

# In Situ FT-IR/ATR Spectroelectrochemistry of Prussian Blue in the Solid State

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**Interfacial oxidation and reduction of Prussian Blue (PB),  $KFe^{III}[Fe^{II}(CN)_6] \cdot nH_2O$  ( $n \approx 10$ ), powder were probed in situ with Fourier transform infrared attenuated total reflection (FT-IR/ATR) spectroscopy. The combination of electrochemistry in the absence of liquid electrolyte with internal reflectance FT-IR spectroscopy was accomplished using a simple two-electrode sandwich-type cell in which a crystalline germanium served both as a working electrode and an infrared transparent element. Application of sufficiently large potential differences to sandwich electrodes led to oxidation and reduction of PB at opposing interfaces. The spectra, which were monitored by difference, clearly show changes in the cyanide stretching frequency range upon oxidation and reduction.**

There has been growing interest in the electrochemical studies in solid state, i.e., in the absence of liquid supporting electrolyte.<sup>1–12</sup> The applicable rigid or semirigid (nonfluid) systems typically contain mixed-valence sites between which electron self-exchange (hopping) is feasible. They also comprise sizable populations of mobile counterions capable of preserving electroneutrality and supporting redox reactions. This research is of potential importance for characterization of materials, development of novel electrocatalytic sensors for gases, construction of rechargeable batteries, and design of electrochemical charge capacitors and molecular electronic devices.

In the present work, we propose coupling solid-state voltammetry with Fourier transform infrared attenuated total reflection

(FT-IR/ATR) spectroscopy.<sup>13,14</sup> The approach permits monitoring of interfacial (i.e., in the vicinity of electrode surface) changes in the infrared spectrum of the investigated material as a function of applied potential. Prussian Blue (PB), iron(III) hexacyanoferrate(II), a prototype of polynuclear mixed-valence metal cyanometallates,<sup>6,15–22</sup> was chosen as a model system due to its suitability for both solid-state electrochemical<sup>23</sup> and IR<sup>15</sup> measurements.

There are two forms of PB, the so-called “soluble” PB,  $KFe^{III}[Fe^{II}(CN)_6] \cdot nH_2O$ , and “insoluble” PB,  $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot nH_2O$ . We focus here only on the “soluble” analogue for the following reasons. While “insoluble” PB cannot show ionic conductivity because it has no structural potassium ions, the “soluble”  $KFe^{III}[Fe^{II}(CN)_6] \cdot nH_2O$  system is characterized by high ionic mobility of hydrated  $K^+$  counterions not only upon exposure to potassium electrolyte but also under solvent-free conditions. Consequently, electrochemical experiments with “soluble” PB in the absence of liquid electrolyte were feasible.<sup>4,6,17,23</sup> A simple two-electrode cell was proposed and applied to monitoring redox reactions of PB powder sandwiched between two opposing electrodes.

PB is particularly attractive for infrared studies since the system contains the strongly absorbing CN functional group. The FT-IR/ATR technique is suited ideally to the analysis of highly absorbing substances and thin films.<sup>13</sup> In ATR sampling mode, the IR incident beam is passed into an infrared-transparent element at an angle so that it is reflected internally a number of times. In the interfacial region, the beam penetrates a small distance into the less dense medium of investigated material and yields its spectrum. ATR does not require special sample pretreatment (e.g., mixing with KBr) and is applicable to granular samples, e.g.,

