

## Supporting information

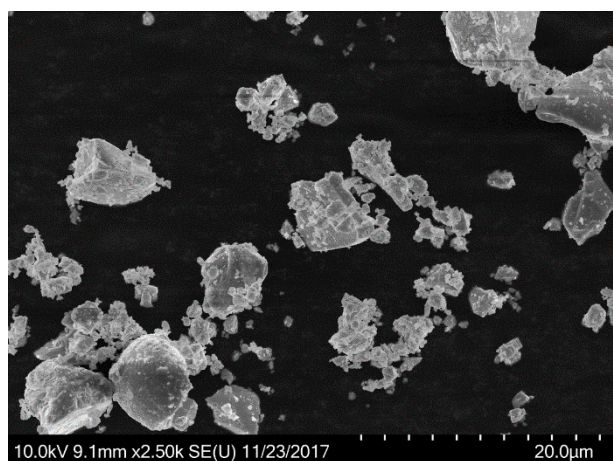


Figure S 1: SEM image of BiVO<sub>4</sub> particles at 2500 times magnification.

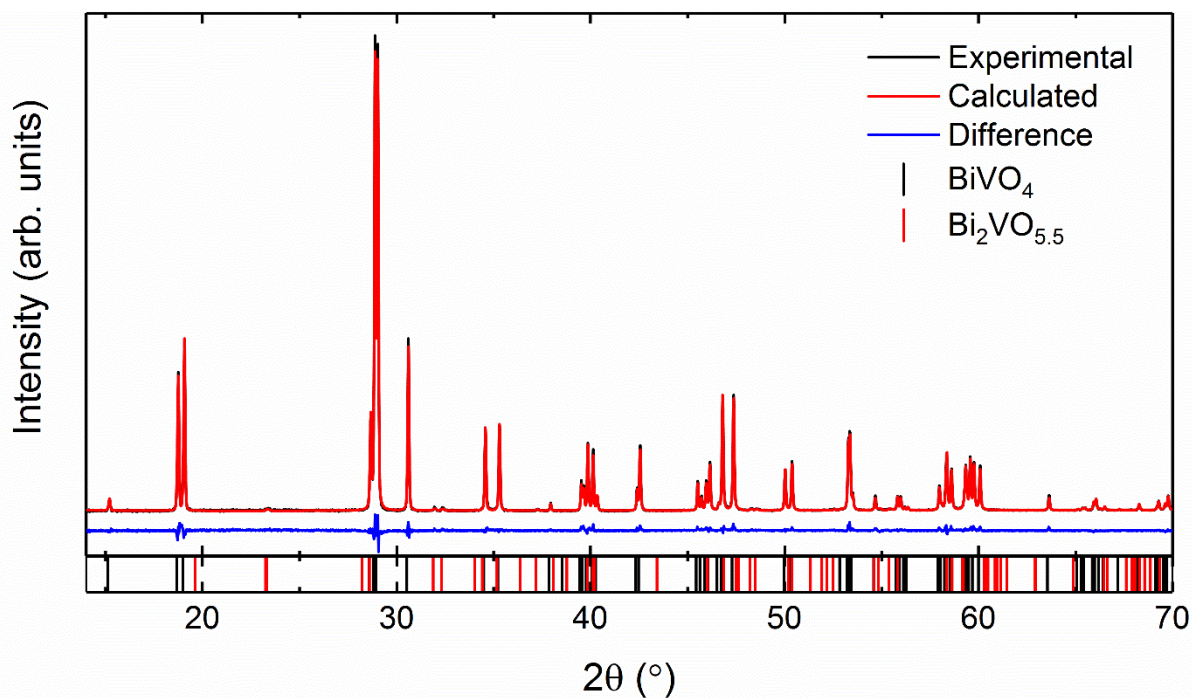


Figure S 2: Rietveld refinement of  $\text{BiVO}_4$  showing experimental, calculated and difference profiles;  $\lambda = 1.54056 \text{ \AA}$ . Bars in lower panel correspond to positions of Bragg reflections from  $\text{BiVO}_4$  (black) (98.05 % phase fraction) and  $\text{Bi}_2\text{VO}_{5.5}$  (red) (1.95 % phase fraction). Cell parameters are summarized in Table S 1.

