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ORIGINAL PAPER

Influence of pencil lead hardness on voltammetric response of graphite reinforcement carbon electrodes

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Abstract This work studied the voltammetric response of graphite reinforcement electrodes made of different pencil lead hardness. The studies showed that harder graphite leads, regardless of their manufacturer, are more appropriate as electrode material for voltammetric purposes due to their higher peak currents, increasing sensitivity and reproducibility, with ΔEp closer to the theoretical value for a reversible system.

Keywords Pencil lead · Graphite reinforcement carbon · Cyclic voltammetry

1 Introduction

Carbon electrodes such as glassy carbon, carbon paste, pyrolytic graphite, carbon fiber and graphite composites have been used extensively as voltammetric sensors in a wide range of applications. A low cost alternative material for hand made voltammetric electrodes is graphite reinforcement carbon (GRC), used as lead in mechanical pencils, available everywhere in different hardness and diameters. It is made by dispersing natural graphite into a mixture of organic binder and spindle oil followed by a thermal treatment [1]. GRC is not as fragile as pyrolytic graphite or carbon paste electrodes and is not as rigid as glassy carbon.

Hardness and blackness can be modified by altering the temperature of the kiln and the proportions of graphite and clay. The more graphite it contains, the softer and thicker it is. Pencil hardness is graded in nineteen degrees ranging from 9H (hardest) to 8B (softest) [2]. The pencil hardness is determined by pencil hardness test ASTM D3363. Instead of clay, the lead contains a macromolecule, i.e. high polymer, a natural material based on organic substance (e.g. cellulose) [1]. During the firing of the lead in an oxygen-free atmosphere (carbonisation), the cellulose is transformed into carbon. The resulting non-ceramic bonding is very resilient and elastic.

The literature describes many applications of GRC electrodes: for determining the titratable acidity in vinegar [3, 4]; in abrasive stripping voltammetry [5]; in determination of ozone [6], dopamine [7], caffeine [8], trepibutone [9], uric acid [10]; in simultaneous determination of nitrite, dopamine and serotonin [11]; as substrate for mercury [12] and bismuth [13] films in trace metal determination; in liquid chromatography for determination of phenols [14]; applied with modified surface for determination of 2,4-dichlorophenol [15]; in voltammetry of microparticles [16]; in studies of copper-chelating properties of flavonoids [17]; in studies of DNA hybridization [18–21]; for discrimination of herpes type [22]; in detection of hepatitis B virus DNA [23, 24] and in studies of interaction between DNA and lycorine [25], arsenic trioxide [26] and *cis*-DDP [27] molecules.

Many of these studies do not state the type of pencil lead used. Other work has been carried out using hardness grades such as 6H, 2H, HB and 2B as working electrode, but there is no information regarding the criteria used to choose the hardness. Moreover, some work describe the cyclic voltammetric behaviour of GRC electrodes [19, 28, 29].

Wang and Kawde [19] studied a pencil-based renewable biosensor for label-free electrochemical detection of DNA hybridization and evaluated different types of pencil leads (B, F, HB, 4H and 6H) for transducing the hybridization event. Substantial differences in the target guanine signals

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and background response were observed at the various types of pencil leads, with the 6H pencil lead displaying the most favourable signal-to-background characteristics. Large background signals and inferior signal-to-background characteristics accompany the large guanine response observed at the other leads.

Aoki et al [28] studied the application of GRC as a voltammetric electrode, describing its polarized domain in H_2SO_4, KCl and NaOH solutions. The cyclic voltammetric response for $[Ru(NH_3)_6]^{2+/3+}$ and $[Fe(CN)_6]^{4-/3-}$ showed a peak separation of about 60 and 70–110 mV with an increase in scan rating, and the slopes of the plot of the peak current against $v^{1/2}$ were 15–20% lower than the theoretical value, probably because of the limitation of the effective area in comparison with the geometrical one. No variation of the voltammograms in terms of GRC hardness was noticed.

