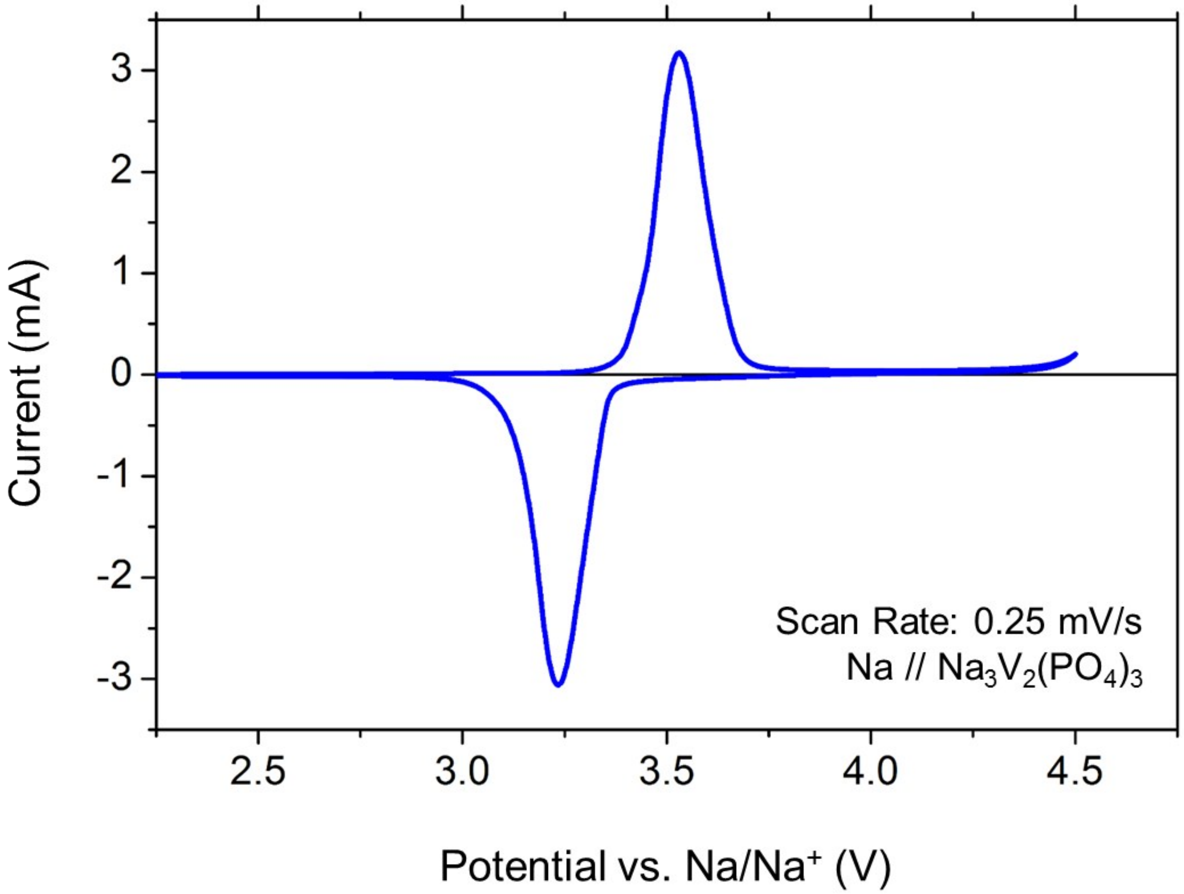


Figure S8. Cyclic voltammogram of $Na_3V_2(PO_4)_3$ half cell performed at 0.25 mV/s to 4.5 V vs. Na/Na^+ using an electrolyte of 1M $NaPF_6$ in diglyme. This test shows the electrochemical window of the 1M $NaPF_6$ in diglyme. To extend the electrochemical window of gylme-based electrolytes beyond what is shown here for 1M $NaPF_6$ in diglyme, the replacement of diglyme with tetraglyme[1] and the use of higher salt concentrations[2] can be carried out. Such electrolyte modifications should provide improved stability for the use of higher voltage cathodes.