Table S 1: Cell parameters from fit of as-bought  $\text{BiVO}_4$  fitted to  $\text{BiVO}_4$  (C12/c1) and  $\text{Bi}_2\text{VO}_{5.5}$  (Aba2). to as-bought sample of  $\text{BiVO}_4$ . Resulting R-factors:  $R_{\text{wp}}$  9.37 (%),  $R_p$  6.72 (%),  $R_{\text{exp}}$  11.23 (%).

	a (Å)	b (Å)	c (Å)	$\beta$ (°)	Size (nm)	Phase fraction (%)
<b><math>\text{BiVO}_4</math> (I2/b)</b>	7.250(1)	11.700(9)	5.195(1)	135.392(1)	100.5(0)	98.05
<b><math>\text{Bi}_2\text{VO}_{5.5}</math> (Aba2)</b>	5.610(0)	15.292(6)	5.538(6)	-	-	1.95

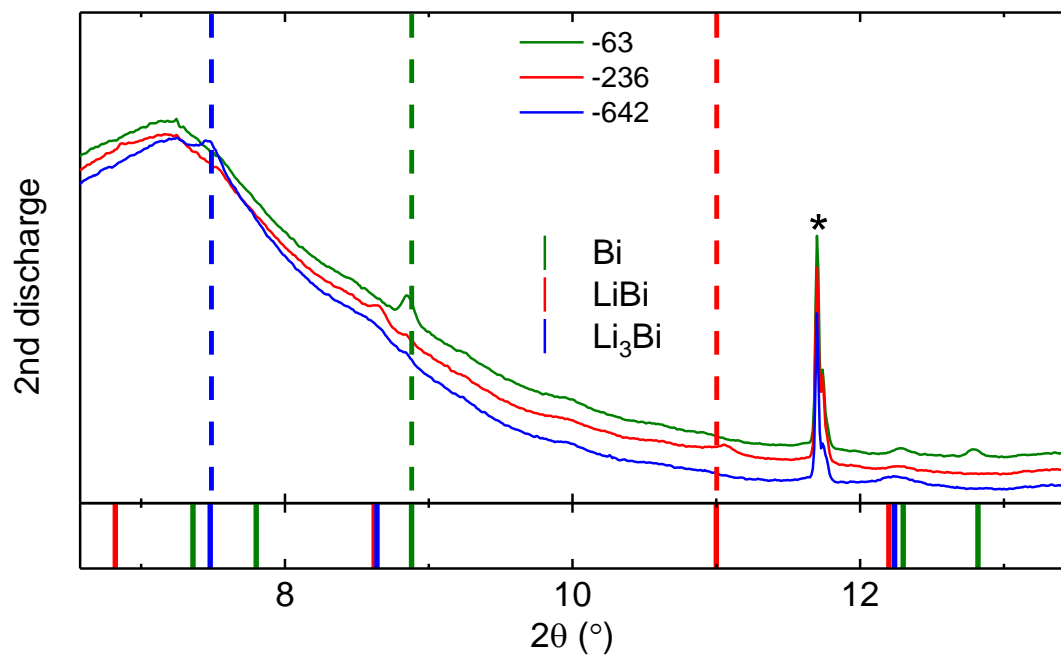


Figure S 3: Selected synchrotron powder X-ray diffractograms collected *operando* during 2<sup>nd</sup> discharge with emphasis on the three distinct phases Bi, LiBi and  $\text{Li}_3\text{Bi}$ .  $\lambda = 5053 \text{ \AA}$ .

