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Electrochemistry of Prussian Blue in silica sol-gel electrolytes doped with polyamidoamine dendrimers

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Abstract The inclusion of a generation-4 polyamidoamine (G4-PAMAM) dendrimer in a silica sol-gel yielded a solid electrolyte that was used to encapsulate Prussian Blue (PB), iron(III) hexacyanoferrate(II), and cobalt hexacyanoferrate. The PB was synthesized in the doped silica by sequential immersion of a monolith in 0.1 M $K_4Fe(CN)_6$, water, and 0.1 M $FeCl_3$. Inclusion of G4-PAMAM resulted in a nanoporous anion-exchange material with a capacity of 10.1 mmol g^{-1} , which is about four times greater than the capacity of silica alone. Relative to its G0 counterpart, the G4-PAMAM doped silica increased the rate of formation of PB by a factor of ca. 20. The solid state voltammetry of PB in the doped silica had the usual features for this compound. At 0.1 V vs. a Ag quasi-reference electrode, a reversible reduction was seen; the relationship between current and scan rate was that for a surface-confined redox couple. The quasi-reversible oxidation of PB was observed at 0.85 V. Inclusion of G4-PAMAM increased the lifetime of silica as a solid electrolyte from a few days to at least three months. Raman microprobe mapping analysis demonstrated that PB was homogeneously distributed across the entire width (ca. 1 mm) of the G4-doped monolith with 20-h immersions.

Keywords Prussian Blue · Cobalt hexacyanoferrate · Voltammetry · Sol-gel electrolyte · Iron hexacyanoferrate

Introduction

Metal hexacyanoferrate modified electrodes have been investigated intensively for a variety of applications such as electrochromism [1, 2, 3, 4], electrocatalysis [5, 6, 7, 8], ion selectivity and the ability to store cations [9, 10, 11, 12, 13], solid state batteries [14, 15], and molecular magnetism [16, 17]. Methods for modifying electrodes with these compounds include electrodeposition, absorption, and entrapping them in polymers [18]. The immobilization of hexacyanoferrates as powder particles on an electrode surface also is used ([19, 20] and citations therein). The use of silica sol-gels as hosts for electroactive species is gaining attention because this medium is compatible with a wide range of interrogation methods, including spectrophotometry, mass spectrometry, and NMR [21, 22]. In addition, the sol-gels can be synthesized to have a pore structure that is controlled over a wide range [21, 23]. The encapsulation of metal hexacyanoferrates in sol-gel matrices has been reported [24, 25].

Silica that is formed by sol-gel processing has been shown to serve as an electrolyte for solid state voltammetry [26, 27, 28, 29]. Because it is not an intrinsic conductor, the combination of pore size and residual water content is important to the behavior of silica as a solid electrolyte. When prepared by the hydrolysis, condensation, and polycondensation of simple alkoxides such as tetramethylorthosilicate, room temperature processing produces a microporous solid [21]. Inclusion of a surfactant at levels well above the critical micelle concentration provides a template that yields a nanostructured solid [23]. The importance of the pore size on its properties as a solid electrolyte was demonstrated in studies with polyoxometalates as electroactive dopants; effective diffusion coefficients were increased from the $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ level to the $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ range, which is near the physical diffusion coefficient in water [26, 27]. The presence of about 11–13% water along with the pore width being greater than the physical size of the polyoxometalates accounted for the facile diffusion in the templated silica.

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Limiting factors on the use of sol-gel materials are their mechanical strength and their physical stability upon exposure to water, including a rapid change in humidity of a surrounding gas. Recently, we demonstrated that inclusion of a polyamidoamine (PAMAM) dendrimer can increase the strength of silica sol-gel materials and decrease their tendency to fracture when either immersed in water or dried rapidly [30]. Moreover, the generation of the PAMAM influenced the pore width of the material. As platforms for electrochemical studies, including electrochromism, charge storage, and catalysis, silica sol-gels also are limited in terms of the concentration of redox centers that can be incorporated. Without concentrations on the order of 0.2 M, communication between redox centers is not efficient, and attempts to attain loads of at this level can result in fracturing [25]. The present study was initiated to determine whether PAMAM-doped silica was suited as a solid state electrolyte. In addition, the influence of the doping, which was predicted to change the matrix from an anion-exchange (silica sites) to a cation-exchange (amine sites) material, on the uptake of anionic complexes was investigated. Of particular interest was whether doping with PAMAM circumvents the problem of fracturing when silica sol-gels are prepared with high populations of metal hexacyanoferrate redox centers [25].