- (1) Dalton, E. F.; SurrIDGE, N. A.; Jernigan, J. C.; Wilburn, K. O.; Facci, J. S.; Murray, R. W. *Chem. Phys.* **1990**, *141*, 143.
- (2) SurrIDGE, N. A.; Jernigan, J. C.; Dalton, E. F.; Buck, R. P.; Watanabe, M.; Zhang, H.; Pinkerton, M.; Wooster, T. T.; Longmire, M. L.; Facci, J. S.; Murray, R. W. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 1.
- (3) Sullivan, M. G.; Murray, R. W. *J. Phys. Chem.* **1994**, *98*, 4343.
- (4) Rosseinsky, D. R.; Tonge, J. S.; Bertholt, J.; Cassidy, J. F. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 231.
- (5) Kulesza, P. J. *Inorg. Chem.* **1990**, *29*, 2395.
- (6) Kulesza, P. J.; Chelmecki, G.; Galadyk, B. *J. Electroanal. Chem.* **1993**, *347*, 417.
- (7) Kulesza, P. J.; Faulkner, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 11878.
- (8) Gorski, W.; Cox, J. A. *J. Electroanal. Chem.* **1992**, *323*, 163.
- (9) Jaworski, R. K.; Cox, J. A. *Electrochim. Acta* **1992**, *37*, 5.
- (10) Creasy, K. E.; Shaw, B. R. *J. Electrochem. Soc.* **1990**, *137*, 2353.
- (11) Kupis, D.; Ochmanska, J.; Galus, Z. *Pol. J. Chem.* **1992**, *66*, 1789.
- (12) Parthasarathy, A.; Martin, C. R.; Srinivasan, S. *J. Electrochem. Soc.* **1991**, *138*, 916.

- (13) Beden, B.; Lamy, C. In *Spectroelectrochemistry, Theory and Practice*; Gale, R. J., Ed.; Plenum: New York, 1988; Chapter 5.
- (14) von Felde, A.; Kern, K.; Higashi, G. S.; Chabal, Y. J.; Christman, S. P.; Blair, C. C.; Cardillo, M. J. *Phys. Rev. B* **1990**, *42*, 5240.
- (15) Itaya, K.; Uchida, I.; Neff, V. D. *Acc. Chem. Res.* **1986**, *19*, 162.
- (16) Hammett, A.; Higgins, S. J.; Mortimer, R. S.; Rosseinsky, D. R. *J. Electroanal. Chem.* **1988**, *255*, 315.
- (17) Feldman, B. J.; Murray, R. W. *Inorg. Chem.* **1987**, *25*, 1702.
- (18) Lin, R.-J.; Tushima, N. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 136.
- (19) Humphrey, B. D.; Sinha, S.; Bocarsly, A. B. *J. Phys. Chem.* **1987**, *91*, 586.
- (20) Xidis, A.; Neff, V. D. *J. Electrochem. Soc.* **1991**, *138*, 3637.
- (21) Habib, M. A.; Maheswari, S. P. *J. Electrochem. Soc.* **1992**, *139*, 2155.
- (22) Kulesza, P. J.; Brajter, K.; Zlotorzynska-Dabek, E. *Anal. Chem.* **1987**, *59*, 2776.
- (23) Kulesza, P. J. *J. Electroanal. Chem.* **1990**, *289*, 103.
- (24) Harrick, N. J. *Internal Reflection Spectroscopy*; Interscience: New York, 1967.

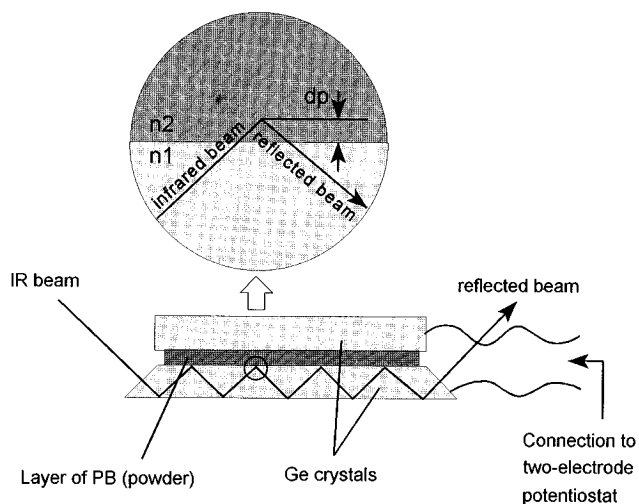


Figure 1. Cross-sectional view of the spectroelectrochemical cell combining a sandwich two-electrode design and ATR apparatus.

coal, without any significant scattering effects.<sup>25</sup> By analogy to the earlier spectroelectrochemical studies,<sup>13,14</sup> in which a multiple internal reflectance FT-IR experiment was performed at the electrode/liquid electrolyte interface, we utilize crystalline germanium as both a transparent material of high refractive index and as a working electrode.