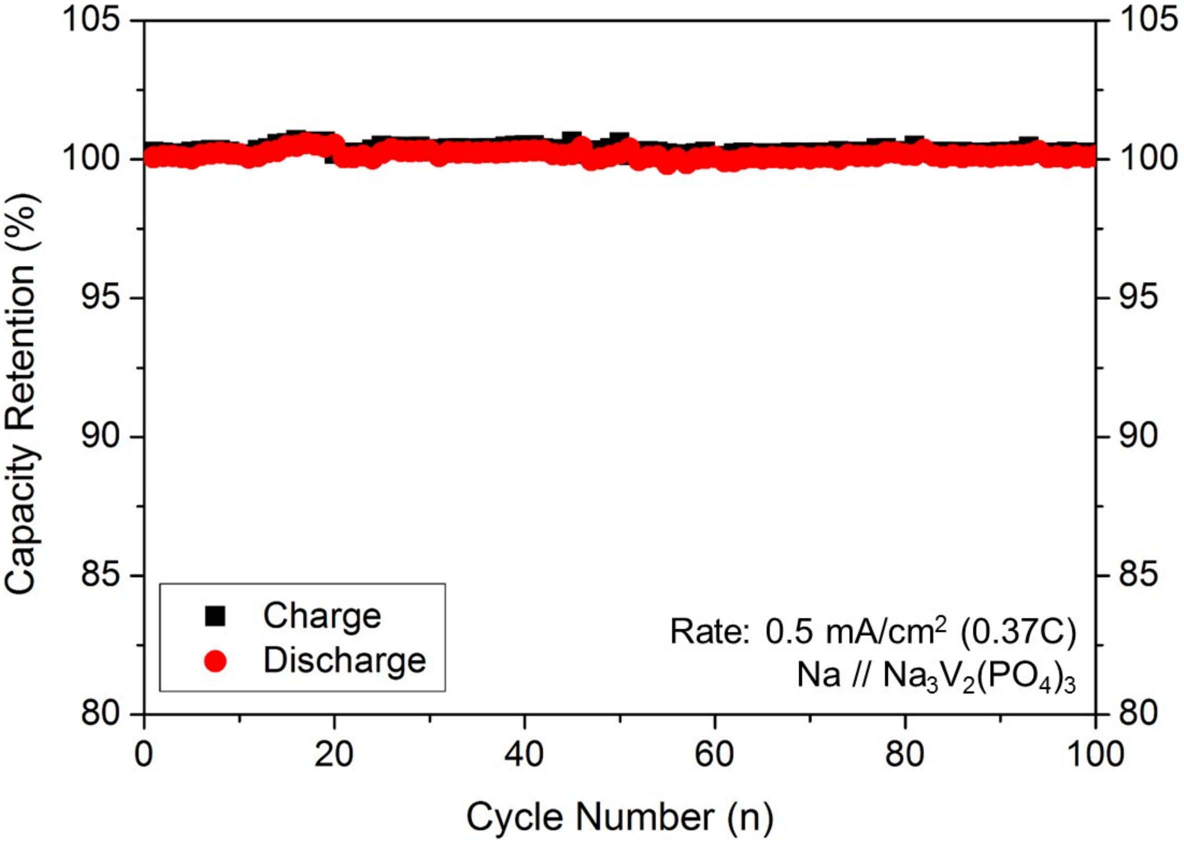


Figure S9. Cycling of $Na_3V_2(PO_4)_3$ in a half-cell configuration performed at 0.5 mA/cm^2 (0.37C) for 100 cycles.

