

Supporting Information for:

New high capacity anodes based on nanoparticle vanadium phosphides

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Synthesis Procedure.

*Synthesis of (nanoparticle) ball milled VP_x.*¹

Materials. Vanadium powder (325 mesh powder, 99.5% metal basis, Aldrich); red Phosphorous powder, (99% metal basis, Aldrich). *VP_x Synthesis.* Alloyed Vanadium phosphides (VP_x) were synthesized by mechano-chemical synthesis using a ball mill (Fritsch Pulverisette 7 Mill). Vanadium (2.0 g, 0.039 mol, 1 equiv) and red phosphorous (4.86 g, 0.157 mol, 4 equiv) were added to *each* of the two bowls (Hard Metal Tungsten Carbide grinding bowls, 80mL capacity) in an argon filled glovebox. (Note, the reaction is carried out identically in two bowls so as to have a balanced system.) 1.6 mm tungsten carbide balls (6.86 g) were then added to each of the grinding bowls and the lids were secured and locked in place. The bowls were removed from the glovebox and inserted into the ball mill. The ball mill was run at 1000 rpm for 96 cycles with each cycle consisting of 60 minutes with 10 minute resting intervals. The temperature was monitored using an IR gun to ensure the external temperature of the bowls did not rise above 100 °C. Periodically the reaction was paused and the surface fittings all tested for tightness. Upon completion of the reaction the powder was isolated from the balls by sieving and analyzed by XRD and BET.

Materials Characterization

Powder X-ray Diffraction (PXRD). VP_x powder was placed onto a zero background holder purchased from The Gem Dugout, State College, PA 16803. Samples were scanned at a rate of 0.024°/15 s in the 2θ range of 10–80° on a Bruker D8 Advance diffractometer in Bragg-Brentano geometry with Cu Kα radiation and a diffracted beam graphite monochromator. Phase identification was determined from the PXRD patterns using Jade 9 software suite. PXRD spectrum is shown in Figure S1.

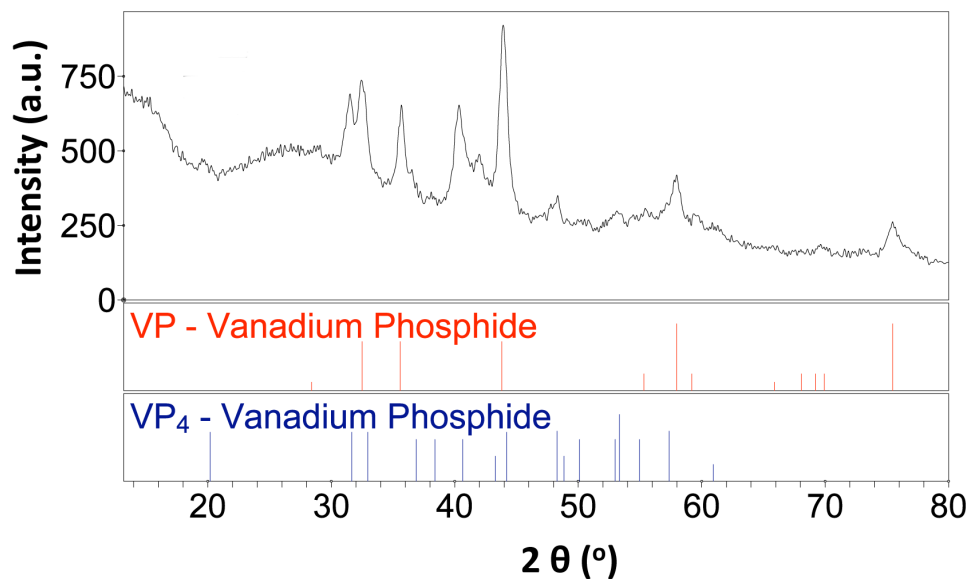


Figure S1. PXRD spectrum for VP_x from ball milling reaction. VP_4 (JCPDS file no. 00-035-1461), and VP (JCPDS file no. 00-038-0943) indexes are shown.

Scanning Electron Microscopy (SEM). VP_x powder was dispersed onto carbon tape from TedPella and imaged using a Zeiss Supra 55VP field emitter gun scanning electron microscope (FEGSEM).

Brunauer-Emmett-Teller (BET) surface area analysis. N₂ adsorption/desorption on composite samples was measured using a Micrometrics Tristar 3000 sorptometer, Figure S2. A BET value of 11.6 m²/g was obtained.

