

Supporting information

On the compatibility of high mass loading bismuth anodes for full-cell sodium-ion Batteries

Lars Olow Simon Colbin¹, Tochukwu E. Nwaforonso¹, Yunjie Li¹, and Reza Younesi¹

¹Department of Chemistry-Ångström Laboratory, Uppsala University, Box 538, SE-75121 Uppsala, Sweden

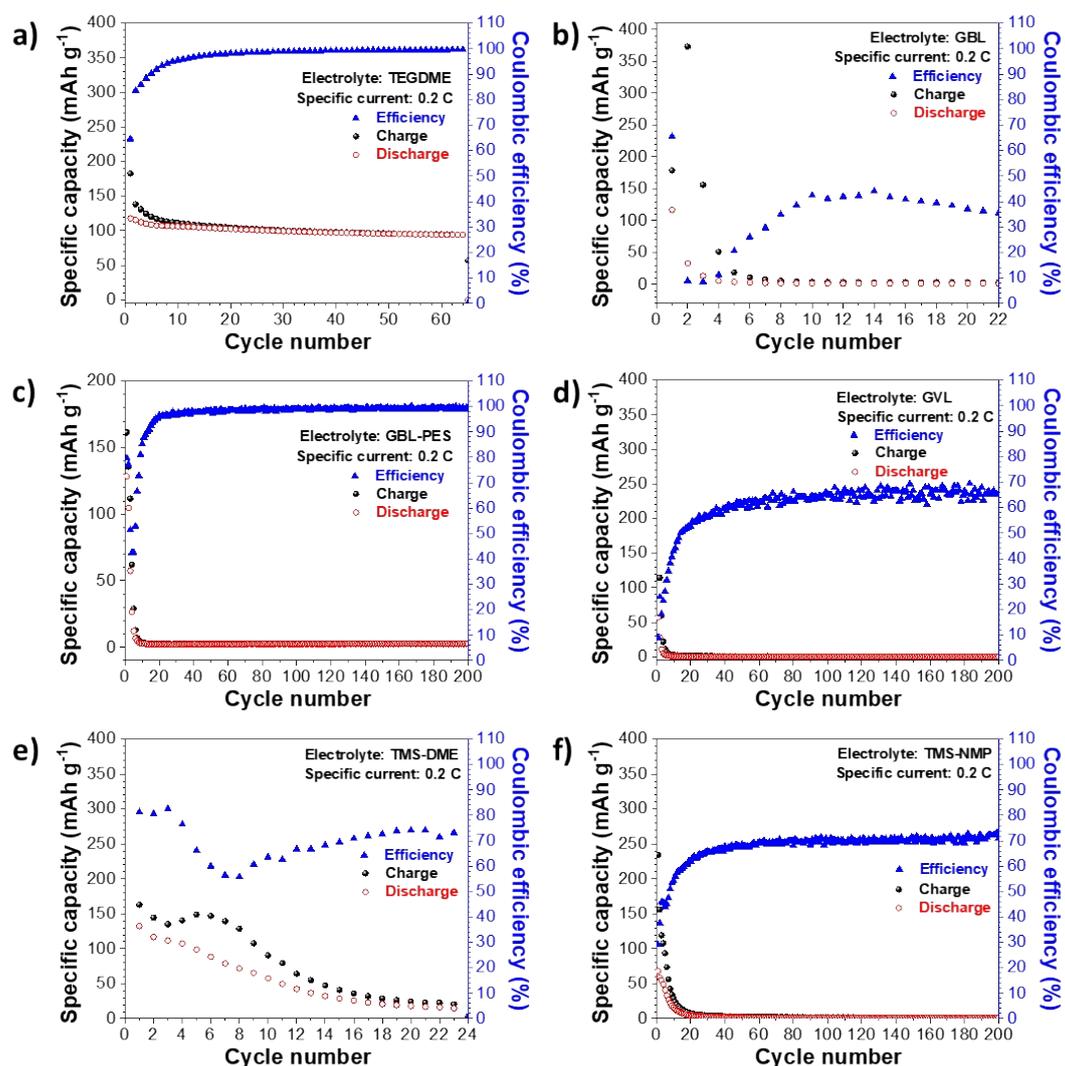


Figure S1. Cycling performances of Bismuth-Prussian white full-cells in different electrolytes. (a) NaPF₆ in TEGDME, (b) NaPF₆ in GBL, (c) NaPF₆ in GBL-PES, (d) NaPF₆ in GVL, (e) NaPF₆ in TMS-DME, (f) NaPF₆ in TMS-NMP.