Prussian Blue (PB), $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$, is a prototype of metal hexacyanoferrates. It is used commonly as a model redox-active solid for both fundamental and applied studies. For this reason and because its voltammetry in a silica sol-gel material has been elucidated [25], the PB system was selected for the present study. In previous work [25], 2×10^{-3} M $\text{K}_3\text{Fe}(\text{CN})_6$ and 2×10^{-3} M FeCl_3 were included in the sol so that Prussian Yellow (PY), $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$, was distributed throughout the resulting gel. The selection of PY rather than PB as the dopant was because the rate of formation of the latter is fast relative to the rate of gelation, resulting in a heterogeneous mixture that yields a poor distribution of PB in the silica. In contrast, PY forms more slowly than does PB. The subsequent voltammetry at a carbon fiber electrode yielded redox behavior that is typical for PB in a film in contact with a liquid phase.

A second factor that suggests the use of PB as a test system is that its formation in a solid matrix can be by a stepwise procedure. For example, Honda and co-workers [14, 31] reported the formation of PB inside a Nafion membrane, a perfluorinated polymer with sulfonate functionality, by initial immersion in FeCl_2 followed by reaction with $\text{K}_3\text{Fe}(\text{CN})_6$. Scanning electron microscopy showed that the PB domain was limited to the region near the surface. Subsequently, solid state electrochemistry that was performed by sandwiching the modified Nafion membrane between two indium tin oxide electrodes showed the characteristic oxidation of PB to Berlin Green and the reduction of PB to Prussian White. When the immersion order was reversed the PB formation was limited to the outer surface of the Nafion [31],

which is consistent with electrostatic repulsion of $\text{Fe}(\text{CN})_6^{3-}$ by the sulfonate.

The hypothesis that is tested in this study is that PAMAM-doped silica will provide a means of forming PB (or Turnbull's Blue, TB) in a physically strong, nanoporous material by, first, strong interaction of $\text{Fe}(\text{CN})_6^{3-}$ [or $\text{Fe}(\text{CN})_6^{2-}$] with the amine sites and, second, reaction with Fe^{II} (or Fe^{III}) in a fresh aliquot of contacting solution. A question to be addressed is whether the PAMAM alters the redox characteristics of PB.

Experimental

Tetramethylorthosilicate, TMOS (99% pure), and polyamidoamine (PAMAM) dendrimers were purchased from Aldrich (Milwaukee, Wis., USA). The generation 0 (G0) PAMAM (molecular mass, 517 Da; four surface amine groups) and generation 4 (G4) PAMAM (molecular mass, 14,215 Da; 64 surface amine groups) were 20 wt% and 10 wt% solutions in methanol, respectively. Other chemicals were reagent grade from Fisher Scientific (Pittsburgh, Pa., USA). The water was purified with a Barnstead NANOpure II system to a conductivity of $17.5 \text{ M}\Omega \text{ cm}^{-1}$.

The voltammetric experiments were performed with a CHI model 630 Electrochemical Workstation (CH Instruments, Austin, Tex., USA). The cell design for the solid state voltammetry is shown in Fig. 1. The working and auxiliary electrodes were 52-mesh Pt (99.9% purity) gauze comprising 0.07-mm (dia.) wire (Aldrich). The silver wire served as a quasi-reference electrode. The UV-visible spectra were collected with an 8453A HP diode array spectrophotometer (Agilent Technologies, Waldbronn, Germany).