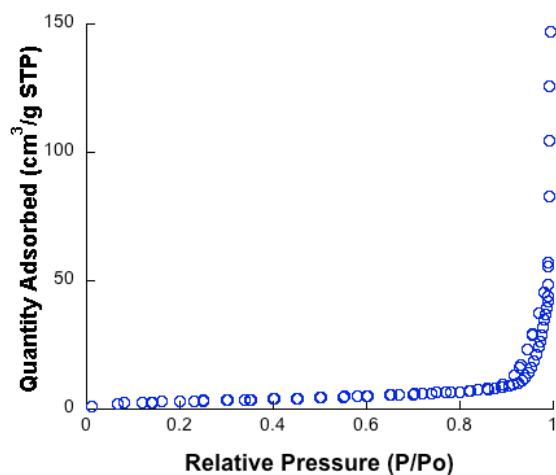


Figure S2. Nitrogen sorption isotherm for VP_x

Electrode Preparations and Discharge

Electrodes were prepared by drop-casting an aliquot of VP_x ink (200 μL) onto a nickel disc (diameter = 5/8", 8 μm thickness) via micropipette and allowed to dry at room temperature for approximately 4 to 6 hours. Aliquots were taken from a homogeneously dispersed ink prepared as follows: 90.0 mg of VP_x and 10.0 mg of SAB Carbon were mixed with 2.4 mL 5% Nafion and 1.6 mL isopropanol. The mixture was sonicated (bath sonicator) at room temperature for a minimum of 1 hour.

For electrochemical testing, electrodes were placed in a PTFE holder exposing 1 cm² of surface to the electrolyte solution. The electrodes were discharged galvanostatically in one of two formats: Format 1.) A three-electrode format: with VP_x as the working electrode with Platinum foil (~ 2.5 cm²) and Hg/HgO (0.1M KOH) serving as the counter and reference electrodes, respectively. Format 2.) A two-electrode format: with Electric FuelsTM E4 air cathode as the working electrode and the VP_x (reference shorted) as the counter. Supporting electrolyte was either aqueous 30% KOH or 2 M K₂CO₃. Galvanic discharges were performed on either a PAR 273 or Solatron 1287 potentiostat controlled with CorrwareTM software from Scribner Associates. In all cases, discharge capacities are reported for discharge to 0 V. Data was processed using Kaleidagraph for presentation purposes.

Corrosion Analysis

In order to improve the discharge capacities, methods to prevent the competing chemical corrosion reaction of the VP_x anode surface were desired. ZrO_2 coatings on VB_2 (referred to here as $ZrO_2:VB_2$), and other electrode surfaces, has been offered as one method to improve electrode performance by acting as a hydroxide shuttle/barrier layer.² While we found this method was useful in lowering the average corrosion currents for VB_2 from $25.1 \mu A cm^{-2}$ (VB_2) to $10.7 \mu A cm^{-2}$ ($ZrO_2:VB_2$), it was found to be ineffective when used analogously with VP_x , Tables S1 and S2. Obtained corrosion currents were very similar at $42 \mu A cm^{-2}$ (VP_x) and $47.1 \mu A cm^{-2}$ ($ZrO_2:VP_x$) in 30% KOH and $16.4 \mu A cm^{-2}$ (VP_x) and $16.0 \mu A cm^{-2}$ ($ZrO_2:VP_x$) in 2 M K_2CO_3 . Notably, submersion of $ZrO_2:VP_x$ in 30% KOH still gave visible gas generation on the electrode surface, suggestive of incomplete coverage with ZrO_2 , consistent with the high rate of corrosion.

Corrosion measurements were performed on either a VoltaLab 40 or VoltaLab 10 potentiostat (Radiometer Analytical), controlled by the VoltaMaster software. Samples were held in a PTFE holder, exposing $1 cm^2$ area to the solution, with a Pt counter electrode and Hg/HgO (0.1 M KOH) reference electrode. Samples were typically immersed in the electrolyte for approximately 1-2 hours to equilibrate prior to measurements. A minimum of three independent samples was used for each material of interest. Potentiodynamic polarization measurements were performed at 0.2 mV/s. Polarization resistance, corrosion current and Tafel slopes were all determined by fitting with the VoltaMaster software (e.g. Figure S3). Electrochemical impedance spectroscopy (EIS) measurements were run at open circuit potential from 100 kHz to 10 mHz, with a 5 mV signal. Polarization resistances were determined by fitting this data to a circuit model using ZView software (Scribner Associates) (e.g. Figure S4). $ZrO_2:VP_x$ and $ZrO_2:VB_2$ (5% ZrO_2) were prepared following a literature procedure.²

Unfortunately, corrosion measurements on AEM: VP_x proved problematic and could not reliably be obtained.