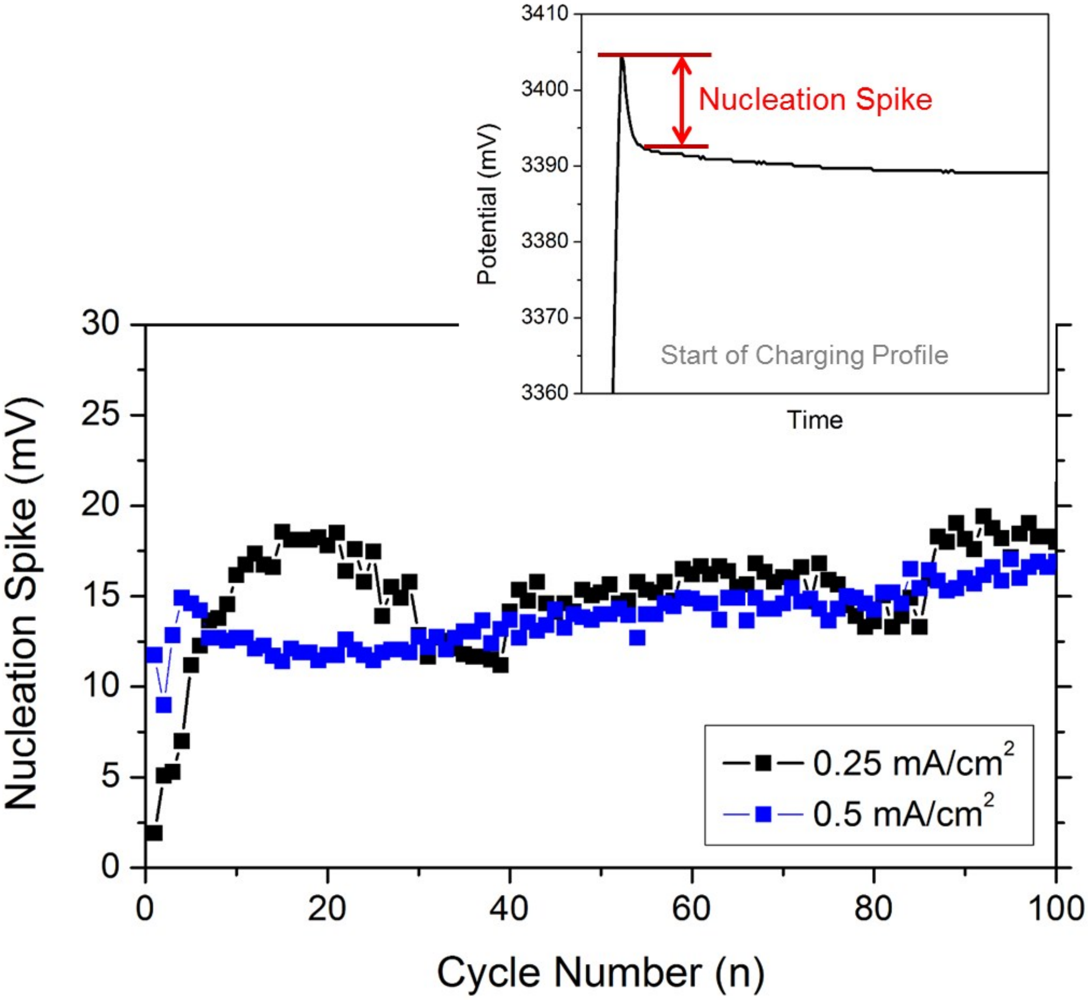


Figure S10. Nucleation spike voltage for anode-free cells cycled at 0.25 mA/cm^2 and 0.5 mA/cm^2. Above the panel is an example plot of the nucleation spike measurement. The slow loss of sodium in the cell causes the alignment of the cathode plateau and the nucleation events to slowly shift with cycle number. Whereas this can explain the initial change in the nucleation spike, the gradual increase over longer cycles could be related to more subtle changes at interfaces during cycling of the full cell device. Such a gradual increase in the spike magnitude was not observed in half-cell testing with carbon black nucleation layers.