#### EXPERIMENTAL SECTION

Electrochemical experiments (in the absence of contact with liquid electrolyte) were carried out in a sandwich configuration analogous to that described elsewhere.<sup>23</sup> The solid-state spectroelectrochemical design utilized the sandwich cell within a conventional internal reflectance apparatus. A schematic diagram is shown in Figure 1. The sandwich electrodes were two transparent crystalline germanium slides (from Harrick Corp., Ossing, NY). The germanium slide, which was connected as a working electrode, served also as an infrared-transparent element for ATR. Because the system operated in two-electrode mode, the second germanium slide was connected as both counter and reference electrodes. In some experiments, a layer of gold (thickness, 10–100 nm) was evaporated onto Ge slides to increase their conductivity. A sample ( $\sim 60\text{--}70\text{ mg cm}^{-2}$  of PB powder) was placed between these two opposing germanium electrodes (spacing,  $\sim 0.05\text{ mm}$ ). A germanium crystal (dimensions  $52 \times 20 \times 2\text{ mm}$ ) from Harrick was used. By application of the germanium element of relatively high geometric area and by proper adjustment of the incident angle ( $45^\circ$ ), the radiation was capable of undergoing multiple (50) internal reflections at the germanium/PB interface before passing to the detector. Absorption and attenuation took place at each of these reflections since the IR beam penetrated a short distance into the PB powder. The absorbances were independent of sample thickness, because the radiation penetrated only  $\sim 1\text{ }\mu\text{m}$  into the sample. This depth of penetration ( $dp$  in Figure 1) was estimated by the usual means<sup>13,14,20</sup> upon consideration of wavelength, indexes of refraction for germanium ( $n_1$ ) and PB ( $n_2$ ), and the angle of incidence. Depending on the potential difference applied to sandwich electrodes, PB could be oxidized or reduced in the interfacial region contacting the working electrode/ATR element.

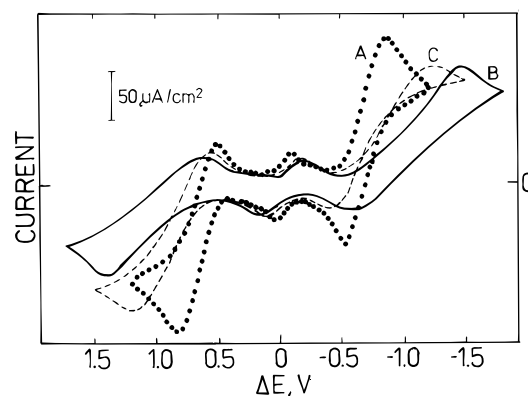


Figure 2. Solid-state voltammetric responses of PB powder sandwiched between two germanium electrodes. Curves were recorded when (A) a layer ( $\sim 50\text{ nm}$ ) of gold was deposited onto germanium surfaces, (B) bare germanium substrates were used, and (C) only a counter/reference germanium electrode was covered with a thick layer of gold ( $\sim 50\text{ nm}$ ). Scan rate,  $20\text{ mV s}^{-1}$ .

Electrochemical measurements were performed with the use of BAS 100 B/W electrochemical analyzer (West Lafayette, IN) or a conventional potentiostatic system. Before use, germanium electrodes were polished with diamond paste. IR measurements were done using a Perkin-Elmer 1615 FT-IR system equipped with a thermally stable DTGS detector. The investigated spectral range was from  $4400\text{ to }700\text{ cm}^{-1}$ . The signal was obtained by averaging 32 scans at resolution of  $4\text{ cm}^{-1}$ .

All chemicals were of analytical grade quality and were used as received. The samples were prepared by precipitation as reported earlier.<sup>23</sup> Based on determination of hydrogen content,  $n$  (i.e., number of stoichiometric water molecules in PB) has been found to be approximately equal to 10. The PB layers were fabricated on electrode slides by spreading finely, and freshly, ground PB powder (grain size,  $20 \pm 10\text{ }\mu\text{m}$ ; estimated using microsieves).