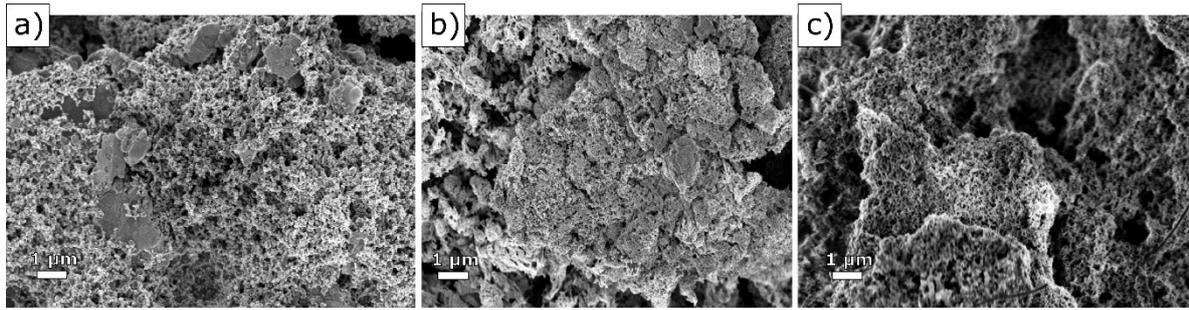


Figure S2: Scanning electron microscopy images of a high mass loading bismuth electrode. A pristine electrode is shown in (a). Electrodes cycled in a full cell using NaPF_6 in Diglyme as the electrolyte solution are shown in (b) for an electrode cycled 3 times, and (c) for an electrode that underwent 52 cycles.

Table S1: The different current scales for selected cycles from the full-cell rate test experiment (Figure 4b). The C-rates and gravimetric current densities are based on the bismuth anode.

Cycle	C-rate	Gravimetric current density (mA/g)	Current density (mA/cm ²)
10	0.1	40	0.23
20	0.5	200	1.2
40	2	800	4.6
55	4.5	1800	10
100	0.1	40	0.23

Table S2: The different current scales for selected cycles from the symmetrical-cell rate test experiment (Figure 5b).

Cycle	C-rate	Gravimetric current density (mA/g)	Current density (mA/cm ²)
10	0.1	38	0.32
20	0.5	190	1.6
40	2	770	6.4
55	8	3100	26
100	0.5	190	1.6

Table S3: The different current scales for selected cycles from three-electrode rate test experiment (Figure 6). The C-rates and gravimetric current densities are based on the bismuth anode.

Cycle	C-rate	Gravimetric current density (mA/g)	Current density (mA/cm ²)
5	0.079	30	0.55
10	0.079	30	0.55
20	0.40	150	2.7
30	0.79	310	5.5
40	1.6	610	11
50	4.8	1800	33
60	7.9	3100	55

Table S4: A comparison of the rate capability of full cells at different bismuth mass loadings at two different cycles a and b. The compared cells all use NaPF₆ in diglyme as the electrolyte solution.

Full-cell System and publication	Bi mass loading (mg/cm ²)	Cycle # [a]	Gravimetric current density (A/g) [cycle a]	Discharge capacity (mAh/g) [cycle a]	Cycle # [b]	Gravimetric current density (A/g) [cycle b]	Discharge capacity (mAh/g) [cycle b]
Bi/Na ₂ Fe ₂ (CN) ₆ present work	17.9	1	0.03	324	42	1.2	20
Bi/Na ₂ Fe ₂ (CN) ₆ present work	5.79	1	0.04	349	42	1.2	180
Bi/Na ₃ V ₂ (PO ₄) ₃ Wang et al. ¹	1.03	1	0.1	265	18	1.2	245

Experimental description

Electrolyte preparation

NaFP₆ was purchased from stella-chemifa (99 %). The solvents were: trimethyl phosphate (TMP) (Acros organics 99 %), Dimethoxyethane (DME) (BASF), Tetraethylene glycol dimethyl ether (TEGDME) (Sigma-Aldrich ≥99 %), γ -valerolactone (GVL) (Sigma-Aldrich 99 %), N-methyl-2-pyrrolidone (Acros Extra Dry ≥99.5 %), sulfolane (TMS) (Sigma-Aldrich 99 %), γ -butyrolactone (GBL) (Merck, Selectipur anhydrous), and NN-Dimethylacetamide (DMAC) (Sigma-Aldrich, 99.8 %, anhydrous). Prop-1-ene-1,3-sultone (PES) was ordered as 97 % from Sigma-Aldrich, produced by Manchester organics. All solvents were dried using molecular sieves before use. The sodium bis(oxalato)borate and NaFP₆ salts were dried separately under vacuum at 120 °C for 12 hours before use. The mixed solvent systems were prepared to 50 w% of each solvent. PES was added as 5 vol% when used as an additive. All solutions were prepared to approximately 1 molal.