Bond et al. [29] developed a renewable graphite pencil electrode for voltammetric purposes. Three different degrees of hardness were tested (HB, H and 3H Pentel pencil leads, 0.5 mm diameter) in 2 mol L^{-1} H_2SO_4 and, since pencil lead contains clay and polymers, peaks occurred in the cyclic voltammograms. The cyclic voltammograms for oxidation of potassium hexacyanoferrate(II), in 2 mol L^{-1} H_2SO_4 using a 3H graphite lead, showed a significant contribution from a thin-layer effect which arises from the solution penetrating the thin gap between the pencil lead and the PTFE body. Furthermore, this electrode leads to high reproducibility and sensitivity for mercury thin-film anodic stripping voltammetry, but no information about the influence of hardness was provided.

As can be seen, there is little information about the cyclic voltammetric behaviour of graphite reinforcement carbon electrode as a function of its pencil lead hardness. The correct choice of its hardness is very important in the construction of appropriate electrodes to enhance its analytical purposes.

2 Experimental

2.1 Reagents, electrode materials and preparation

All the chemicals used were of analytical grade and the water was distilled and deionized in a Millipore Simplicity 185 system.

The resistance of graphite reinforcement carbon (pencil lead rods of 60 × 0.5 mm) was measured with a Hewlett Packard 3468A multimeter in triplicate, using three different pencil leads for each degree of hardness, in order to obtain a more accurate value. Thirty-five commercial pencil leads of 12 different manufacturers were studied.

The graphite reinforced carbon electrodes (GRC) were obtained by sealing with epoxy resin, into a disposable polypropylene pipette tip, a 15 × 0.5 mm pencil lead rod with a copper wire rolled on one end to make electric contact. The electrodes were maintained at rest for 24 h to ensure complete curing of the epoxy resin and, after this, the electrodes were submitted to an abrasive process using emery paper until a graphite disc appeared. Three electrodes were constructed with each commercial pencil lead, of different degrees of hardness (4B–4H) and from several manufacturers, to obtain more accurate results.

Before use the electrodes were polished with alumina (0.3 μm), then rinsed thoroughly with water, cleaned in an ultrasonic bath with water and, finally, rinsed with deionized water and ethanol.

2.2 Electrochemical cell, equipment and procedure

The voltammetric measurements were performed with an μAutolab Eco Chemie, and the electrochemical cell was placed in a Faraday cage containing the working electrode (graphite reinforced carbon electrodes or pencil lead rods), an Ag/AgCl double junction electrode, as reference electrode, and a platinum rod (1 × 20 mm) as auxiliary electrode. The voltammograms were obtained and analyzed with GPES (4.6 version) software.

Five millilitres of solution were pipetted into the voltammetric cell and deaerated by purging with nitrogen gas for 5 min. Three measurements were carried out for each sample for evaluation of precision.

The performance of the GRC electrodes was checked by the cyclic voltammetric behaviour of 6 mmol L^{-1} $K_4[Fe(CN)_6]$ in KCl 1 mol L^{-1}, as a supporting electrolyte, in −0.2 to 0.9 V versus $Ag/AgCl,KCl_{(sat)}$ range. All the cyclic voltammograms were performed in triplicate for all the electrodes constructed.

3 Results and discussion

Before the construction of the GRC electrodes, the electrical resistance of 35 commercial pencil leads, of different degrees of hardness and from 12 manufacturers, was measured, as a resistance of hundreds of ohm is not desirable for electrode material [30]. About 80% of the pencil leads showed resistances lower than 5 ohm, and only two led to values higher than 100 ohm. Thus, all pencil leads can be used as electrodes and no correlation was found between hardness and resistance.

To study the relationship between cyclic voltammetric response and hardness, leads from only three manufacturers (Faber Castell, Kappel and Pentel) were used to construct the GRC electrodes, due to their wider variety of degrees of hardness. Epoxy resin was used in electrode sealing because of its low cost and well-known performance for this application. The sealing of the pencil leads was tried with glass too, but the high temperature process damaged the conductance properties of graphite, rendering it unfit as electrode material.

After the polishing and cleaning processes, the charge current of these electrodes was measured, using the difference of current in 0.4 V versus Ag/AgCl,$KCl_{(sat)}$, in cathodic and anodic scans of cyclic voltammograms obtained for a 1 mol L^{-1} KCl solution, from −0.2 to 0.9 V versus Ag/AgCl,$KCl_{(sat)}$, at a scan rate of 100 mV s^{-1}. A significant diminution of the charging current as a function of the number of polishing and cleaning processes (up to 90%) was observed, mainly for the softer lead electrodes, which was probably related to polarized chemical groups in the electrode surface. Thus, the electrodes were polished and cleaned until the charging current reached a constant value of about 0.1 μA. No voltammetric peak was detected during successive cyclic voltammetric scans, showing that clay, polymers and other constituents of pencil leads, of different degrees of hardness and from several manufacturers, were not electroactive in this medium.