Silica monoliths were prepared by combining TMOS with 0.2 M KCl, 0.1 M HCl, and 1 mM PAMAM of the desired generation in a volume ratio of 1:1:1:1. The mixture was stirred for 30 min and dried for at least 10 days in 60×25 mm Falcon (plastic) covered petri dishes (Fisher). The dimensions of the dried cylindrical monoliths were 1 mm thickness and 20 mm diameter. Unless otherwise stated, the doping with PB was by immersion of the dried gel in 0.1 M $\text{K}_4\text{Fe}(\text{CN})_6$ for 5 min followed by a rinse with water and reaction with 0.1 M FeCl_3 for 10 min. It was estimated that this procedure resulted in PB formation in a ca. 0.1-mm layer. For the spectroscopic profiling experiments, the time in the iron-containing solutions was 20 h. In many cases the doping was with a combination of 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.1 M FeCl_2 , which initially yields the structurally identical TB; however, internal electron transfer results in the formation of PB. The results with these two preparation methods were identical.

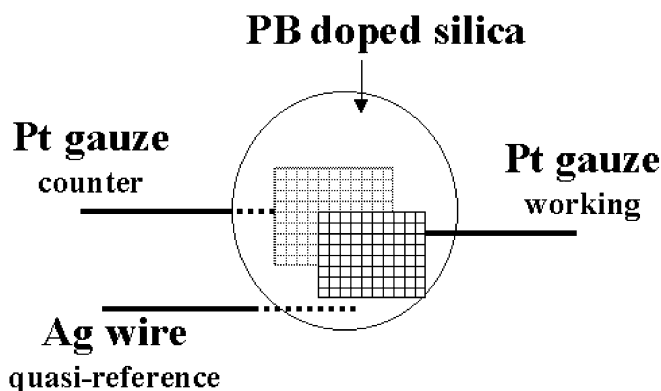


Fig. 1. Solid state electrochemical cell

Mapping analysis was performed with a Renishaw 2000 confocal Raman microprobe interfaced to a Prior mapping stage. Instrument control, data acquisition, and data manipulation were conducted under GRAMS32 and Renishaw WiRE software. Samples were excited with a HeNe (632 nm) laser; power at the sample did not exceed 6 mW. The source was focused onto the sample using a 20 \times (0.46 N.A.) objective, which provided a beam diameter of about 2 μ m at the sample. The same objective was used to collect the scattered radiation. Data were collected in the spectrograph mode at 4 cm^{-1} resolution. Each recorded spectrum represents the average of five individual scans with an integration time of 10 s for each spectral element. The map was generated across the 1-mm monolith by collecting a spectrum every 10 μ m. The samples were hexagonal monoliths, 1-mm thickness and 11-mm edge diameter. The monolith was split and mounted in a plug of non-fluorescing epoxy (EPO-TEK, Epoxy Technology, Billerica, Mass., USA) so that the interior cross-section was exposed. The epoxy was cured for 4 days under ambient laboratory conditions and 12 h in a drying oven at 50 $^{\circ}\text{C}$. The surface was polished with 600-grit silicon carbide paper and 0.05- μ m alumina paste prior to spectroscopic interrogation.