Electrode preparation

The electrodes were prepared from slurries coated on carbon-coated aluminum foil. The bismuth slurries consisted of 90 w% bismuth, 5 w% sodium carboxymethyl cellulose, and 5 w% conducting carbon powder (Super P) in water. The bismuth for the electrodes used in testing different electrolytes was purchased from Sigma-Aldrich (≥99.99 %, 100 mesh), while all other cycling with bismuth was conducted using Bismuth produced by Chempur (99.9 %, 325 mesh). The Prussian white was provided by Altris AB, which was mixed at 90 w% with 5 w% sodium carboxymethyl cellulose, and 5 w% conducting carbon powder (Super P) in deoxygenated water. All electrodes were dried at 140 °C for 25 h before use.

Cell preparation and electrochemical measurements

All cells were assembled as vacuum sealed pouch cells under an argon atmosphere with O₂ < 1 ppm and H₂O < 1 ppm. All cells solely used aluminum current collectors. The electrodes used in half cells had diameters of 13 mm for bismuth and 15 mm for sodium metal and were separated by a 20 mm glass fiber separator (Whatman), containing 100 μ L electrolyte solution. The half cells shown in Figure S1, used modest low mass-loading ~1.5 mg/cm² for bismuth and ~2.5 mg/cm² for Prussian white. The remainder of the galvanostatic cycling was conducted using higher mass loadings: When Prussian white was used in an abundance a mass loading of ~80 mg/cm² Prussian white and ~20 mg/cm² bismuth was used, whereas in the balanced cells

$\sim 15 \text{ mg/cm}^2$ and $\sim 6 \text{ mg/cm}^2$ was active material in the Prussian white and bismuth electrodes respectively. The electrode diameters in these experiments were 10 mm for both electrodes. Regarding reference electrodes, metallic sodium was used as a reference electrode for the three-electrode rate test, while a desodiated Prussian white electrode ($\sim 3.3 \text{ V vs. Na}^+/\text{Na}$) was used as a reference in the intermittent current interruption experiment.² The bismuth electrodes used in symmetrical cells had a diameter of 13 mm, and a mass loading of $\sim 8 \text{ mg/cm}^2$ (desodiated mass). These cells were constructed so that there was a slight overcapacity ($< 5 \%$) on the sodiated electrode.

The cyclic voltammetry experiments were also conducted using pouch cells. Here Prussian white charged to 3.3 V vs. Na^+/Na was used as a reference electrode. The bismuth working electrode had a diameter of 10 mm and a mass loading of $\sim 1.5 \text{ mg/cm}^2$, while the Prussian white counter electrode had a diameter of 13 mm and a mass loading of $\sim 15 \text{ mg/cm}^2$. The scan-rate was varied in the cyclic voltammetry experiment, the first seven cycles were conducted at 0.4 mV/s, which was thereafter increased to 1 mV/s.

All three-electrode experiments were conducted using a *Biologic MPG2* potentiostat, whereas two-electrode galvanostatic cycling was conducted using an Arbin, LANDT (model CT2001A), and Neware battery testing machine.

Scanning electron microscopy

A Zeiss/LEO 1550 scanning electron microscope was used to study the morphology of the bismuth electrodes. The images were recorded using the instrument's in-lens secondary electron detector. equipment was used to obtain morphology information of the bismuth electrode.

References

- 1 C. Wang, D. Du, M. Song, Y. Wang, and F. Li, "A High-Power $\text{Na}_3\text{V}_2(\text{PO}_4)_3\text{-Bi}$ Sodium-Ion Full Battery in a Wide Temperature Range" *Adv. Energy Mater.*, 9, 16, 1900022, 2019.
- 2 M. J. Lacey, "Influence of the Electrolyte on the Internal Resistance of Lithium–Sulfur Batteries Studied with an Intermittent Current Interruption Method" *ChemElectroChem*, 4, 8, 1997–2004, 2017.