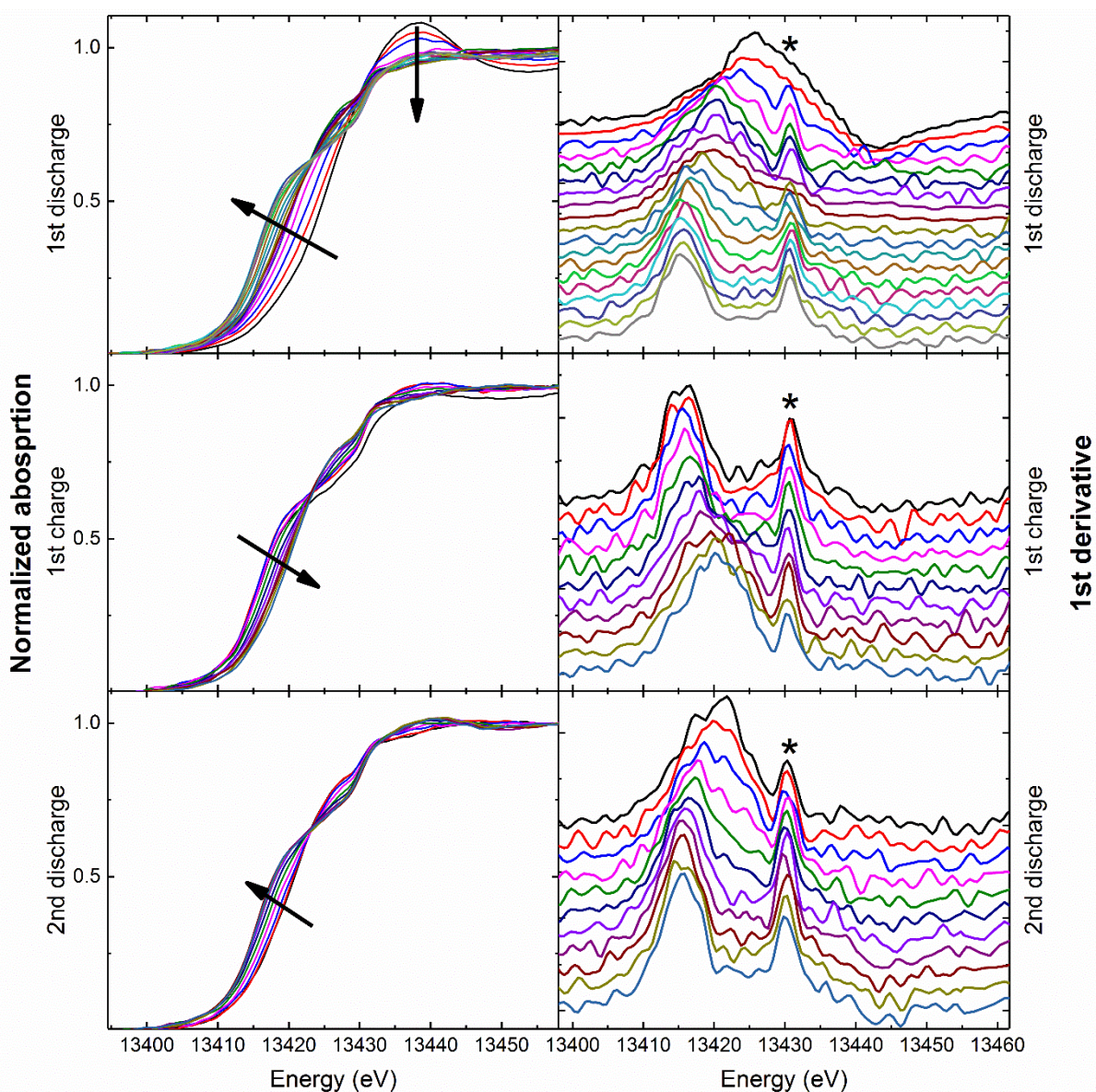


Figure S 4: XANES spectra of the Bi L3 edge for 1<sup>st</sup> discharge (top), 1<sup>st</sup> charge (middle) and 2<sup>nd</sup> discharge (bottom). Normalized absorption is shown in left panels, corresponding 1<sup>st</sup> derivative curves in right panels (downwards cascading from initial to final charge state). Arrows in left panels indicate changes in edge position from initial to final charge state in each half cycle. Asterix \* marks glitch from the monochromator.

### Energetics of possible steps in the reaction pathway between Li and BiVO<sub>4</sub>

1.  $6\text{Li} + \text{BiVO}_4 \rightarrow \text{Li}_3\text{Bi} + \text{Li}_3\text{VO}_4$  -9.234 eV (-891 kJ mol<sup>-1</sup>)
2.  $3\text{Li} + \text{BiVO}_4 \rightarrow \text{Bi} + \text{Li}_3\text{VO}_4$  -7.108 eV (-686 kJ mol<sup>-1</sup>)
3.  $\text{Li} + \text{BiVO}_4 \rightarrow \text{VO} + \text{Li}_3\text{BiO}_3$  -4.962 eV (-479 kJ mol<sup>-1</sup>)
4.  $\text{Li} + \text{BiVO}_4 \rightarrow \text{BiO} + \text{LiVO}_2 + \text{Li}_2\text{O}$  -4.948 eV (-477 kJ mol<sup>-1</sup>)
5.  $\text{Li} + 2\text{BiVO}_4 \rightarrow \text{LiV}_2\text{O}_5 + \text{Bi}_2\text{O}_3$  -2.005 eV (-193 kJ mol<sup>-1</sup>)
6.  $4\text{Li} + 2\text{BiVO}_4 \rightarrow 2\text{BiO} + 2\text{LiVO}_2 + 2\text{LiO}$  -4.070 eV (-393 kJ mol<sup>-1</sup>)
7.  $3\text{Li} + \text{Bi} + \text{Li}_3\text{VO}_4 \rightarrow \text{Li}_3\text{Bi} + \text{Li}_3\text{VO}_4$  -2.126 eV (-205 kJ mol<sup>-1</sup>)

