Negative electrode in aqueous systems (Huggins, ch. 10)

1. Zinc electrode (alkaline battery)

Zn-air battery

2. Cd electrode (Ni-Cd rechargeable battery)
3. Metal hydride electrodes

Positive electrode in aqueous systems (Huggins, ch. 11)

1. MnO_2 electrode
2. Ni electrode

15. Other topics related to electrodes (Huggins, ch. 12)

1. Mixed-conducting host structures
2. Flow batteries
3. Fine particle electrodes

12A Mixed-Conducting Host Structures into Which Either Cations or Anions Can Be Inserted

12A.2 Insertion of Species into Materials with Transition Metal Oxide Bronze Structures

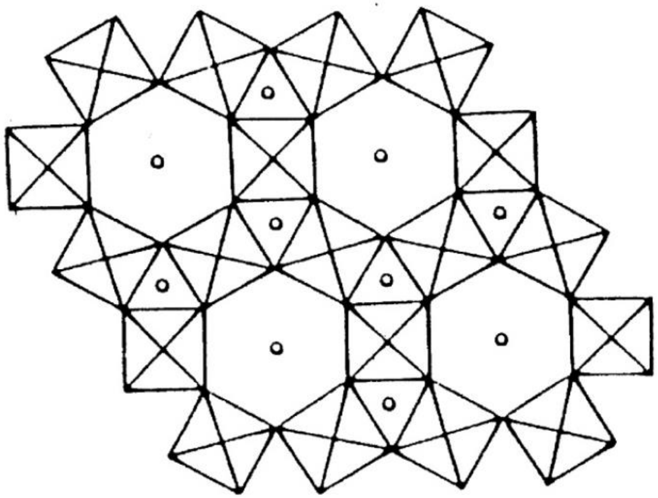


Fig. 12A.1 Representation of the hexagonal tungsten bronze structure in the *c*-direction, *small circles* show the presence of both large and small tunnel sites

Li^+ cations can subsequently be inserted into this structure at room temperature. They go into the set of smaller tunnels that are oriented in the cross-direction, rather than into the large tunnels. The presence of the lithium ions causes the reduction of some of W^{6+} ions to W^{5+}, and the material becomes dark. Thus the low temperature insertion of Li^+ cations, which is both very rapid and reversible, can be employed to make this an interesting electrochromic material [1–4].

12A.4 Hexacyanometallates

There is a family of materials with crystal structures that are analagous to the BX_3 *rhenium trioxide* and ABX_3 *perovskite* materials, but in which the X positions are occupied by cyanide anions, which are appreciably larger than oxide ions. These materials are sometimes called hexacyanometallates, and the B positions are often occupied by transition metal ions. The transition metal hexacyanometallates are examples of the large family of insoluble mixed-valence compounds. An overview of

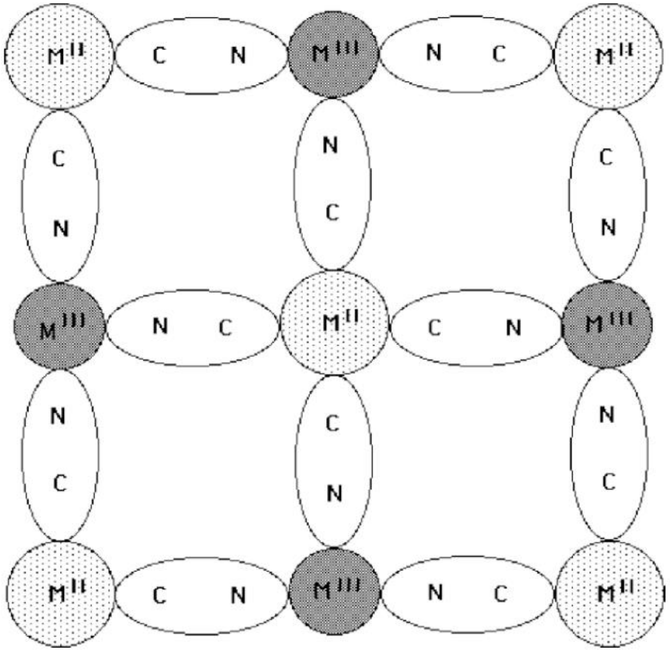


Fig. 12A.2 Schematic representation of one plane in the structure of the hexacyanometallate host lattice

The prototype material is “Prussian blue,” which is also sometimes called “Berlin blue.” Its nominal formula is $KFe_2(CN)_6$, or $K_{0.5}Fe(CN)_3$. It has a dark blue-black color, has been known for a very long time, and has been widely used as a dyestuff. It was evidently the first coordination compound reported in the scientific literature [12]. An account of the early work on the preparation and chemical composition of materials in the Prussian blue family can be found in [13]. They have been studied extensively because of their electrochromic properties, and there has been renewed interest in them in recent years in connection with their use in “modified electrode surfaces” that are interesting for catalytic purposes.