Table S1. Corrosion Summary for VP₄ electrodes^a

Material	Electrolyte	Average R _p from EIS (kΩ)	Average R _p from Tafel (kΩ)	Average corrosion current (μA cm ⁻²) from Tafel
VP _x	30% KOH	0.57(0.19)	0.64(0.18)	42.0(9.3)
ZrO ₂ :VP _x	30% KOH	0.52(0.16)	0.58(0.18)	47.1(15.2)
VP _x	2 M K ₂ CO ₃	1.90(1.52)	1.50(0.53)	16.4(5.0)
ZrO ₂ :VP _x	2 M K ₂ CO ₃	1.44(0.72)	1.60(0.77)	16.0(8.9)

^aValues in parentheses are standard deviations; ^b Assumes 19 e⁻ for VP_{2.8} average composition (60% VP₄ and 40% VP)

Table S2. Corrosion Summary for VB₂ electrodes^a

Material	Electrolyte	Average R _p from EIS (kΩ)	Average R _p from Tafel (kΩ)	Average corrosion current (μA cm ⁻²) from Tafel
Nano VB ₂	30% KOH	0.94(0.27)	0.93(0.10)	25.1(2.8)
ZrO ₂ :VB ₂	30% KOH	1.70(1.03)	3.51(2.65)	10.7(7.6)

^aValues in parentheses are standard deviations

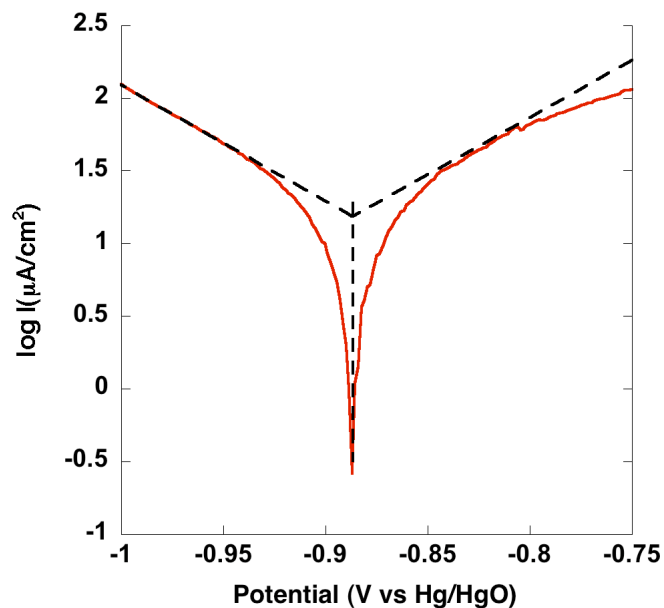


Figure S3. Representative Tafel Plot for VP_x

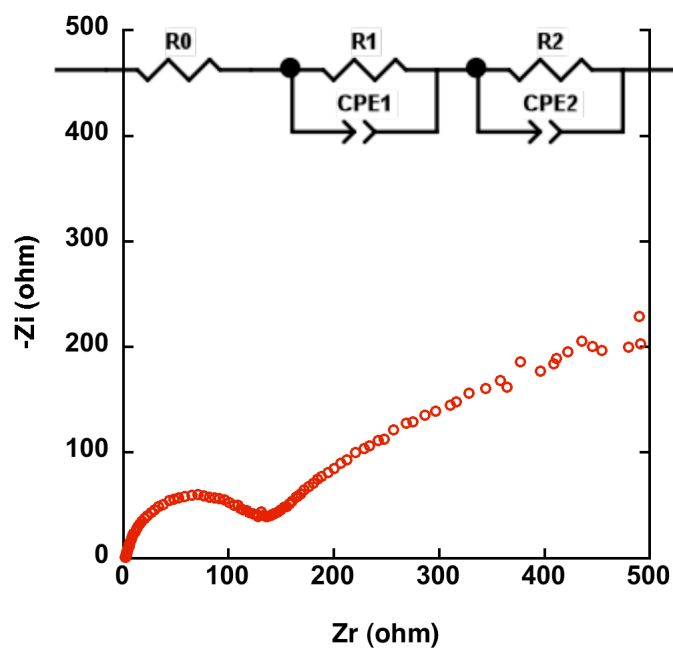
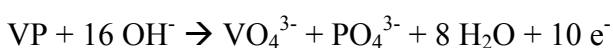


Figure S4. Representative EIS Data with equivalent circuit scheme shown

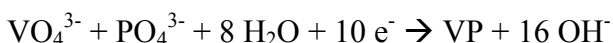
Estimation of Full Cell Voltage for Vanadium monophosphide/air cell (VP/air)

Little thermodynamic data is available for vanadium phosphides.³ However, the overall cell voltage for VP can be calculated from known thermodynamic data as follows.