Figure 1 shows cyclic voltammograms obtained for GRC electrodes and their respective unpolished pencil lead rods, immersed directly in 6 mmol L^{-1} $K_4[Fe(CN)_6]$ and 1 mol L^{-1} KCl solution, for two different degrees of hardness. The cyclic voltammograms obtained for harder pencil lead rods (2H) and their respective GRC electrodes were more similar than for the softer ones (2B). This behaviour was observed for the three different manufacturers, thus indicating that the presence of polarized chemical groups is more evident for soft leads and, therefore, a better voltammetric response requires a more exhaustive polishing and cleaning process. These polarized chemical groups can induce an electrostatic repulsion of anionic species $[Fe(CN)_6]^{4-/3-}$, decreasing the charge transfer rate and, consequently, increasing ΔE_p values.

This fact is better visualized in Fig. 2, which shows ΔE_p values for different GRC electrodes. The polishing and cleaning processes of the electrodes lead to lower values compared to pencil lead rod used directly in the solution. In all the cases ΔE_p values decreased, and are more reproducible, as the degree of hardness increases. In other words, the $[Fe(CN)_6]^{4-/3-}$ system exhibits a more reversible response for harder pencil leads with an ΔE_p value of about 80 mV, but higher than the theoretical value of 59 mV for a reversible system, suggesting a quasi-reversible electron transfer. The i_{pa} plots against $v^{1/2}$ lead to straight lines but do not go through the origin, for all cases, also indicating that the electronic transfer is not completely reversible.

Aoki et al. [28] found no variation of the voltammograms with hardness of GRC, for two different systems, but these results were obtained with very close degrees of hardness (H, HB and B) of only one manufacturer, an insufficient sampling to show any relationship between reversibility and graphite hardness. Bond et al. [29] studied the oxidation of ferrocyanide only with the 3H pencil lead electrode and the contribution from a thin-layer effect from the solution penetrating into the PTFE body, and the pencil lead affected its behaviour.

The i_{pa}/i_{pc} values tend to unit for higher hardness for pencil lead rods (Fig. 3a), indicating a more reversible response for harder ones, and are lower than one for Pentel and Faber-Castell GRC electrodes (Fig. 3b), showing a distinct behaviour from Kappel ones. Figure 4 shows that i_{pa} for the $[Fe(CN)_6]^{4-/3-}$ system, obtained for different GRC electrodes, is dependent on hardness. For the three manufacturers an increase in i_{pa} using harder leads was observed, mainly for the Kappel ones which provided higher values but with less reproducibility. The i_{pa}/i_{pc} values were above one at low scan rates. These values decrease exponentially as scan rate increases and tend to reach unity from 200 mV s^{-1} in all the electrodes constructed (Fig. 5a), thus indicating electron transfer followed by chemical reaction [32].

The current function decreased exponentially with increase in scan rate (Fig. 5b), tending to a constant value as from 200 mV s^{-1} for Faber and Pentel pencil leads,