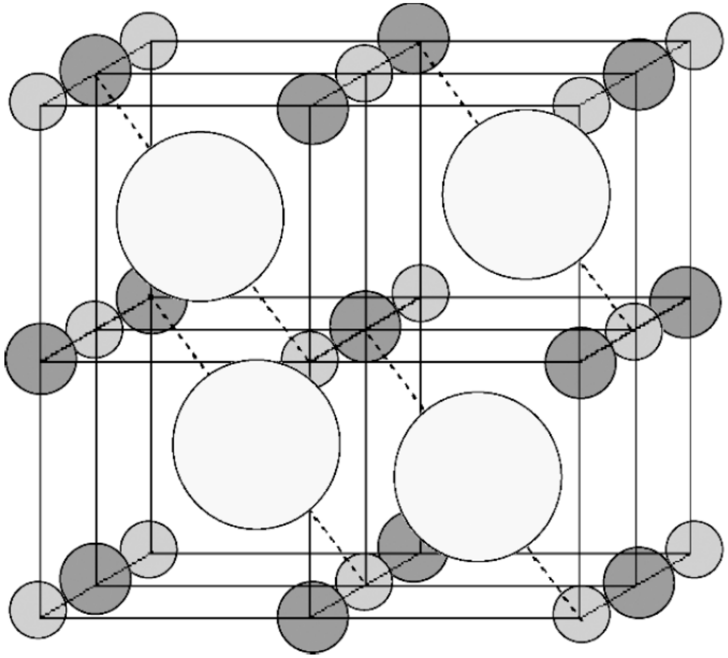


Fig. 12A.3 Schematic representation of the structure of Prussian blue, in which half of the A sites are filled

12A.5 Electrochemical Behavior of Prussian Blue

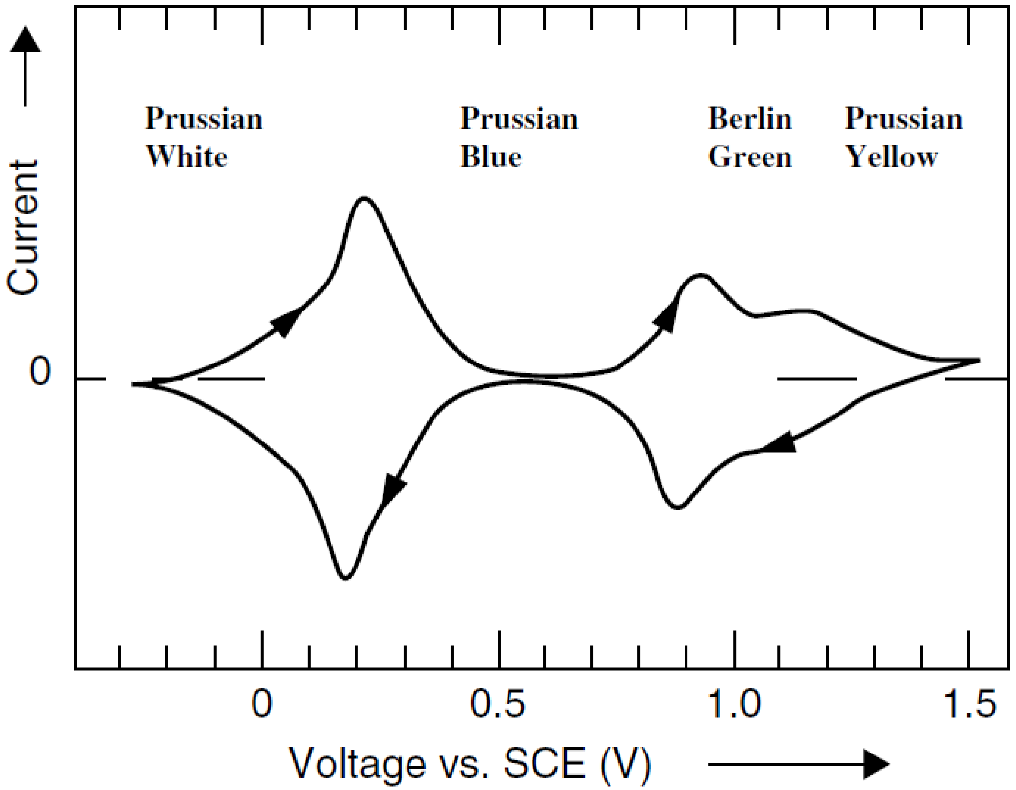


Fig. 12A.6 Voltammogram that also shows the reaction to form Prussian yellow at more positive potentials