8.  $\text{Li} + \text{BiVO}_4 \rightarrow \text{VO}_2 + \text{LiBiO}_2$     -1.875 eV (-181 kJ mol<sup>-1</sup>)
9.  $12\text{Li} + 2\text{BiVO}_4 \rightarrow 3\text{Li}_2\text{O}_2 + 2\text{Li}_3\text{Bi} + 2\text{VO}$     -6.373 eV (-615 kJ mol<sup>-1</sup>)
10.  $\text{Li} + \text{BiVO}_4 \rightarrow \text{V} + \text{Li}_3\text{BiO}_4$     -2.181 eV (-210 kJ mol<sup>-1</sup>)
11.  $\text{Li} + \text{BiVO}_4 \rightarrow \text{BiO}_2 + \text{LiVO}_2$     1.371 eV (-132 kJ mol<sup>-1</sup>)
12.  $\text{Li} + \text{BiVO}_4 \rightarrow \text{LiBi} + \text{VO}_2 + \text{O}_2$     4.792 eV (462 kJ mol<sup>-1</sup>)
13.  $3\text{Li} + \text{BiVO}_4 \rightarrow \text{Li}_3\text{Bi} + \text{VO}_2 + \text{O}_2$     3.417 eV (330 kJ mol<sup>-1</sup>)
14.  $2\text{Li} + \text{BiVO}_4 \rightarrow \text{LiBi} + \text{LiVO}_2 + \text{O}_2$     2.313 eV (223 kJ mol<sup>-1</sup>)
15.  $\text{BiVO}_4 + \text{Li} \rightarrow \text{Li}_2\text{O} + \text{BiO}_2 + \text{VO}$     -1.809 eV (-175 kJ mol<sup>-1</sup>)
16.  $\text{Li} + \text{BiVO}_4 \rightarrow \text{LiBi} + \text{VO}_2 + \text{O}_2$     4.792 eV (462 kJ mol<sup>-1</sup>)
17.  $3\text{Li} + \text{BiVO}_4 \rightarrow \text{Li}_3\text{Bi} + \text{VO}_2 + \text{O}_2$     3.417 eV (330 kJ mol<sup>-1</sup>)
18.  $\text{Li} + 2\text{BiVO}_4 \rightarrow \text{Bi}_2\text{O}_3 + \text{V}_2\text{O}_5 + \text{Li}$     1.578 eV (152 kJ mol<sup>-1</sup>)
19.  $2\text{Li} + \text{BiVO}_4 \rightarrow \text{LiBi} + \text{LiVO}_2 + \text{O}_2$     2.313 eV (223 kJ mol<sup>-1</sup>)
20.  $\text{Li} + \text{BiVO}_4 \rightarrow \text{BiO}_2 + \text{VO}_2 + \text{Li}$     1.108 eV (107 kJ mol<sup>-1</sup>)
21.  $\text{Li} + \text{BiVO}_4 \rightarrow \text{VO} + \text{LiBiO}_3$     0.582 eV (56 kJ mol<sup>-1</sup>)
22.  $4\text{Li} + \text{BiVO}_4 \rightarrow \text{Bi} + \text{Li}_4\text{VO}_4$     -5.645 eV (-545 kJ/mol)