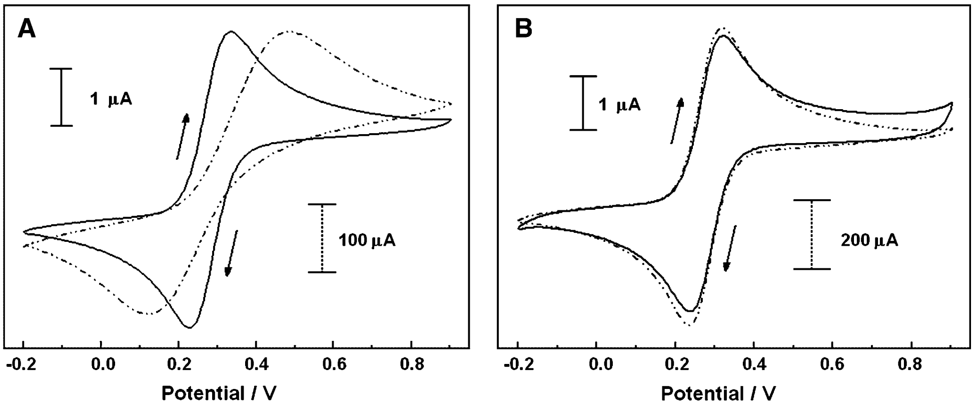

Fig. 1 Cyclic voltammograms of $K_4[Fe(CN)_6]$ 6 mmol L^{-1} in KCl 1 mol L^{-1} for Faber-Castell pencil lead rods (–··–) and their respective GRC electrodes (——) of different hardness. (**a**) 2B; (**b**) 3H. v = 100 mV s^{-1}

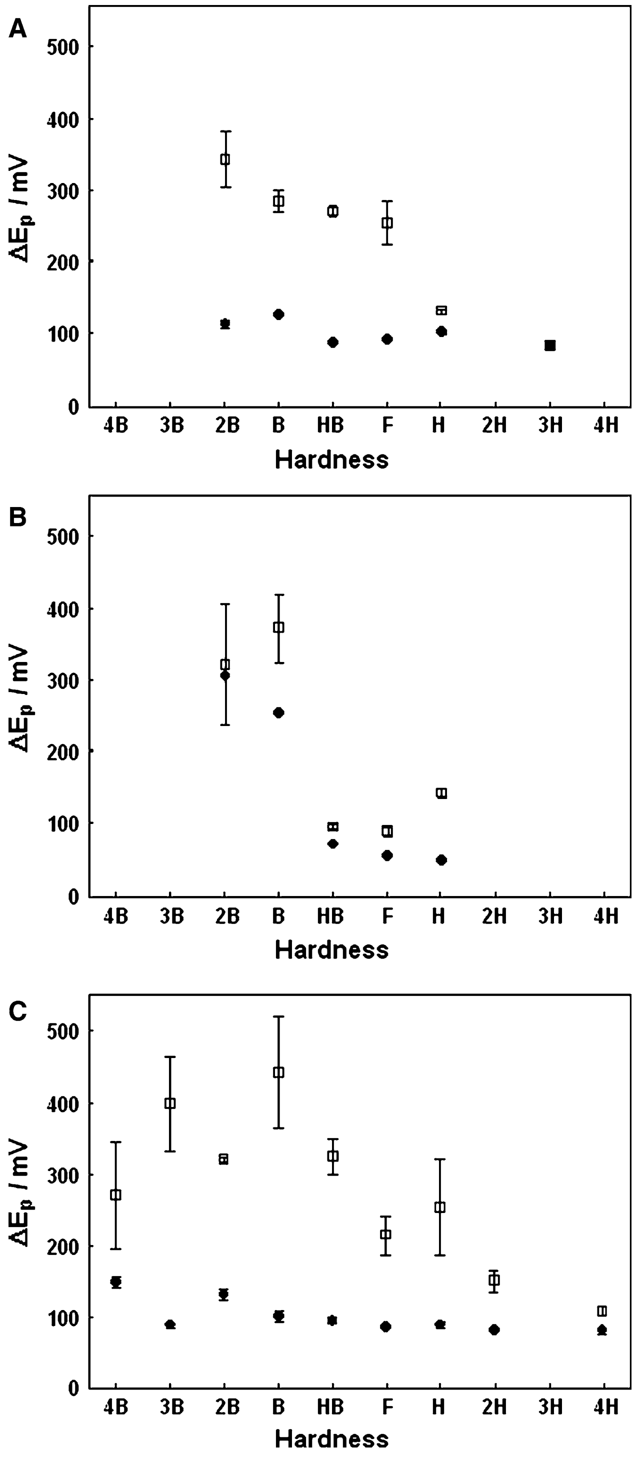

Fig. 2 Variation of ΔE_p, values as a function of hardness for pencil lead rods (□) and their respective GRC electrodes (●) of different manufacturers, for a $K_4[Fe(CN)_6]$ 6 mmol L^{-1} and 1 mol L^{-1} KCl solution. (**a**) Faber-Castell; (**b**) Kappel and (**c**) Pentel. $v = 100$ mV s^{-1}

indicating a catalytic reaction after the electron transfer. For Kappell the values increase exponentially suggesting electron transfer after a reversible chemical reaction [32].