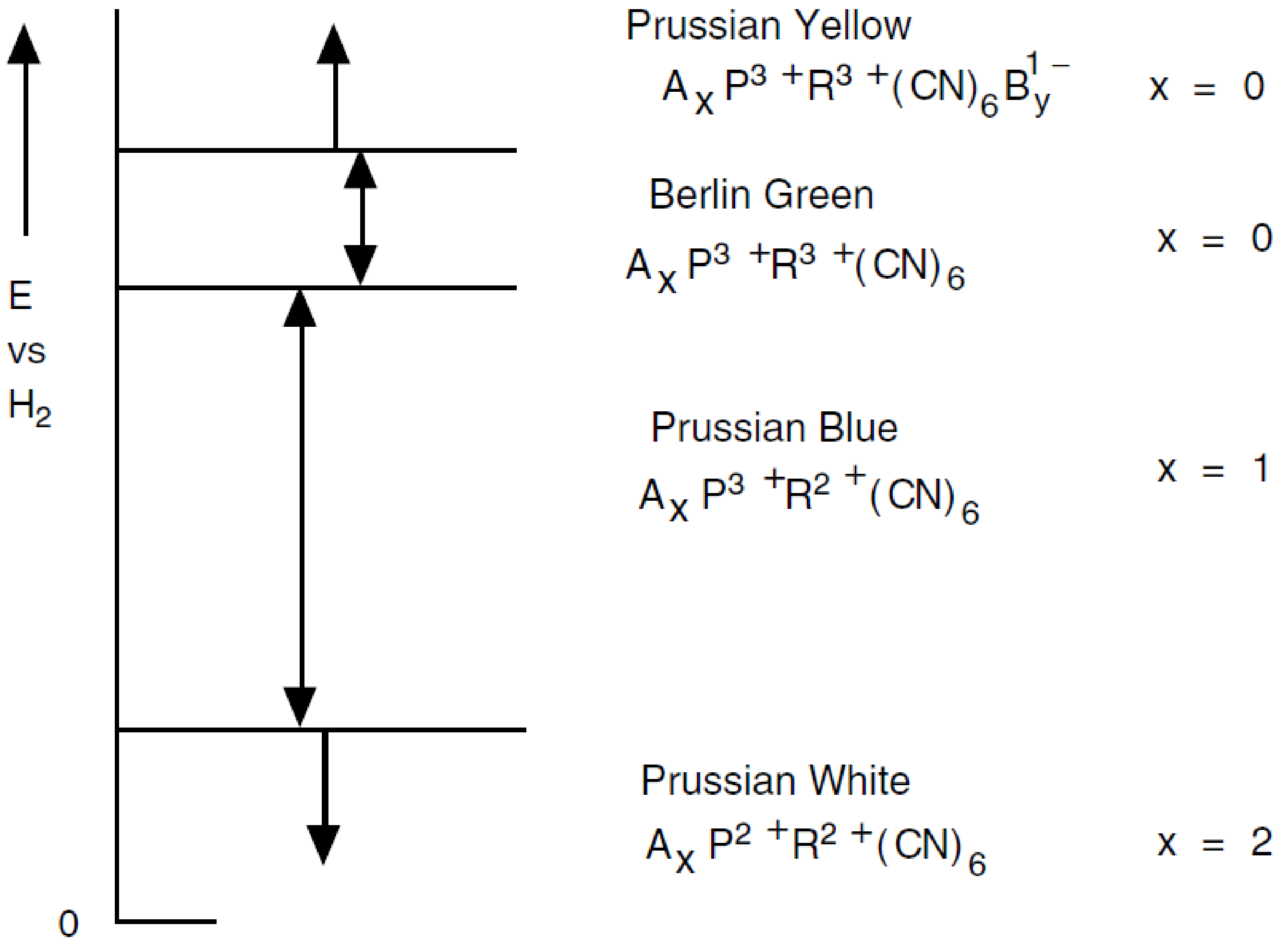


Fig. 12A.7 Schematic representation of the potentials at which the several reactions occur in Prussian blue