Species	VP	OH ⁻	VO ₄ ³⁻	PO ₄ ³⁻	H ₂ O
Δ _f G (kJ/mol)	-270	-157.2	-899	-1018.7	-237.1
Source	Ref ⁴	CRC Handbook ⁵	CRC Handbook	CRC Handbook	CRC Handbook



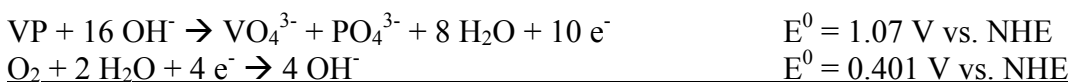
Written as a reduction:



$$\begin{aligned} \Delta_{\text{reaction}}G &= \Delta_{\text{formation}}G(\text{products}) - \Delta_{\text{formation}}G(\text{reactants}) \\ &= \Delta_{\text{f}}G(\text{VP}) + 16\Delta_{\text{f}}G(\text{OH}^-) - \Delta_{\text{f}}G(\text{VO}_4^{3-}) - \Delta_{\text{f}}G(\text{PO}_4^{3-}) - 8\Delta_{\text{f}}G(\text{H}_2\text{O}) \\ &= (-270) + 16(-157.2) - (-899) - (-1018.7) - 8(-237.1) \\ &= 1029.3 \text{ kJ/mol} \end{aligned}$$

$$\Delta_{\text{r}}G = -nFE^0$$

$$E^0 = -\Delta_{\text{r}}G/nF = 1.0293\text{e}6 \text{ (J mol}^{-1}\text{)} / [(10)(96485 \text{ C mol}^{-1})] = -1.07 \text{ V vs. NHE}$$



Theoretical volumetric capacities of VP, VP₂ and VP₄ were calculated using known MW, the respective number of electrons from equations 1-3 in the main text and the x-ray densities obtained from the JCPDS index data files.

Membrane Preparation

Anion exchange membranes (AEMs) based on a poly(phenylene) backbone prepared by a Diels-Alder reaction as previously described.⁶ Select data for polymers used in this study are presented in Table S3. Polymers 7-30-B and 7-90-F were homo-polymers with the ionic groups randomly distributed.

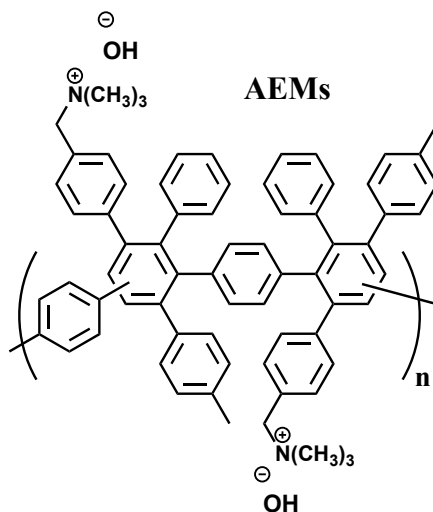


Table S3. Properties for Alkaline Exchange Membranes used in this study.^a

Membrane	Thickness (μm)	Measured IEC (mequiv g ⁻¹)	Conductivity (mS/cm)	Water uptake (%)
07-30-B	90	2.25	44	114
07-90-F	90	2.31	45	118

^aMeasurements were made with the polymers in hydroxide form. The thickness is for hydrated membranes. Conductivities were measured in water at room temperature.

Additional Membrane Studies

Cyclic voltammetry was conducted on Nickel (Ni) foil (working electrode) and AEM:Ni foil assembly in 30% KOH versus a Platinum counter, Figure S5. In the case of Nickel foil, the oxidation/reduction for $\text{Ni}^{2+}/\text{Ni}^{3+}$ is observed. When the AEM is placed in between the electrolyte and the Ni foil, there is a decrease in capacitive charging at the Nickel surface and an obvious lack of oxidation/reduction occurring, consistent with a lower effective concentration of hydroxide at the Ni surface.