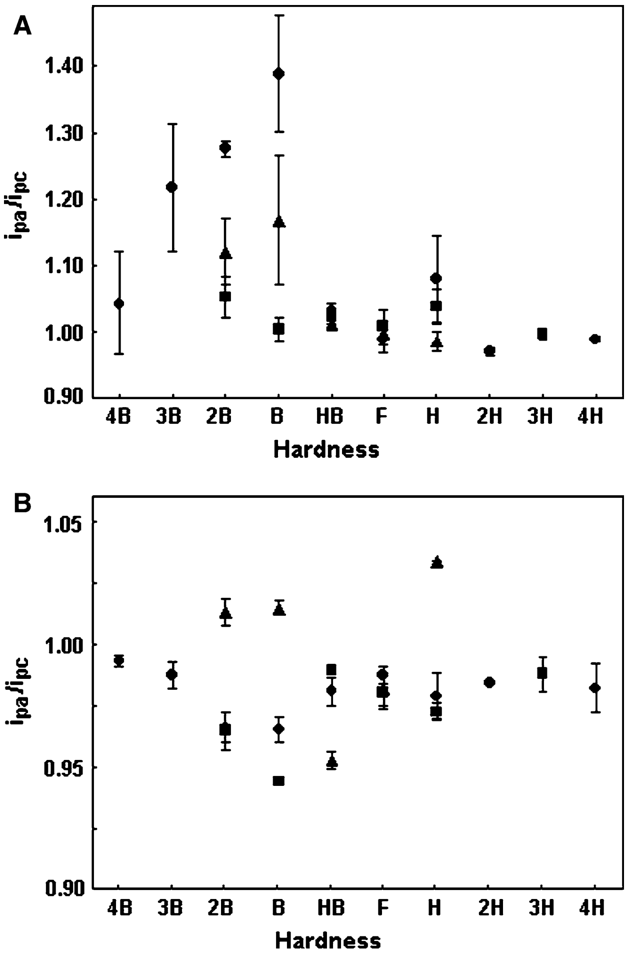

Fig. 3 Variation of i_{pa}/i_{pc} values as a function of hardness for pencil lead rods (**a**) and their respective GRC electrodes (**b**) of different manufacturers, for a $K_4[Fe(CN)_6]$ 6 mmol L^{-1} in KCl 1 mol L^{-1} solution. (■) Faber-Castell; (▲) Kappel and (●) Pentel. $v = 100$ mV s^{-1}

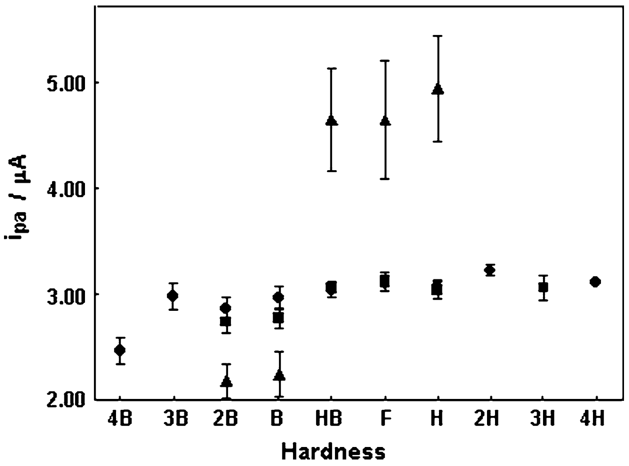

Fig. 4 Variation of i_{pa} values as a function of hardness for GRC electrodes of different manufacturers, for a $K_4[Fe(CN)_6]$ 6 and 1 mol L^{-1} KCl solution. (■) Faber-Castell; (▲) Kappel and (●) Pentel. $v = 100$ mV s^{-1}