#### RESULTS AND DISCUSSION

**Voltammetric Experiments.** We have performed preliminary experiments to establish the practical utility of germanium elements as sandwich electrodes for solid-state electrochemistry. By analogy to earlier FT-IR/ATR spectroelectrochemical studies involving liquid electrolytes,<sup>13,14</sup> in order to improve conductivity of electrodes, we have considered evaporation of a thin layer of metal (Au) onto the semiconducting germanium elements. Figure 2 shows the solid-state (i.e., obtained in the absence of liquid electrolyte) voltammetric responses of a fairly thick layer ( $\sim 0.05\text{ mm}$ ) of PB powder pressed between two sandwich electrodes. Curve A stands for the voltammetric curve obtained with use of germanium electrodes covered (on one side) with gold. Since the two-electrode cell operates without any reference system, the applied potential differences ( $\Delta E$ ) polarize both electrodes in opposite directions. The actual sign of  $\Delta E$  implies only polarization of that Ge-slide electrode which was connected as working electrode. When  $\Delta E$  exceeds the value of  $\pm 0.7\text{ V}$ , which is approximately equivalent to the difference between the formal potentials for PB oxidation and reduction,<sup>15,23</sup> the system yields well-defined peaks (Figure 2A). Since both sandwich electrodes are virtually identical, the PB voltammetric peaks are symmetrical around  $\Delta E = 0\text{ V}$ . Regardless the direction of potential scan, PB (i.e.,  $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ ) undergoes (when  $\Delta E$  exceeds  $\pm 0.75$

(25) Mielczarski, J. A.; Denca, A.; Strojek, J. W. *Appl. Spectrosc.* **1986**, *40*, 998.

V) simultaneous oxidation to Prussian Yellow,  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ , and reduction to Everitt's salt,  $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ , at the interfaces formed by opposing electrodes. The respective equations describing PB redox reactions have been reported earlier.<sup>23</sup>

A typical voltammetric response of PB, recorded with the use of a sandwich cell (Figure 2A), also includes a set of fairly low peaks in the vicinity of 0 V (in addition to much larger peaks at  $\sim\pm 0.80$  V). The low currents appearing at  $\sim\pm 0.1$  V are believed to reflect electron transfer between  $\text{Fe}^{\text{III}}(\text{CN})_6$  and  $\text{Fe}^{\text{II}}(\text{CN})_6$ .<sup>23</sup> Application of small potential difference would be sufficient to drive electron self-exchange (hopping) between such hexacyanoferrate-(III,II) redox centers. The  $\text{Fe}^{\text{III}}(\text{CN})_6$  sites exist in PB at low levels because they originate from the  $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$  "impurity" in the  $\text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$  reagent used for preparation of PB.

The cyclic voltammetric response shown in Figure 2A strongly resembles the data reported earlier for PB investigated with use of the analogous sandwich design utilizing glassy carbon electrodes.<sup>23</sup> It can be concluded that, in such a solid-state electrochemical experiment, gold-covered germanium has similar operational characteristics similar to a carbon substrate.

We found that, following deposition of gold overlayer (having a thickness in excess of 15–20 nm) onto the germanium substrate, the transparency of the ATR element to infrared radiation was significantly (more than 2 orders of magnitude) lower so that investigation of PB by internal reflectance was practically precluded. Even when thinner gold layers, 5–15 nm, were used the FT-IR/ATR measurements of PB yielded spectra with a signal-to-noise ratio much lower in comparison to the result obtained with the use of bare germanium (Figure 3). Therefore, we favored bare crystalline germanium as a substrate for sandwich electrodes, particularly for the ATR element in the spectroelectrochemical cell. This approach produced the largest FT-IR/ATR response but at the cost of quality of an electrochemical measurement.

It is apparent from Figure 2, curve B, that due to the semiconducting properties of Ge and its higher resistivity in comparison to metallic (Au) or glassy carbon electrodes, the voltammetric characteristics of PB suffers from Ohmic effects. Nevertheless, upon application of sufficiently large potential differences ( $\Delta E$ ) across the PB layer, the system has produced voltammetric peaks. Although these peaks are flat and drawn out, their development implies that PB can be oxidized and reduced in the interfacial regions existing near the positively and negatively biased germanium electrodes.