Results and discussion

Initial experiments were spectrophotometric measurements on the uptake of $\text{Fe}(\text{CN})_6^{3-}$ into silica monoliths doped with G0-PAMAM (Fig. 2A) and monoliths that were doped with G4-PAMAM (Fig. 2B). When G4-PAMAM was present, the absorbances at characteristic bands for $\text{Fe}(\text{CN})_6^{3-}$ at 304 nm and 420 nm increased with the time of immersion in 0.1 M $\text{Fe}(\text{CN})_6^{3-}$. In contrast, the G0-PAMAM doped silica monoliths (Fig. 2A) showed significantly less uptake of $\text{Fe}(\text{CN})_6^{3-}$. With undoped silica, measurable uptake of $\text{Fe}(\text{CN})_6^{3-}$ was not observed over the time scale of Fig. 2. Moreover, a repeat of the experiments in Fig. 2B, except with doped sol-gels immersed in 0.1 M $\text{Fe}(\text{CN})_6^{3-}$ at pH 10, did not show uptake of the anionic complex. As a result, the spectral changes in Fig. 2B were attributed to reaction between protonated amine sites and $\text{Fe}(\text{CN})_6^{3-}$. From the data in Fig. 2, it is apparent that the rate of sorption of $\text{Fe}(\text{CN})_6^{3-}$ was greater into the G4-PAMAM doped silica than into its G0 counterpart. More facile diffusion into G4-PAMAM is expected because it templates the silica structure into the nanoporous domain [30]. However, the greater population of amine sites with the G4-PAMAM than with G0-PAMAM is a second factor to consider. In this regard, the powdered silica sol-gel materials that were doped with G0-PAMAM and G4-PAMAM sorbed 7.7 and 20.5 mmol g^{-1} $\text{Fe}(\text{CN})_6^{3-}$, respectively, during a 20-h equilibration. The capacity of the latter may be an underestimate in that 98% of the $\text{Fe}(\text{CN})_6^{3-}$ was removed from the solution in that period. In contrast, a control experiment with undoped silica yielded an uptake of 6.2 mmol g^{-1} $\text{Fe}(\text{CN})_6^{3-}$. Based on these results, subsequent experiments were focused primarily on G4-PAMAM as the dopant.

The PB was synthesized in the doped silica as described in the Experimental section. In accord with the reaction scheme in Fig. 3, a blue color forms immediately upon reaction of the bound $\text{Fe}(\text{CN})_6^{3-}$ with Fe^{2+} . Spectrophotometric interrogation showed an absorption

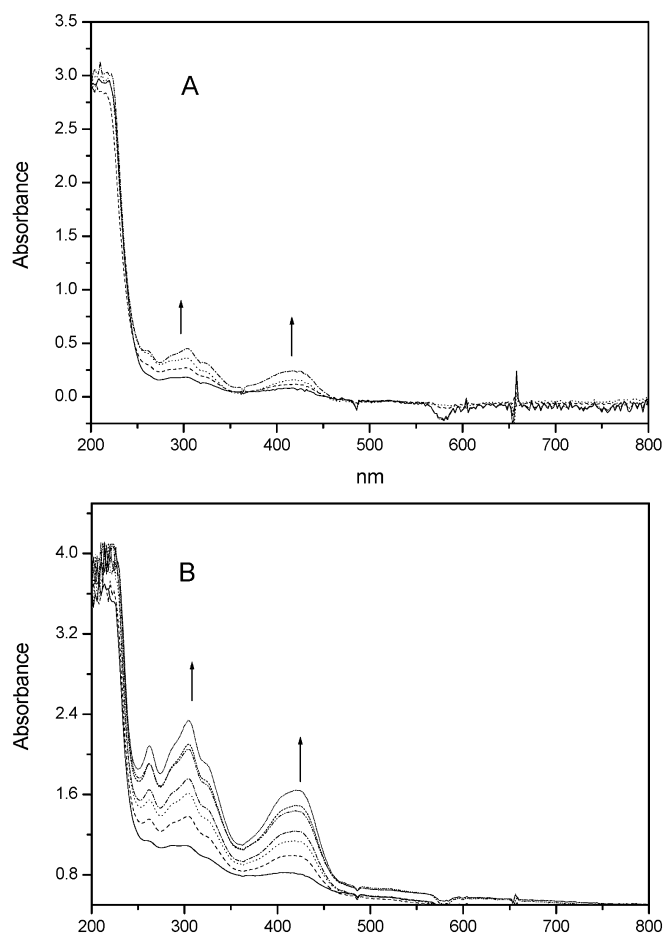


Fig. 2. Spectrophotometric study of the uptake of $\text{Fe}(\text{CN})_6^{3-}$ into a silica sol-gel doped with (A) G0-PAMAM or (B) G4-PAMAM. The times in contact with a 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$ solution were 60–250 s in A and 10–80 s in B

band centered at 690 nm, which supports the assignment of the reaction product to PB. The Raman spectrum also matched that of a PB standard. Additional evidence for the formation of PB is that immersion of the monolith in a sodium dithionite solution bleached the blue color, presumably by reduction of PB to Prussian White, PW (Everitt's Salt); exposure to atmospheric dioxygen for 1 h restored the blue color. Of importance is that this experimental cycle, as well as other work in which the monoliths were soaked in aqueous solutions for several days, did not show evidence of leaching of PB or its oxidized and reduced forms from the PAMAM-doped sol-gel material.