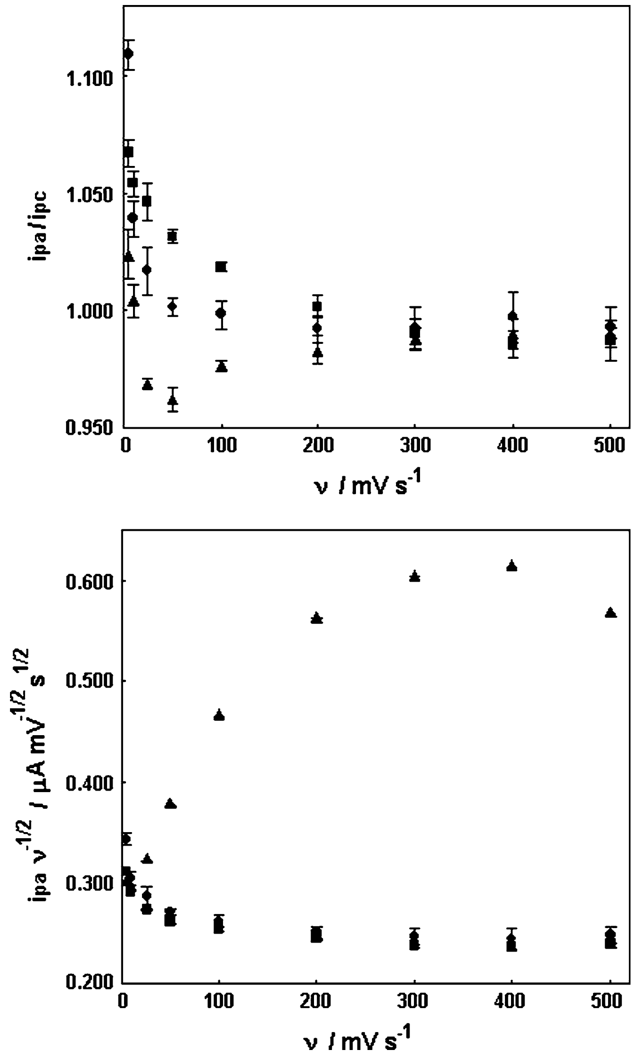

Fig. 5 Variation of i_{pa}/i_{pc} and $i_{pa}v^{-1/2}$ values as a function of scan rate for 2B GRC electrodes for a $K_4[Fe(CN)_6]$ 6 and 1 mol L^{-1} KCl solution. (■) Faber-Castell; (▲) Kappel and (●) Pentel

This behaviour is due to the different interactions between the electroactive species and the typical components of each brand of pencil lead.

This means that the electron transfer process for the $[Fe(CN)_6]^{4-/3-}$ system is accompanied by a chemical reaction [31, 32], which has a more significant role at low scan rates (lower than 200 mV s^{-1}).

These results agree with the redox mechanism proposed by Zhang et al. [33], who used infrared spectrometry and cyclic voltammetry (using a basal plan graphite electrode), and Kunimatsu et al. [34], where ferricyanide adsorbs onto the electrode surface, followed by a reduction and formation of an intermediate, and its transformation into ferrocyanide. For glassy carbon electrodes a similar behaviour was observed [35, 36].

Scholl et al. [37] investigated the electrochemical behaviour of graphite-epoxy composite electrodes, with various load ratios (40–70 wt.%), and reached an optimal graphite: epoxy ratio of 60 wt.% to obtain well-defined peaks and a maximum ratio between peak current and charge current, at the same potential, for ferrocyanide in KCl 0.4 mol L^{-1} solution. The rest of the load ratios are strongly deformed by the composite resistance or the double layer capacitance effects. Temperature studies showed that the peak shifts are not only due to the resistive component of the electrode. Because the electrical and mechanical properties are related to shape, size and spatial distributions of conductive particles, the surface properties are modified. When in a composite there is higher concentration of conductive powder, the double-layer structure depends on the surface roughness and the nature of the electroactive substances.

According to the mass percentage of graphite for different pencil grades described by Sousa and Buchanan [2], a 60 wt.% of graphite in pencil lead corresponds to 2H hardness. Therefore, the results obtained in this paper are similar to those for graphite-epoxy composite electrodes, where hardness, i.e. graphite amount and roughness affect the voltammetric response, and a well polished surface is necessary to obtain reversible cyclic voltammograms.

Despite the quasi-reversible electrochemical response of the GRC electrodes, the studies showed that harder graphite leads, regardless of their manufacturer, are more appropriate as electrode material for voltammetric purposes due to their higher peak currents, providing more sensitivity and reproducibility.

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