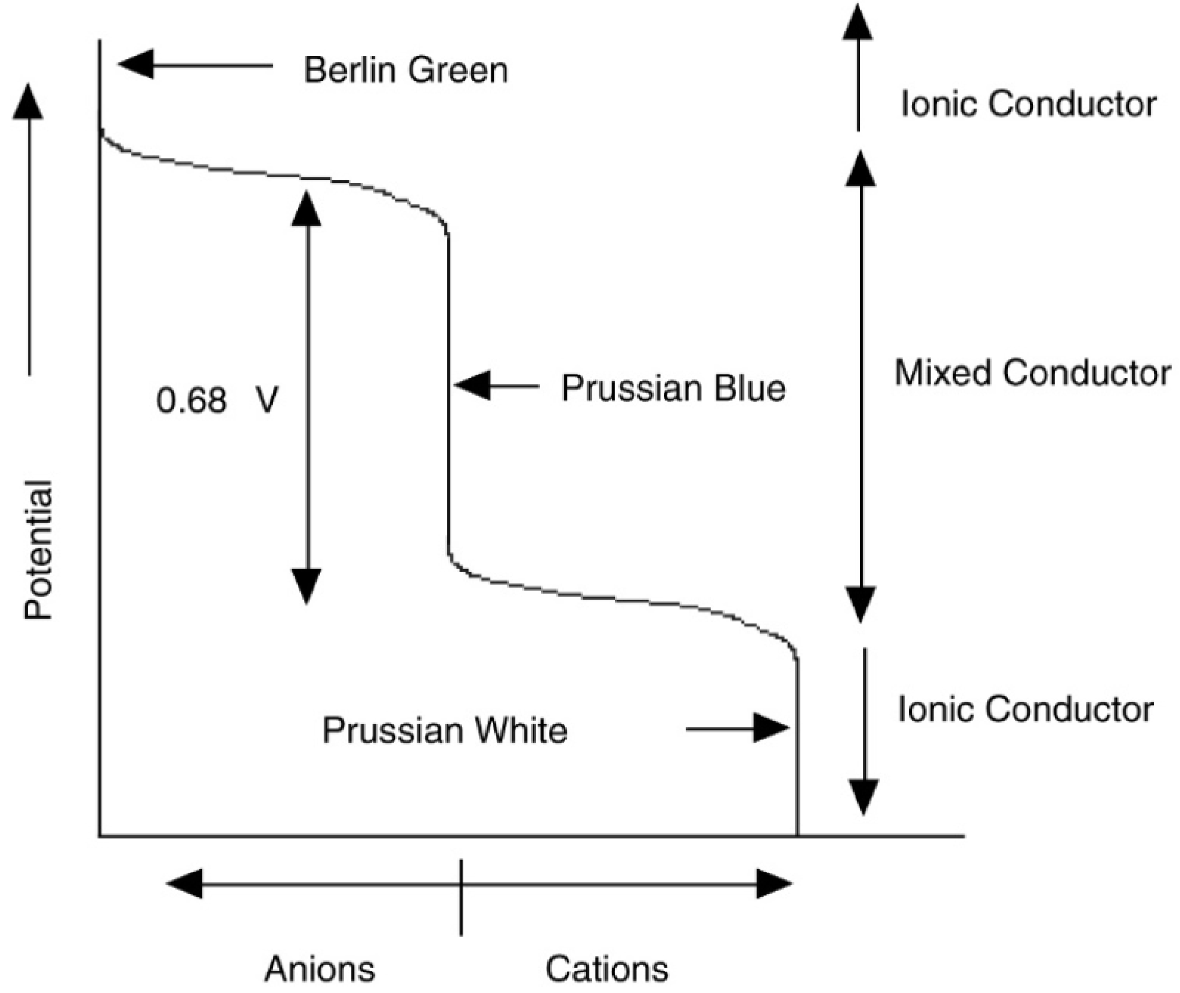


Fig. 12A.8 Schematic equilibrium electrochemical titration curve for the Prussian blue system

12A.6 Various Cations Can Occupy the A Sites in the Prussian Blue Structure

A number of different cations can be present in the A positions in the hexacyanometallate structure. Monovalent examples include Li^+, Na^+, K^+, NH_4^+, Rb^+, and Cs^+ ions. The ability of these various ions to reversibly enter the structure has been interpreted in terms of their size when hydrated. These are shown in Table 12A.1, which also includes the hydrated divalent Ba^{2+} ion.

Table 12A.1 Assumed radii of hydrated cations

Cation	Radii (Å)
Li^+	2.37
Na^+	1.83
K^+	1.25
$NH_4{}^+$	1.25
Rb^+	1.18
Cs^+	1.19
Ba^{2+}	2.88

12A.9 The Electronic Properties of Members of the Prussian Blue Family

Table 12A.2 Examples in which Fe ions have been replaced by other species

Substitution for Fe^{3+}	Substitution for Fe^{2+}
Mn^{3+}	Cu^{2+}
Co^{2+}, M^{+}	Os^{2+}
Ni^{3+}	Ru^{2+}
In^{3+}	Alkaline earth ions
Cu^{2+}, M^{+}	

Electrochromism (EC) ?

Reversible change its optical properties under applied voltage

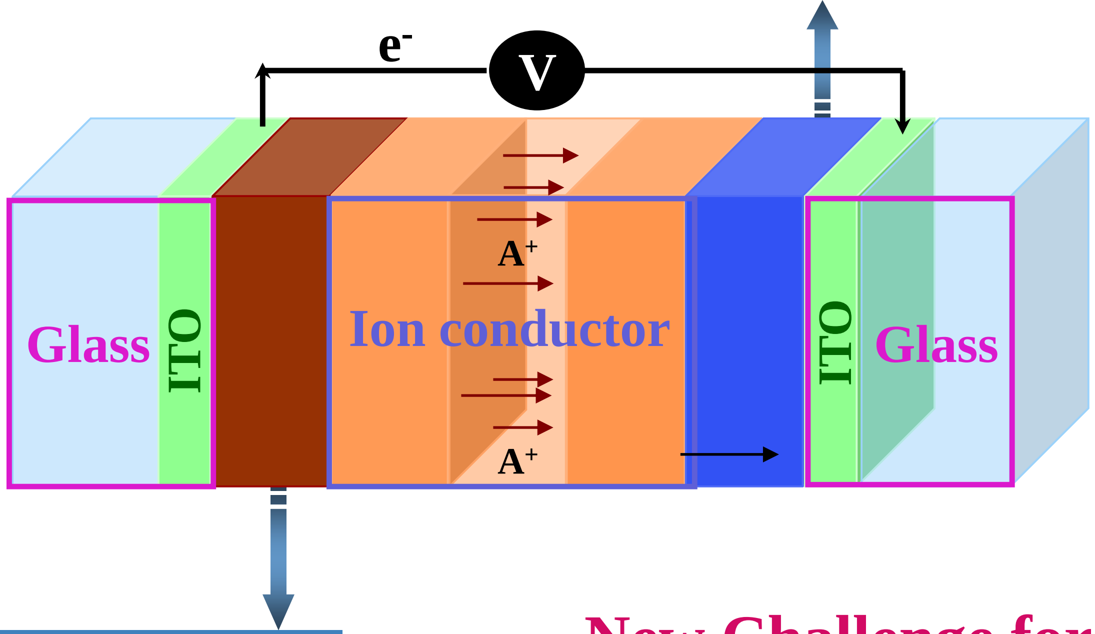
$MO_x + yA^+ + ye^- \leftrightarrow A_yMO_x$

(bleached) (colored)

($A^+ = H^+, Li^+, Na^+$, etc)

Cathodic coloration

Oxides of W, Ta, Mo, Nb, Cu, etc.