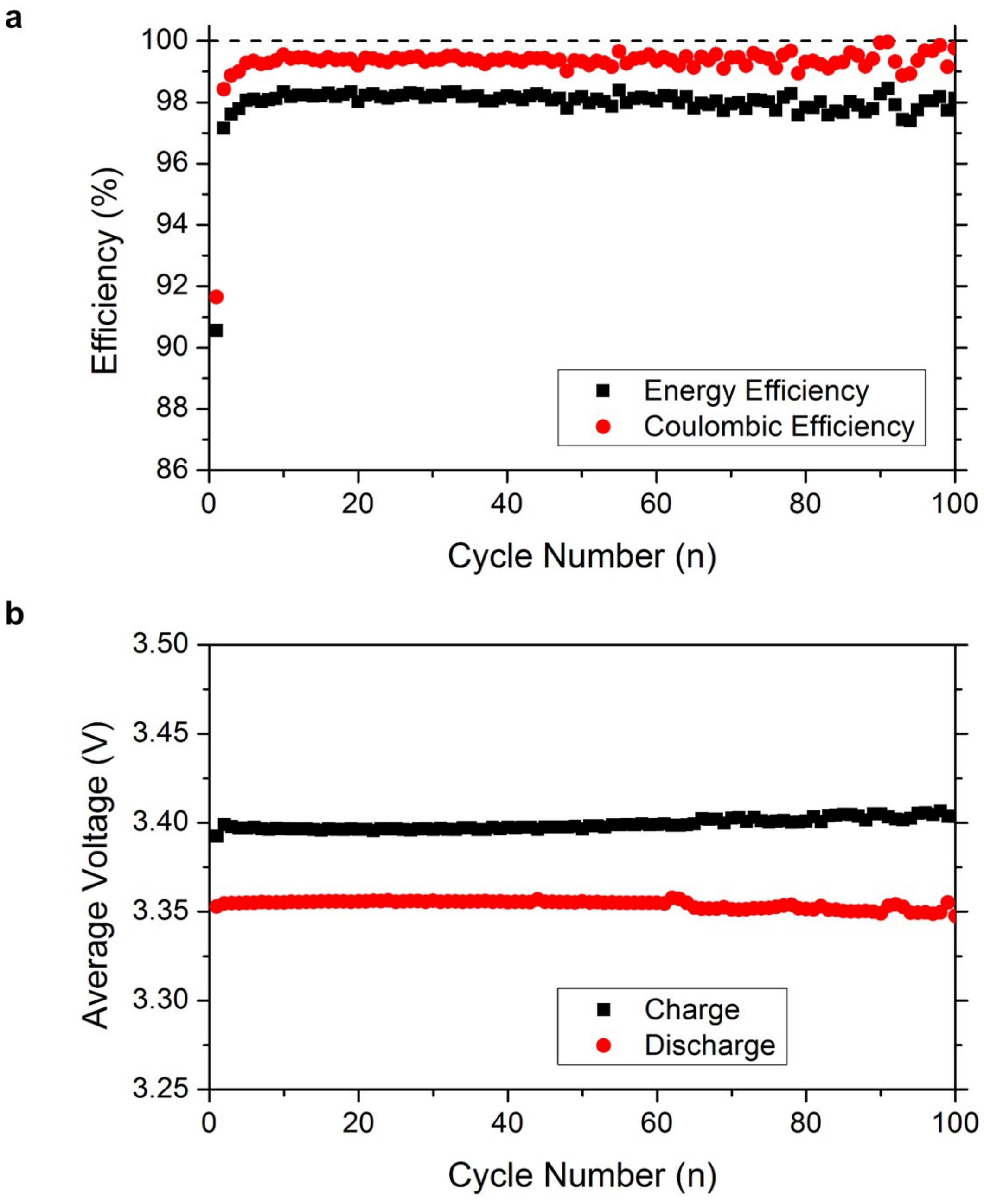


Figure S11. (a) Cycling efficiency and (b) average voltage for anode-free cell cycled at 0.25 mA/cm^2.