The distribution of the PB across a monolith was measured by Raman microspectroscopy. With a sample prepared and mounted as described in the Experimental section, the profiles shown in Fig. 4 were obtained. The peaks at 2092 and 2152 cm^{-1} arise from $\nu(\text{CN})$ stretching modes. The presence of two peaks is related to the mixed transition metal oxidation states in the samples prepared as described. To estimate the homogeneity of the PB distribution, the integrated peak intensity from 1950 to 2350 cm^{-1} was obtained for each spectrum in the map.

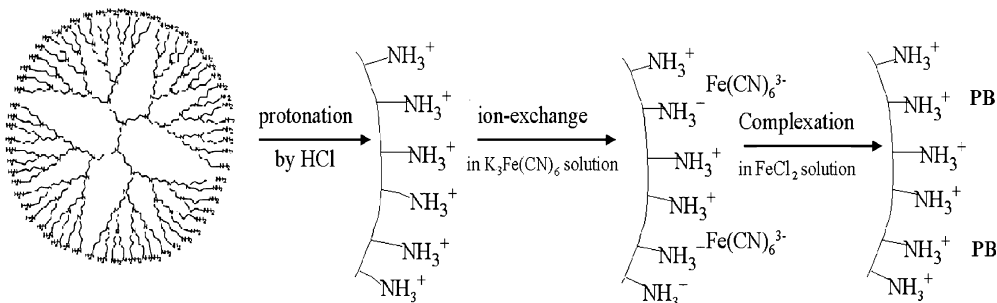
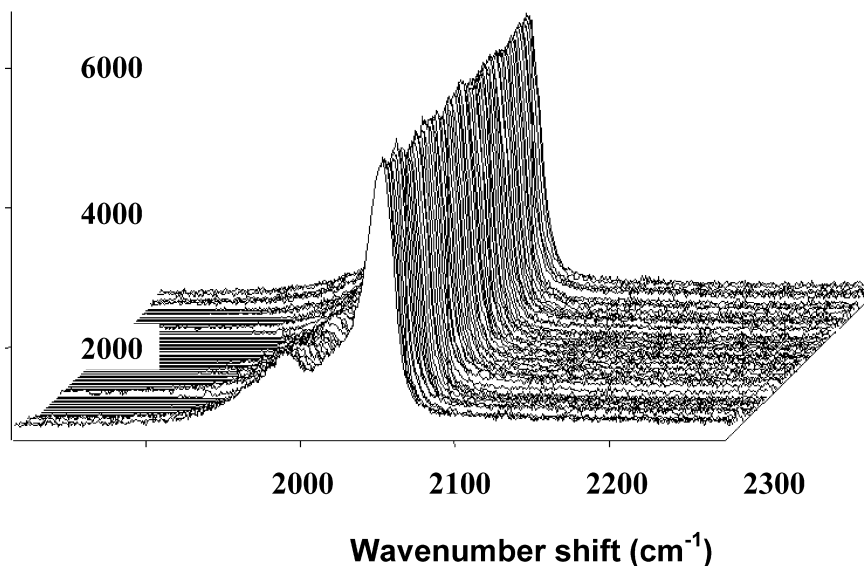


Fig. 3. Reaction scheme for the formation of PB by sequential immersion of silica doped with G4-PAMAM into $\text{Fe}(\text{CN})_6^{3-}$ and Fe^{2+}