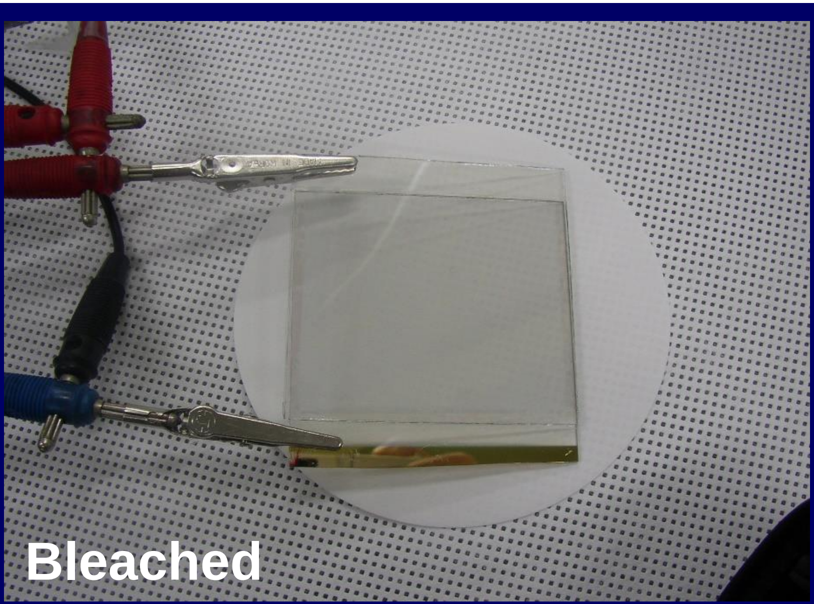
Anodic coloration

Oxides of Ni, V, Ti, Co, Mn, Fe, Ru, Ir, etc.

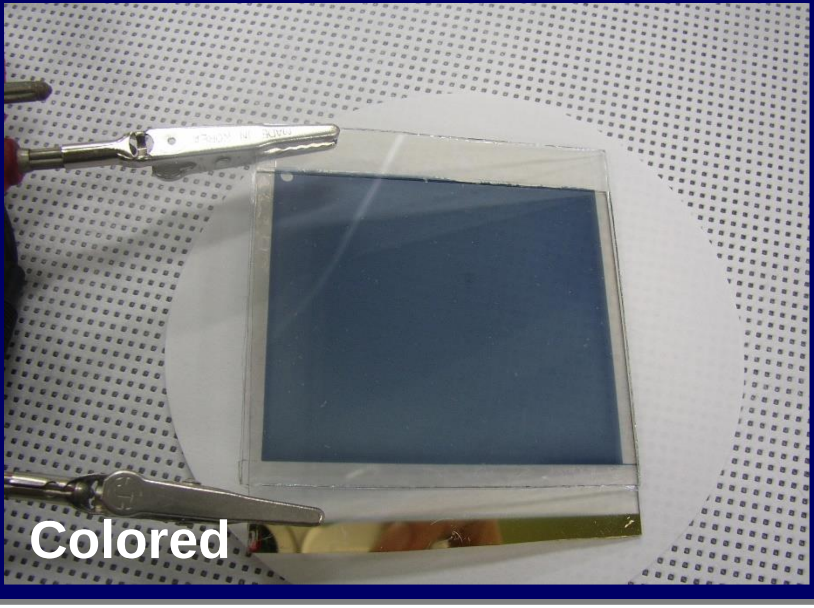
New Challenge for EC

- ✓ Battery Technologies
- ✓ Nanotechnology

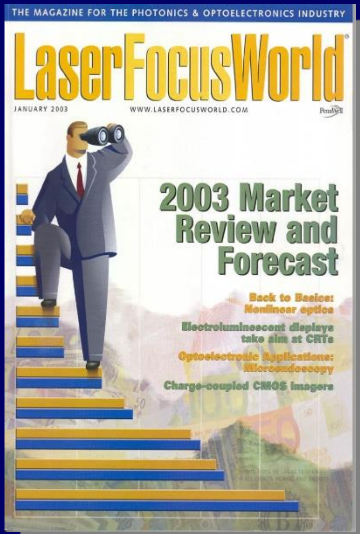
All-Solid-State Electrochromic Device (10×10 cm^2 area)



Bleached



Colored



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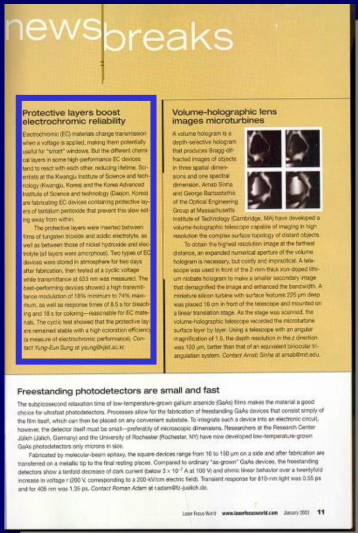

newsbreaks

Protective layers boost electrochromic reliability

Electrochromic (EC) materials change transmission when a voltage is applied, making them potentially useful for "smart" windows. But the different chemical layers in some high-performance EC devices tend to react with each other, reducing lifetime. Scientists at the Kwangju Institute of Science and technology (Kwangju, Korea) and the Korea Advanced Institute of Science and technology (Daejon, Korea) are fabricating EC devices containing protective layers of tantalum pentoxide that prevent this slow eating away from within.