Because only one germanium electrode is used for spectral measurements, the opposing electrode does not have to be bare germanium. To improve conductivity, we have also considered a cell in which the counter/reference substrate is covered with a thin coating of gold ( $\sim 50$  nm). The resulting cyclic voltammogram (Figure 2, curve C) produces better defined voltammetric peaks (in comparison to Figure 2, curve B). Some distortion observed in the reverse scan following application of negative  $\Delta E$ s (Figure 2C) may have originated from the fact that electrodes are not identical. Since the interfaces formed by PB with Au and Ge may not be equivalent, the cyclic voltammogram is not so perfectly symmetrical as before (Figure 2, curves A and B). From the viewpoint of the quality of FT-IR/ATR results, both spectroelectrochemical cells (which have been used to record voltammetric curves shown Figures 2B and C) produce virtually identical spectra. Ohmic effects are not expected to affect our spectro-

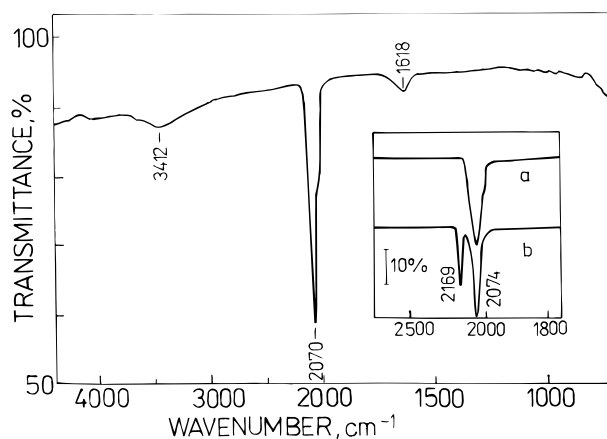


Figure 3. FT-IR/ATR spectrum of PB powder sandwiched (at open circuit) between germanium slides (the  $\text{CO}_2$  signal at  $2370\text{ cm}^{-1}$  was subtracted). The FT-IR/ATR spectra of the cyanide band in (a) PB and (b) Berlin Green are compared in the inset.

electrochemical experiments because the measurements are performed at steady state.

#### SPECTROELECTROCHEMICAL MEASUREMENTS

At open circuit, the whole layer of PB sandwiched between two germanium slide electrodes is neither oxidized nor reduced. In the  $4400\text{--}700\text{ cm}^{-1}$  region, the FT-IR/ATR spectrum of the system (Figure 3) shows a strong absorption band at  $2070\text{ cm}^{-1}$  attributable to the CN functional group as well as weaker bands arising from interstitial water responses near  $1600$  and  $3400\text{ cm}^{-1}$  associated with O–H stretch and H–O–H bend, respectively.<sup>26</sup> The use of germanium, which absorbs below  $700\text{ cm}^{-1}$ , as transparent material for internal reflectance precludes investigation of Fe–C–N–Fe bending modes characteristic of PB in the far-infrared region ( $450\text{--}650\text{ cm}^{-1}$ ).<sup>27</sup> Since the CN signal is predominant in the spectrum of PB (Figure 3), we have limited our spectroelectrochemical study to monitoring changes in the cyanide stretching frequency range.

PB is a "mixed", ionic/mixed-valence, conductor in which transport of structural  $\text{K}^+$  (hydrated) ions provides charge balance and supports electron hopping.<sup>17,23</sup> Application of the sufficiently large potential difference to electrodes in a sandwich cell drives simultaneously both redox reactions of PB: oxidation near the positive electrode and reduction near the negative electrode.<sup>5,23</sup> Diffusional concentration gradients are established at opposing interfaces formed by PB with germanium electrodes. Near the center of the sandwiched PB layer, namely, beyond the diffusional zones, the redox state of PB is effectively unchanged.<sup>28</sup> During the ATR measurement, the IR beam penetrates the PB phase only to a certain depth ( $\sim 1\text{ }\mu\text{m}$ ) from the interface, so that the reflected beam carries the surface information. By performing the electrolytic experiment for a fairly long time (60 s), and by choosing the appropriate potential difference (and polarization of the germanium element connected as the working electrode), we have been able to generate a sufficiently thick zone of largely oxidized or reduced PB so that the spectroelectrochemical changes can be detected in FT-IR/ATR. To enhance sensitivity of infrared monitoring, difference spectra have been recorded.