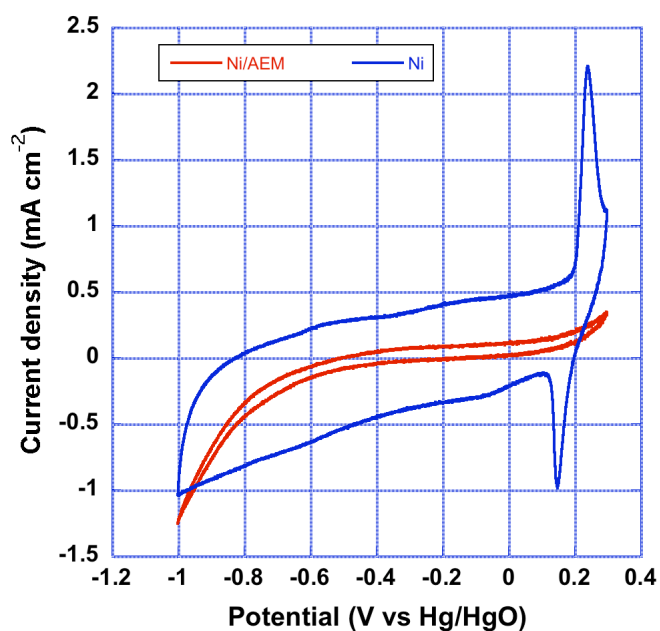


Figure S5. Cyclic voltammogram of (blue) Ni foil and (red) AEM:Ni foil assembly in 30% KOH vs Hg/HgO reference at 20 mV s⁻¹ scan rate.

Similarly for VP_x and AEM: VP_x as shown in Figure S6, a decrease in current and broadening for the VP_x oxidation peak is observed with AEM: VP_x as the concentration of the hydroxide is lowered near the electrode surface. The first half scan was performed in the positive direction starting at OCV. These scans were performed at a 0.05 mV s^{-1} scan rate to allow time for the oxidation of VP_x to occur.

In general, the lack of reduction peak on the return scan, also demonstrates that VP_x is an electrochemically irreversible system applicable to primary battery systems.

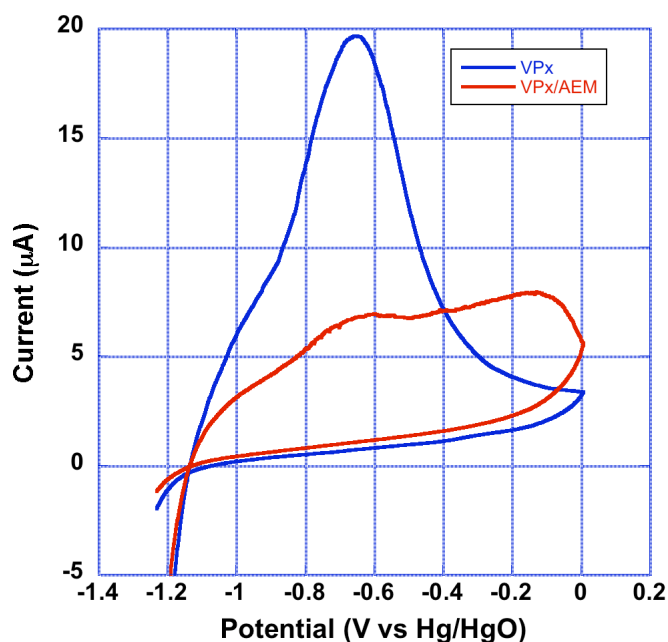


Figure S6. Cyclic voltammogram of (blue) VP_x and (red) AEM: VP_x assembly in 30% KOH vs Hg/HgO reference at 0.05 mV s^{-1} scan rate.

Corrosion reactions are typically accelerated above a certain critical (e.g. hydroxide) concentration⁷ and it is proposed that the AEM results in a lower hydroxide concentration at the VP_x surface with significantly decreased rates of corrosion, while still allowing for discharge to occur (at the rates examined). For a similar Zinc system, higher hydroxide concentrations also lead to enhance corrosion product dissolution, which further enhances corrosion.⁷ Hence, in addition to lowering the hydroxide concentration at the VP_x electrode surface, an additional explanation for reduced

corrosion could be that the membrane also limits diffusion of the corrosion products away from the anode surface, which inhibits the surface corrosion.

References

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