The protective layers were inserted between films of tungsten trioxide and acidic electrolyte, as well as between those of nickel hydroxide and electrolyte (all layers were amorphous). Two types of EC devices were stored in atmosphere for two days after fabrication, then tested at a cyclic voltage while transmittance at 633 nm was measured. The best-performing devices showed a high transmittance modulation of 18% minimum to 74% maximum, as well as response times of 8.5 s for bleaching and 18 s for coloring—reasonable for EC materials. The cyclic test showed that the protective layers remained stable with a high coloration efficiency (a measure of electrochromic performance). *Contact Yung-Eun Sung at ysung@kjist.ac.kr.*

Volume-holographic lens images microturbines

A volume hologram is a depth-selective hologram that produces Bragg-diffracted images of objects in three spatial dimensions and one spectral dimension. Arnab Sinha and George Barbastathis of the Optical Engineering Group at Massachusetts Institute of Technology (Cambridge, MA) have developed a volume-holographic telescope capable of imaging in high resolution the complex surface topology of distant objects.

To obtain the highest resolution image at the farthest distance, an expanded numerical aperture of the volume hologram is necessary, but costly and impractical. A telescope was used in front of the 2-mm-thick iron-doped lithium niobate hologram to make a smaller secondary image that demagnified the image and enhanced the bandwidth. A miniature silicon turbine with surface features 225 μm deep was placed 16 cm in front of the telescope and mounted on a linear translation stage. As the stage was scanned, the volume-holographic telescope recorded the microturbine surface layer by layer. Using a telescope with an angular magnification of 1.5, the depth resolution in the z direction was 100 μm, better than that of an equivalent binocular triangulation system. *Contact Arnab Sinha at arnab@mit.edu.*

Freestanding photodetectors are small and fast

The subpicosecond relaxation time of low-temperature-grown gallium arsenide (GaAs) films makes the material a good choice for ultrafast photodetectors. Processes allow for the fabrication of freestanding GaAs devices that consist simply of the film itself, which can then be placed on any convenient substate. To integrate such a device into an electronic circuit, however, the detector itself must be small—preferably of microscopic dimensions. Researchers at the Research Center Jülich (Jülich, Germany) and the University of Rochester (Rochester, NY) have now developed low-temperature-grown GaAs photodetectors only microns in size.

Fabricated by molecular-beam epitaxy, the square devices range from 10 to 150 μm on a side and after fabrication are transferred on a metallic tip to the final resting places. Compared to ordinary "as-grown" GaAs devices, the freestanding detectors show a tenfold decrease of dark current (below 3×10^{-7} A at 100 V) and ohmic linear behavior over a twentyfold increase in voltage r (200 V, corresponding to a 200-kV/cm electric field). Transient response for 810-nm light was 0.55 ps and for 405 nm was 1.35 ps. *Contact Roman Adam at r.adam@fz-juelich.de.*

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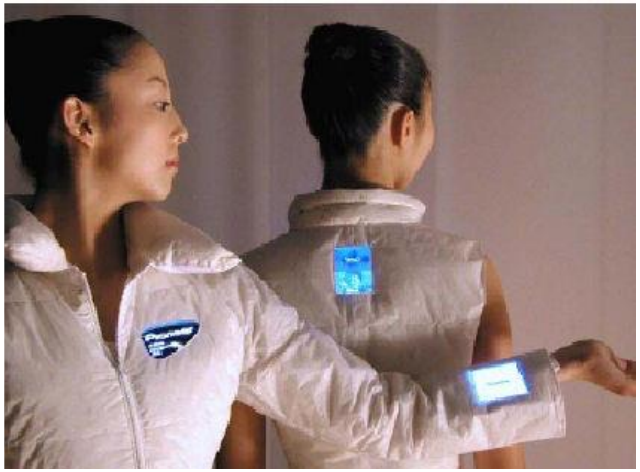
Applications of Electrochromic Devices

[Rear View Mirror]

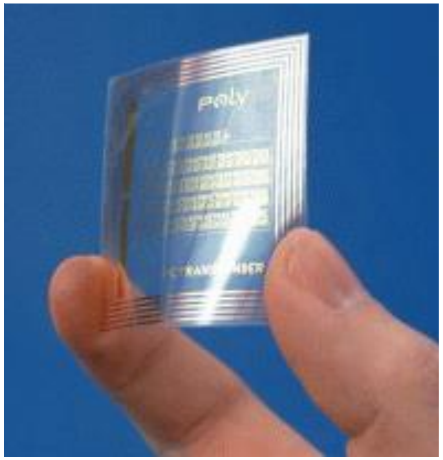
[Portable Screen]



[Smart Textile]

Electrochromic devices

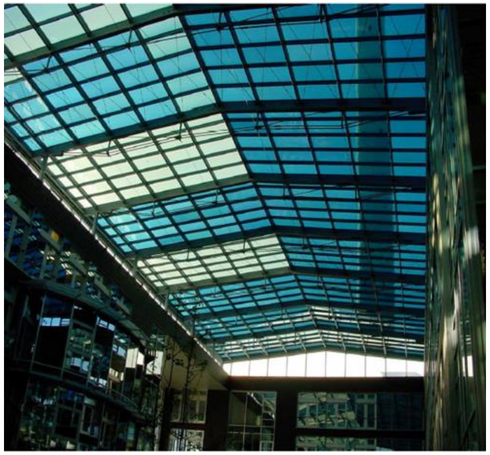
[RFID tag]



[Smart Card]

[e-Paper]

[Smart Window]