(26) Hurditch, R. J. *Electron Lett.* **1975**, *11*, 142.

(27) Wilde, R. E.; Ghosh, S. N.; Marshall, B. J. *Inorg. Chem.* **1970**, *9*, 2512.

(28) Carpenter, M. K.; Conell, R. S. *J. Electrochem. Soc.* **1990**, *137*, 2464.

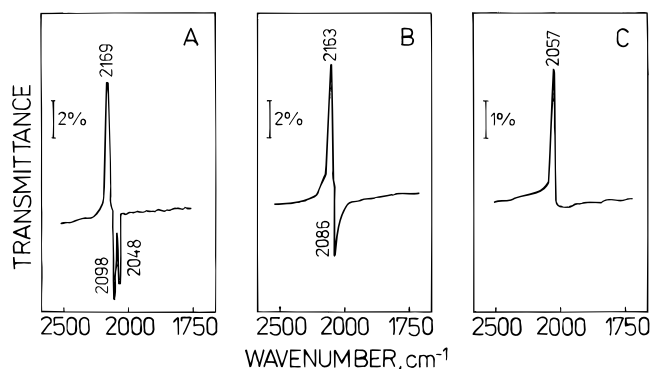


Figure 4. Spectroelectrochemical characterization of PB powder sandwiched between two germanium electrodes. Difference FT-IR/ATR spectra were recorded. To obtain (A) and (B): the response of oxidized PB (at  $\Delta E = 1.6$  V) was subtracted (A) from the spectrum of PB recorded at open circuit and (B) from the response of reduced PB (at  $\Delta E = -1.6$  V). (C) was obtained by subtracting the response of PB (at open circuit) from the response of the reduced system (at  $\Delta E = -1.6$  V).

We observed changes in the CN band following in situ oxidation and reduction of PB in a solid-state spectroelectrochemical cell. When  $\Delta E$  was equal to 1.6 V, PB ( $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ ) underwent oxidation to Berlin Green ( $\{\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]\}_x \cdot \{\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]\}_{1-x}$ , where  $0.6 < x < 0.8$ ) or Prussian Yellow ( $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ ) in the vicinity of the Ge element (working electrode). We already established from the ex situ FT-IR/ATR measurements done on independently prepared powders of PB and the system's largely oxidized form, Berlin Green, that the CN absorption band split upon oxidation (compare spectra a and b in inset to Figure 3). Figure 4A shows the difference spectrum produced upon subtraction of the spectrum, which was obtained after solid-state electrochemical oxidation, from the initial (background) spectrum of PB powder (recorded at open circuit). The difference bands shown in Figure 4A appear at similar wavenumbers, but they do not point in the same direction. The analogous result was obtained when the spectrum of Berlin Green (Figure 3b) was subtracted from the spectrum of PB (Figure 3a). We attribute the upward-going band appearing at  $2169 \text{ cm}^{-1}$  (Figure 4A) to cyanide band splitting which accompanies oxidation. Such a phenomenon was previously observed by others during ex situ external reflectance investigations of electrodes modified with oxidized indium and palladium hexacyanoferrates.<sup>29,30</sup> The peak splitting may suggest strong cyanide bridging between two equivalent Fe(III) ions within the Fe–C–N–Fe units of Prussian Yellow. In view of the data shown in Figure 3 (spectra a and b), the smaller, downward-going, bands at  $2098$  and  $2048 \text{ cm}^{-1}$  (Figure 4A) are expected to be produced upon subtraction of a relatively narrow band appearing in the oxidized form at  $2074 \text{ cm}^{-1}$  (Figure 3b) from the broader band existing in PB at  $2070 \text{ cm}^{-1}$  (Figure 3a).