23.  $4\text{Li} + \text{BiVO}_4 \rightarrow \text{LiBi} + \text{Li}_3\text{VO}_4$     -7.108 eV (-686 kJ mol<sup>-1</sup>)
24.  $\text{Li} + \text{Bi} + \text{Li}_3\text{VO}_4 \rightarrow \text{LiBi} + \text{Li}_3\text{VO}_4$     -0.752 eV (-73 kJ mol<sup>-1</sup>)
25.  $\text{Li} + \text{LiBi} + \text{Li}_3\text{VO}_4 \rightarrow \text{LiBi} + \text{Li}_4\text{VO}_4$     -0.55 eV (-53 kJ/mol)
26.  $2\text{Li} + 2\text{LiBi} + \text{Li}_3\text{VO}_4 \rightarrow \text{LiBi} + \text{Li}_3\text{Bi} + \text{Li}_3\text{VO}_4$     -1.374 eV (-133 kJ mol<sup>-1</sup>)
27.  $2\text{Li} + \text{LiBi} + \text{Li}_4\text{VO}_4 \rightarrow \text{Li}_3\text{Bi} + \text{Li}_4\text{VO}_4$     -0.91 eV (-87 kJ/mol)
28.  $\text{Li} + \text{Bi} + \text{Li}_3\text{VO}_4 \rightarrow \text{Bi} + \text{Li}_4\text{VO}_4$     -0.171 eV (-17 kJ/mol)
29.  $2\text{Li} + \text{Bi} + \text{Li}_3\text{VO}_4 \rightarrow \text{LiBi} + \text{Li}_4\text{VO}_4$     -1.1708 eV (-112 kJ/mol)
30.  $4\text{Li} + 2\text{Bi} + \text{Li}_3\text{VO}_4 \rightarrow \text{LiBi} + \text{Li}_3\text{Bi} + \text{Li}_3\text{VO}_4$     -1.67 eV (-160 kJ/mol) -2.879 eV (-278 kJ mol<sup>-1</sup>)
31.  $3\text{Li} + \text{Bi} + \text{Li}_3\text{VO}_4 \rightarrow \text{Li}_3\text{Bi} + \text{Li}_3\text{VO}_4$     -1.53 eV (-147 kJ/mol) -2.126 eV (-205 kJ mol<sup>-1</sup>)
32.  $\text{Li} + \text{Li}_3\text{Bi} + \text{Li}_3\text{VO}_4 \rightarrow \text{Li}_3\text{Bi} + \text{Li}_4\text{VO}_4$     -0.171 eV (-17 kJ/mol)
33.  $4\text{Li} + 2\text{BiVO}_4 \rightarrow 2\text{BiO} + 2\text{LiVO}_2 + 2\text{LiO}$     -1.589 eV (-153 kJ/mol) -4.070 eV (-393 kJ mol<sup>-1</sup>)
34.  $6\text{Li} + \text{BiVO}_4 \rightarrow \text{Li}_3\text{Bi} + \text{Li}_3\text{VO}_4$     -6.901 eV (-645 kJ/mol) -9.234 eV (-891 kJ mol<sup>-1</sup>)
35.  $\text{Li} + \text{Bi} + \text{Li}_3\text{VO}_4 \rightarrow \text{Li}_3\text{Bi} + \text{Li}_3\text{VO}_4$     -1.527 eV (-147 kJ/mol) -2.126 eV (-205 kJ mol<sup>-1</sup>)