12B Cells with Liquid Electrodes: Flow Batteries

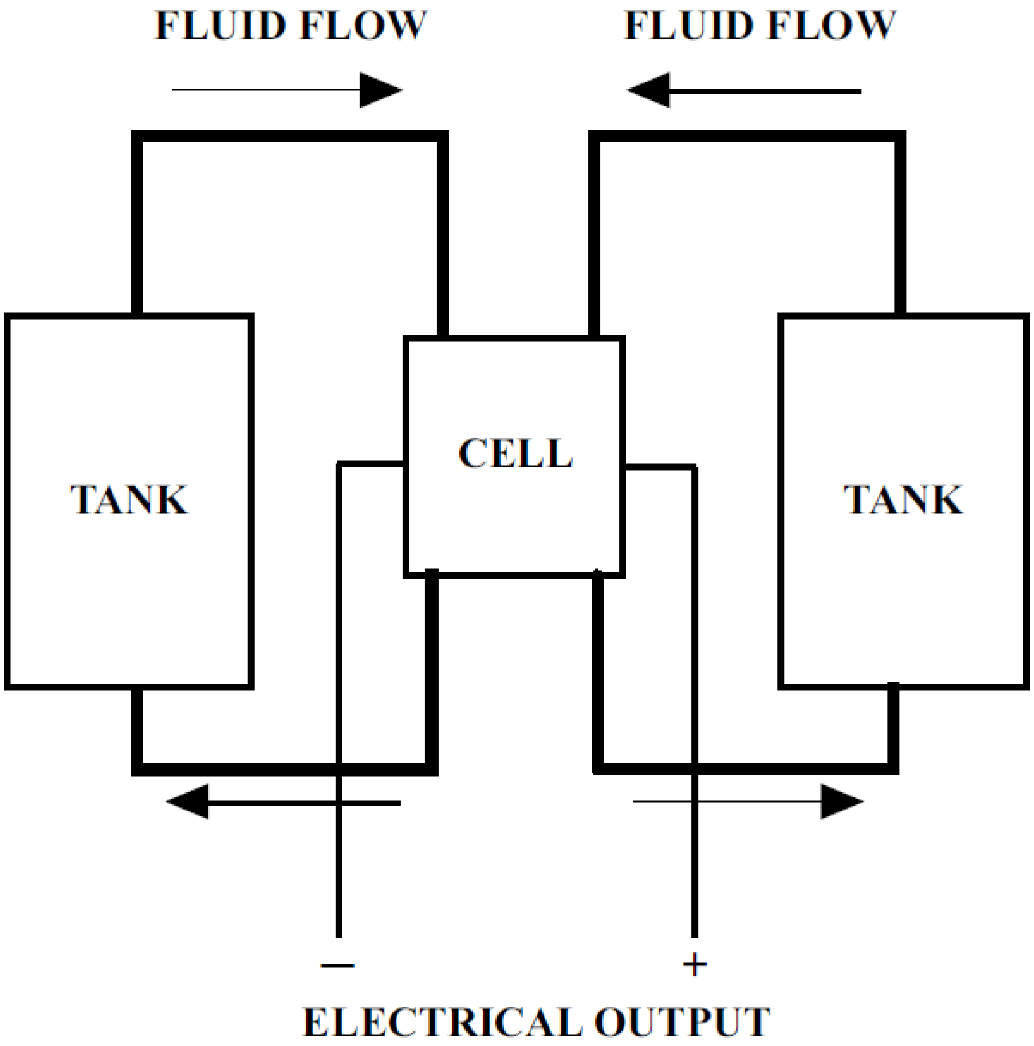


Fig. 12B.1 General physical arrangement of a flow battery

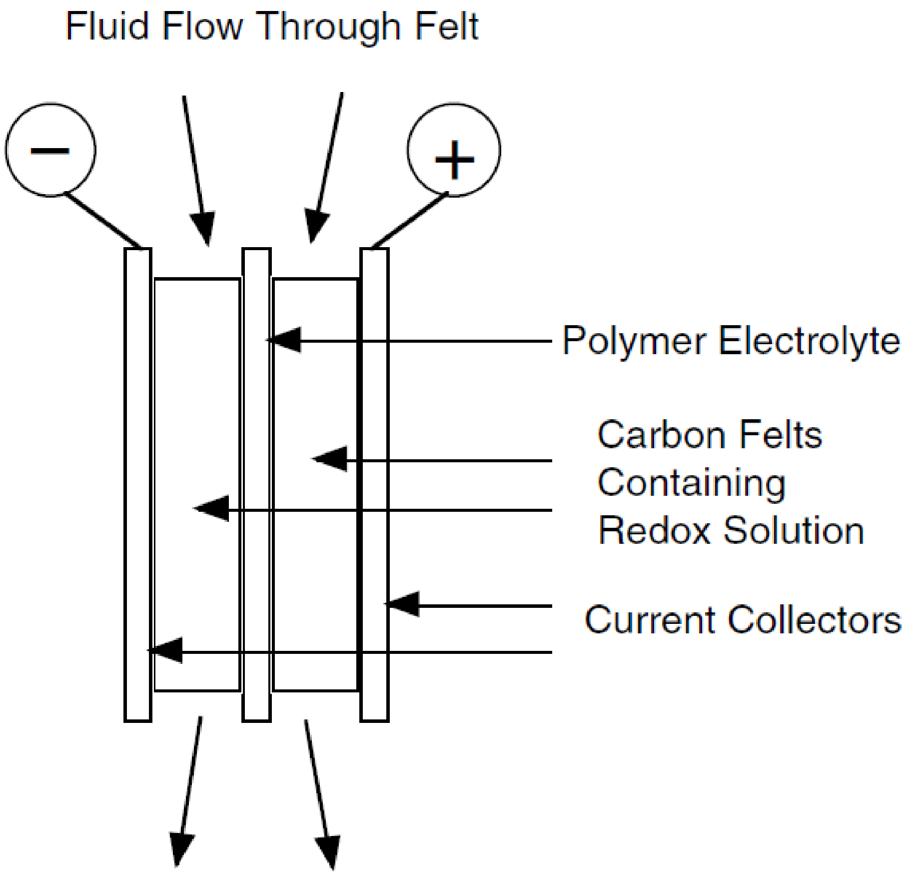


Fig. 12B.2 The cell portion of the system. In some cases there are multiple bipolar cell configurations

Table 12B.1 Various redox systems used in flow batteries

System	Negative electrode reactant	Positive electrode reactant	Nominal voltage
V/Br	V	Bromine	1.0
Cr/Fe	Cr	Fe	1.03
V/V	V	V	1.3
Sulfide/Br	Polysulfide	Bromine	1.54
Zn/Br_2	Elemental Zinc	Bromine	1.75
Ce/Zn	Zn	Ce	<2

12B.2 Redox Reactions in the Vanadium/Vanadium System

One can write the reactions in the electrode solutions of the vanadium system as

$$VO_2{}^+ + 2H^+ + e^- = VO^{2+} + H_2O \tag{12B.1}$$

or in terms of the vanadium ions