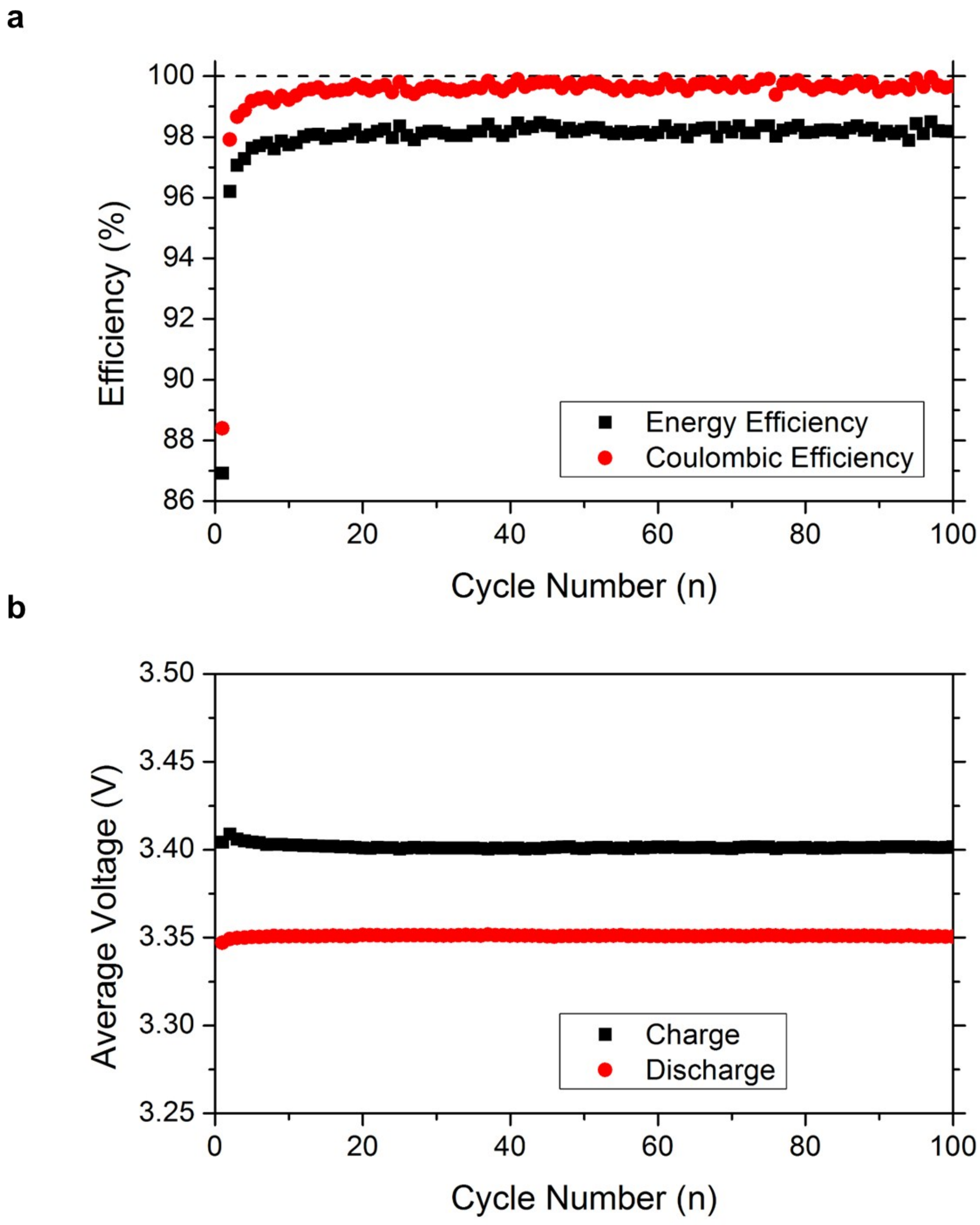


Figure S12. (a) Cycling efficiency and (b) average voltage for anode-free cell cycled at 0.5 mA/cm^2.

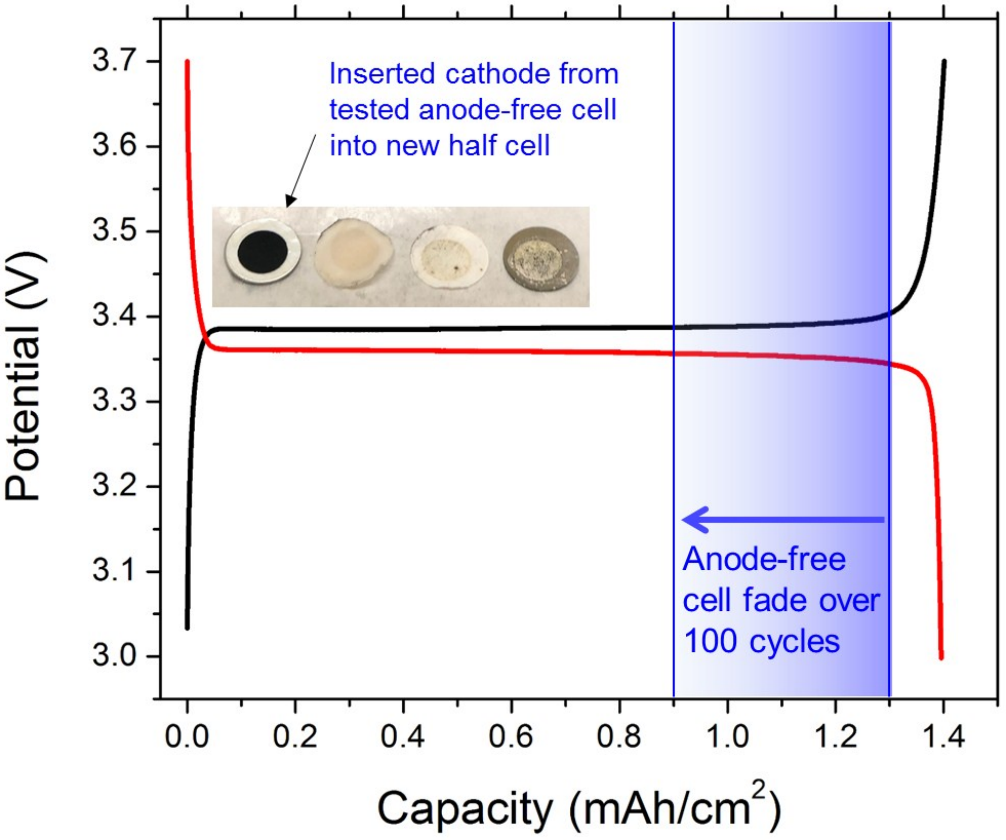


Figure S13. Potential profile of cathode from cell cycled 100+ times at 0.25 mA/cm^2 that was inserted back into a new half cell, indicating capacity fade during cycling was due to a loss of sodium.

References

1. Z. W. Seh, J. Sun, Y. Sun and Y. Cui, *ACS Cent. Sci.*, 2015, **1**, 449-455.
2. K. Yoshida, M. Nakamura, Y. Kazue, N. Tachikawa, S. Tsuzuki, S. Seki, K. Dokko and M. Watanabe, *J. Am. Chem. Soc.*, 2011, **133**, 13121-13129.