The average integrated peak intensity was 1.73×10^5 counts cm^{-1} , and the relative standard deviation was 7.6%. A repeat with an optically smooth standard yielded a relative standard deviation of 0.2% at a fixed position. The difference in the relative standard deviations is a reflection of a combination of surface roughness and the heterogeneity. In contrast, when the PB is formed in an identical manner except in a sol-gel in the absence of the G4-PAMAM, visual inspection revealed areas in the center of the cross-section where PB was absent. Microspectroscopic mapping was not performed because of the highly heterogeneous distribution of the PB formation in this case. Even reversing the immersion order did not eliminate the propensity for formation of PB primarily in regions near the surface of the undoped silica. In the absence of G4-PAMAM, the behavior was comparable to that reported for the formation of PB in Nafion [14, 31].

Solid state voltammetric experiments were performed in the cell illustrated in Fig. 1. A typical voltammogram is shown in Fig. 5. The general features are in accord

Fig. 4. Raman spectroscopic mapping of PB across a cross-section of a silica sol-gel doped with G4-PAMAM. The scans on the z -axis dimension are across the 1.0-mm thickness of the sol-gel



with the known voltammetry of PB films [32, 33, 34, 35, 36]. Moreover, the peak potentials agree with those for the voltammetry of PB in silica that is not processed in the presence of a dendrimer [25]. However, the redox process at about 0.85 V yielded peaks which were more drawn out than expected from the above-cited studies. A possible factor is that this process is the one-electron oxidation of $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ to $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{III}}(\text{CN})_6]_3\text{Cl}_3$ [33, 36], rather than that of $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ to $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$. The involvement of the anion in the former case was postulated as the cause of slow electron-transfer kinetics for the PB analogue, nickel hexacyanoferrate [37]. An alternative explanation is that the PB forms on the G4-PAMAM in a manner where NH_3^+ replaces K^+ , consequently diminishing the ability of K^+ to penetrate PB during the voltammetry.

The illustrated experiment was performed on a sol-gel that was aged for 10 days; however, doped gels that were aged for up to three months yielded similar behavior. In the absence of PAMAM, our previous studies showed that aging the silica for longer than five days yielded voltammetry of hosted compounds that was severely distorted. The system shows two redox couples, namely the oxidation of PB to PY, which occurs through the mixed intermediate form, Berlin Green, and the reduction of PB to PW. The voltammetric behavior for the reduction of PB is consistent with a reversible process for a surface confined species in that the peak potentials

are virtually coincidental. At 1.0 and 100 mV s^{-1} , the peak potential differences are 15 and 35 mV, respectively. That the ideal behavior, coincidental peak potentials, is not observed probably results from some ohmic distortion of the voltammogram. Consistent with a study in undoped silica sol-gels [25], the voltammetry for the oxidation of PB is not well defined; the appearance of the peaks suggests that this redox couple, which has a formal potential of ca. 0.9 V, is a diffusional, quasi-reversible process.

The above interpretation of the voltammetry in Fig. 5 was supported by an analysis of the influence of scan rate on the voltammetric peaks. Linear least-squares analysis of plots of $\log i_p$ vs. $\log v$, where i_p and v are peak current and scan rate, respectively, was performed on the cathodic peaks in Fig. 5. The cathodic currents were analyzed because of the difficulty in measuring the peak current for the oxidation of PB. For the peak near 0.85 V, the slope was 0.51 ($r=0.999$), a value in agreement with the theoretical relationship of i_p proportional to $v^{1/2}$ for a diffusion-limited system. In this solid state system, physical diffusion of the electroactive species is not necessarily the limiting process; instead, a combination of physical diffusion of the electroactive species and the counterion along with electron self-exchange govern the electrode process. Regarding the latter, the quantity of iron that is loaded into the silica which is doped with G4-PAMAM is on the order of 10 mmol g^{-1} ; hence, the PB probably occurs as a solid along the pores that are templated by inclusion of G4-PAMAM in the sol [30]. The dendrimer also may have templated the formation of colloidal PB. In this regard, a previous attempt to load undoped silica sol-gels with high concentrations of PB weakened the solid [25], whereas in the present study no change in strength was observed. For the peak near 0.1 V in Fig. 5, the analogous analysis yielded a slope of 0.71 ($r=0.998$), which suggests that a combination of diffusion and surface behavior limit the current. The importance