$$V^{5+} + e^- = V^{4+} \tag{12B.2}$$

in the positive electrode reactant solution, and

$$V^{2+} = V^{3+} + e^- \tag{12B.3}$$

in the negative electrode reactant solution.

So that the overall reaction is

$$VO_2{}^+ + 2H^+ + V^{2+} = VO^{2+} + H_2O + V^{3+} \tag{12B.4}$$

or

$$V^{5+} + V^{2+} = V^{4+} + V^{3+} \tag{12B.5}$$

12B.3 Resultant Electrical Output

The variation of the open circuit cell potential with the state of charge in the case of the V/V system with concentrations of 2 mol l^{-1} of each V species is shown in Fig. 12B.3. Typical operation would involve cycling between 20 and 80% of capacity, and thus at voltages between 1.3 and 1.58 V.

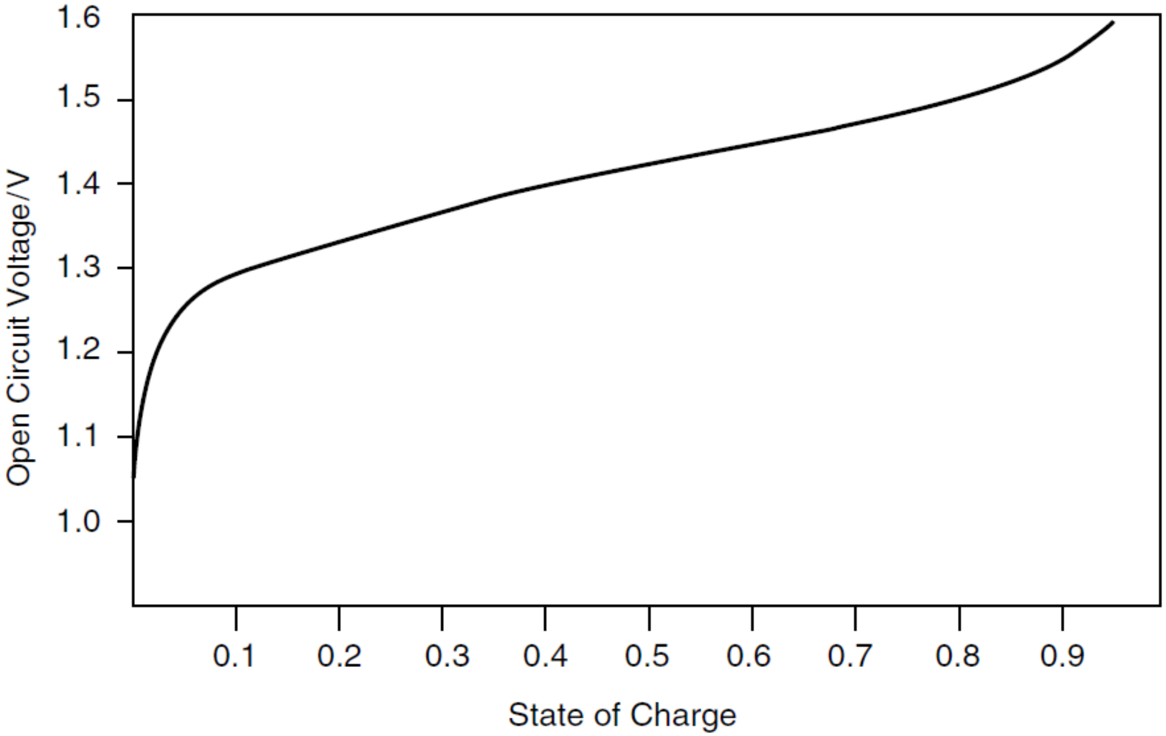


Fig. 12B.3 Variation of the open circuit potential vs. state of charge for the case of V/V flow cell at 298 K