36.  $4\text{Li} + 3\text{BiVO}_4 \rightarrow \text{LiV}_3\text{O}_8 + \text{Li}_3\text{Bi} + 2\text{BiO}_2$        $-0.278 \text{ eV} (-27 \text{ kJ mol}^{-1})$
37.  $6\text{Li} + 9\text{BiVO}_4 \rightarrow 3\text{LiV}_3\text{O}_8 + \text{Li}_3\text{Bi} + 4\text{Bi}_2\text{O}_3$        $-3.159 \text{ eV} (-305 \text{ kJ mol}^{-1})$
38.  $2\text{Li} + 3\text{BiVO}_4 \rightarrow \text{LiV}_3\text{O}_8 + \text{LiBi} + 2\text{BiO}_2$        $1.097 \text{ eV} (106 \text{ kJ mol}^{-1})$
39.  $4\text{Li} + 9\text{BiVO}_4 \rightarrow 3\text{LiV}_3\text{O}_8 + \text{LiBi} + 4\text{Bi}_2\text{O}_3$        $-1.785 \text{ eV} (-172 \text{ kJ mol}^{-1})$
40.  $2\text{Li} + 18\text{BiVO}_4 + 4\text{LiBi} \rightarrow 3\text{Li}_2\text{V}_6\text{O}_{13} + 11\text{Bi}_2\text{O}_3$        $-7.512 \text{ eV} (-725 \text{ kJ mol}^{-1})$
41.  $18\text{BiVO}_4 + 4\text{Li}_3\text{Bi} \rightarrow 6\text{Li} + 3\text{Li}_2\text{V}_6\text{O}_{13} + 11\text{Bi}_2\text{O}_3$        $-2.014 \text{ eV} (-194 \text{ kJ mol}^{-1})$
42.  $2\text{Li} + 6\text{BiVO}_4 \rightarrow \text{Li}_2\text{V}_6\text{O}_{15} + 3\text{Bi}_2\text{O}_3$        $-1.528 \text{ eV} (-147 \text{ kJ mol}^{-1})$
43.  $5 \text{ Li} + 18\text{BiVO}_4 + 4\text{LiBi} \rightarrow 3\text{Li}_3\text{V}_6\text{O}_{13} + 11\text{Bi}_2\text{O}_3$        $-14.308 \text{ eV} (-1380 \text{ kJ mol}^{-1})$
44.  $18\text{BiVO}_4 + 4\text{Li}_3\text{Bi} \rightarrow 3\text{Li} + 3\text{Li}_3\text{V}_6\text{O}_{13} + 11\text{Bi}_2\text{O}_3$        $-8.810 \text{ eV} (-850 \text{ kJ mol}^{-1})$
45.  $3\text{Li} + 2\text{BiVO}_4 \rightarrow 2\text{LiVO}_3 + \text{LiBi} + \text{BiO}_2$        $-3.578 \text{ eV} (-345 \text{ kJ mol}^{-1})$
46.  $4\text{Li} + 3\text{BiVO}_4 \rightarrow 3\text{LiVO}_3 + \text{LiBi} + \text{Bi}_2\text{O}_3$        $-6.636 \text{ eV} (-640 \text{ kJ mol}^{-1})$
47.  $6\text{Li} + 3\text{BiVO}_4 \rightarrow 3\text{LiVO}_3 + \text{Li}_3\text{Bi} + \text{Bi}_2\text{O}_3$        $-8.011 \text{ eV} (-773 \text{ kJ mol}^{-1})$
48.  $5\text{Li} + 2\text{BiVO}_4 \rightarrow 2\text{LiVO}_3 + \text{Li}_3\text{Bi} + \text{BiO}_2$        $-4.953 \text{ eV} (-478 \text{ kJ mol}^{-1})$
49.  $5\text{Li} + 4\text{BiVO}_4 \rightarrow 2\text{LiV}_2\text{O}_5 + \text{Li}_3\text{Bi} + 3\text{BiO}_2$        $-2.847 \text{ eV} (-275 \text{ kJ mol}^{-1})$
50.  $3\text{Li} + 4\text{BiVO}_4 \rightarrow 2\text{LiV}_2\text{O}_5 + \text{LiBi} + 3\text{BiO}_2$        $-1.473 \text{ eV} (-142 \text{ kJ mol}^{-1})$
51.  $\text{Li} + 2\text{BiVO}_4 \rightarrow \text{LiV}_2\text{O}_5 + \text{Bi}_2\text{O}_3$        $-2.005 \text{ eV} (-193 \text{ kJ mol}^{-1})$
52.  $14\text{Li} + 5\text{BiVO}_4 \rightarrow \text{Li}_5\text{BiO}_5 + 4\text{LiBi} + 5\text{LiVO}_3$        $-20.553 \text{ eV} (-1983 \text{ kJ mol}^{-1})$
53.  $22\text{Li} + 5\text{BiVO}_4 \rightarrow \text{Li}_5\text{BiO}_5 + 4\text{Li}_3\text{Bi} + 5\text{LiVO}_3$        $-26.051 \text{ eV} (-2514 \text{ kJ mol}^{-1})$
54.  $41\text{Li} + 10\text{BiVO}_4 \rightarrow 3\text{Li}_5\text{BiO}_5 + 7\text{Li}_3\text{Bi} + 5\text{LiV}_2\text{O}_5$        $-48.125 \text{ eV} (-4643 \text{ kJ mol}^{-1})$
55.  $27\text{Li} + 10\text{BiVO}_4 \rightarrow 3\text{Li}_5\text{BiO}_5 + 7\text{LiBi} + 5\text{LiV}_2\text{O}_5$        $-38.505 \text{ eV} (-3715 \text{ kJ mol}^{-1})$