Figure 4B illustrates the difference spectrum obtained upon subtraction of the FT-IR/ATR response of the material oxidized at  $\Delta E = 1.6$  V from the spectrum of the system reduced (at  $\Delta E = -1.6$  V) to Everitt's salt,  $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ . As in the case of Figure 4A, the upward-going band at  $2163 \text{ cm}^{-1}$  is consistent with the definite splitting of CN band following oxidation. The difference spectrum of Figure 4B resembles the data presented

in Figure 4A except that, instead of two peaks appearing at  $2048$  and  $2098 \text{ cm}^{-1}$  (Figure 4A), only a small peak occurred at  $2086 \text{ cm}^{-1}$  in Figure 4B. This discrepancy originates from the fact that the spectrum of the oxidized material was subtracted, in Figures 4A and B, from two distinct background spectra, of PB and Everitt's salt, respectively.

We demonstrate in Figure 4C that a single, upward-going, peak at  $2057 \text{ cm}^{-1}$  is produced upon subtraction of the spectrum of PB from the spectrum of Everitt's salt. Apparently, a cyanide band in Everitt's salt has lower intensity in comparison to PB. It seems that the reduced form of PB, Everitt's salt, is dominated like PB by a single cyanide band near  $2060\text{--}2070 \text{ cm}^{-1}$ . These observations are consistent with the recent in situ FT-IR study<sup>31</sup> in which the spectral responses of PB film during reduction in KCl electrolyte were monitored.

## CONCLUSIONS

We propose a simple method for combining solid-state electrochemistry with internal reflectance FT-IR/ATR spectroscopy. This in situ approach has proved to be a useful tool for monitoring spectral (IR) changes upon oxidation or reduction of PB powder. The cyanide stretching frequency range has been chosen for infrared analysis. We observe definite splitting of a cyanide band following oxidation of PB. Some decrease of the cyanide band intensity seems to accompany reduction of PB.

The solid-state spectroelectrochemical characterization of PB has some practical significance. Under normal conditions, the oxidized and reduced forms of PB are unstable. A solution precipitate, obtained upon mixing of potassium hexacyanoferrate(III) with iron(III) sulfate is not completely the oxidized  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$  structure, Prussian Yellow, since the latter system decomposes easily in solution<sup>32</sup> and degrades to the mixed form of Berlin Green,  $\{\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]\}_x \cdot \{\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]\}_{1-x}$  ( $0.6 < x < 0.8$ ). Also handling of the reduced  $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$  sample, Everitt's salt (Prussian White), is difficult in conventional IR measurements because the material is air-sensitive and becomes rapidly oxidized. Our report is parallel to the recent attempts of others aimed at utilizing ex situ and in situ FT-IR measurements to study spectroelectrochemistry of ferrocyanides and metal hexacyanoferrates.<sup>30,31,33–35</sup>

In the present study, we simply utilized commercially available, germanium ATR elements as sandwich electrodes. Our intention was to find conditions that would permit obtaining the largest possible FT-IR/ATR signal following interfacial electrolysis of PB. On the whole, the measurement system was well behaved since the results of experiments described in Figure 4 could be virtually indefinitely reproduced.

Ohmic complications, originating from semiconducting properties of germanium electrodes, were not severe in the case of PB, but they could cause problems in other samples. To improve conductivity of electrodes, we considered deposition of an ultrathin ( $\sim 5\text{--}15 \text{ nm}$ ) layer of gold onto germanium slides. This treatment did not lead to reliable (clear from background noise) FT-IR/ATR spectra of PB, and the respective results are, therefore, not shown

(31) Hamnett, A.; Christensen, P. A.; Higgins, S. J. *Analyst* **1994**, *119*, 735.

(32) Sharpe, A. G. *The Chemistry of Cyano Complexes of Transition Metals*, Academic Press: New York, 1976.

(33) Wu, Y.; Pfenning, W.; Bocarsly, A. B.; Vicenzi, E. P. *Inorg. Chem.* **1995**, *34*, 4262.

(34) Fan, Q.; Ng, L. M. *J. Electrochem. Soc.* **1994**, *141*, 3369.

(35) Zhang, J.; Yin, Q.; Cai, S.; Fujishima, A. *Electroanalysis* **1993**, *5*, 517.

(29) Kulesza, P. J.; Faszynska, M. *J. Electroanal. Chem.* **1988**, *252*, 461.

(30) Jiang, M.; Zhao, Z. *J. Electroanal. Chem.* **1990**, *292*, 281.

here. Deposition of thicker (>50 nm) gold films on germanium elements made ATR monitoring of PB practically impossible.

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