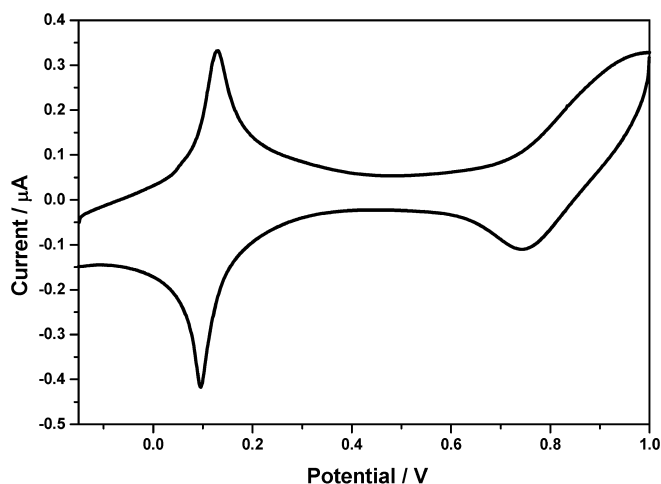


Fig. 5. Cyclic voltammetry of PB in a silica sol-gel doped with G4-PAMAM. The PB was formed as described in the Experimental section. Scan rate, 0.1 V s^{-1}

of these results is that the G4-PAMAM does not degrade the utility of the silica sol-gel as a solid state electrolyte.

The study was extended to the voltammetry of cobalt hexacyanoferrate, CoHCF. This substance is of growing interest because, depending on the counterion and oxidation state, it has magnetic properties that can be induced either electrochemically or photochemically [17]. Two overlapping anodic processes related to hexacyanoferrate oxidations were observed (Fig. 6). Presumably they originated from the existence of two forms of CoHCF that have been approximated as $\text{K}_2\text{Co}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ and $\text{KCo}_{1.5}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ [38, 39]. The one-electron oxidation of these forms was accompanied by loss of one potassium ion [38, 39]. The result in Fig. 6 demonstrated that the results for PB in silica were not unique to that particular metal hexacyanoferrate, MHCF, which allows the projection of application of platforms comprising MHCF-doped sol-gel materials to the variety of areas described in the Introduction.

Conclusions

This study demonstrates the utility of G4-PAMAM as a dopant for silica sol-gel materials in the preparation of solid electrolytes that serve as host materials for metal hexacyanoferrates. The anion exchange capacity of this material was more than three times higher than that of silica alone, and the dopant had no deleterious effects on the voltammetry of PB. Thus, this material is well suited for studies that require impregnation with anionic complexes. For general application to solid state voltammetry, the most important result is that the G4-PAMAM markedly increases the lifetime of the silica in terms of its ability to act as a solid electrolyte. Presently, we are extending our studies of the lifetime of these solid electrolytes to determine the reasons for the stabilization of silica by G4-PAMAM.

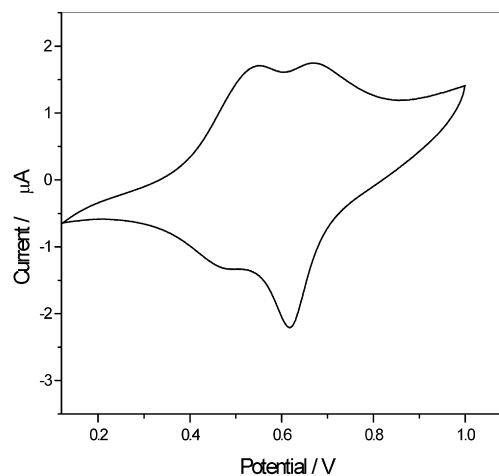


Fig. 6. Cyclic voltammetry of cobalt(II) hexacyanoferrate(II) in a silica sol-gel doped with G4-PAMAM. Scan rate, 20 mV s^{-1}

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