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Liquid-free alkaline gel filled reference electrode based on Cr₂O₃ spheres

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Ball yarn-like Cr₂O₃ non-agglomerated spheres have been synthesized through electrochemical route and fabricated into a new kind of polymer gel filled reference electrode. The potential stability and reproducibility in varying pH have been evaluated. Results demonstrate stable potential, independent of pH and extended self-life for the intensive usage for the fabricated electrode. Electrochemical studies show excellent potential over a wide range of pH in aqueous medium. This fabricated liquid-free reference electrode/sensor opens up new possibilities for multi-orientation usage.

Keywords: Electrochemistry, Electrodes, Reference electrodes, Gel electrolytes, Electroanalysis, Chromium oxide

Reference electrodes play an important part in many electrochemical measurements and are used to evaluate the potential of the working electrode¹. It should give stable, accurate and reproducible potential, independent of the composition of analyte solution and working electrode. Established on its elements, reference electrodes are classified into two types. One is the liquid filled reference electrode (calomel, Ag/AgCl and Hg/HgO) and other one is the solid state reference electrodes (SSRE) such as printed carbon based Ag/AgCl and metal oxides². The liquid-filled reference electrodes have numerous drawbacks and disadvantages³ such as requiring periodic maintenance, unstable for long-term use, evaporation of inner filling solution, leakage leading to contamination of the surrounding environment and difficulty in miniaturization, etc. The liquid-free electrode has important features and resolves most of the problems due to the liquid part of the reference electrodes⁴⁻⁶. It provides a new platform for the development of SSREs over a variety of application and miniaturization. Gel electrolyte or metal salt containing gel filled electrodes have been used instead

of liquid electrolyte¹. The liquid free reference electrodes such as gel electrolyte^{7,8} and molten salt⁹ filled electrodes give maintenance-free use and minimize the liquid junction potential^{10,11}.

Chromium exists in nature in the form of hexavalent and trivalent states, which greatly differ in their chemistry and toxicology¹². The higher oxidation state, Cr(VI), is a well established human carcinogen¹³ as compared to Cr(III) due to high solubility and easily adsorbable form of Cr(VI) in the form of hydrogen chromate (HCrO₄⁻), chromates (CrO₄²⁻) and dichromates (Cr₂O₇²⁻). On the other hand, Cr(III) has low solubility due to formation of Cr(OH)₃ and resistance to further oxidation¹⁴. Of the oxides of chromium(VI) (CrO₃) and chromium(III) (Cr₂O₃), Cr₂O₃ is of increasing interest to researchers due to its lower toxicological effects and unusual characteristics^{15,16} which includes high specific surface area¹⁷, wide band gap energy (3.4 eV) and resistance to oxidation¹⁸. Cr₂O₃ is widely used in the area of catalysis^{19,20}, anode materials for Li ion batteries²¹, hydrogen storage²², green ceramic pigments in industries²³, wear resistant coatings in steels and photocatalyst²⁴. Cr₂O₃ has also been widely studied in the field of gas sensors (mixed potential)^{25,26-29}. A recent study reports a Cr₂O₃ based Ni/NiO composite catalyst to be a potentially interesting material for hydrogen evolution in alkaline electrolyte³⁰. The combination of gas sensor and the alkaline catalyst is more interested and it inspired to elaborate the use of Cr₂O₃ for reference electrode. Cr₂O₃ commonly synthesized by the reduction and subsequent thermal decomposition of alkaline dichromate salt by sulfur or ammonium salt and by the thermal decomposition of CrO₃, Cr(OH)₃.xH₂O and CrOOH³¹.

In this study, an attempt has been made towards the preparation and characterization of Cr₂O₃ spheres and its utilization in a liquid-free alkaline gel filled reference electrode. The possible mechanism of sphere formation is also discussed. In order to utilize the as-prepared Cr₂O₃ material, a new kind of polyvinyl alcohol-alkaline (PVA-KOH) gel filled reference electrode has been fabricated using a micropipette tip as substrate and evaluated for its performance in aqueous medium. The performance of

the fabricated electrode is also compared with conventional reference electrodes.

Experimental

Potassium hydroxide, sodium hydroxide, sulphuric acid were purchased from Fischer Scientific. CaO was purchased from Otto Chem. Ltd. Potassium dichromate was purchased from the Indian Drugs and Pharmaceuticals Ltd. Nickel foam (purity >99.99%) was purchased from MTI Co, USA. All the chemicals were used as such and without further purification. All solutions were prepared using deionized water. Solutions of the desired pH were prepared using phosphate buffer and acid-base mixture of sodium hydroxide and hydrochloric acid.

Ball yarn-like Cr₂O₃ spheres were prepared through electrochemical route as described elsewhere³². K₂Cr₂O₇ (0.3 M) was mixed with sulphuric acid in the ratio 4:1 (v/v). Pt foil (1 cm²) and Pt coated titanium mesh (3 cm²) were immersed in the solution and used as cathode and anode respectively. Constant potential of ~12 V was applied between the electrodes using Aplab (LD 6405) regulated dual DC power supply until the change/transformation from reddish orange to green (Supplementary data, Fig. S1). Then the solution was kept in an air oven to evaporate the excess water content. This solid material was ground into a powder and washed with deionized water several times to remove the soluble products and then calcinated at various temperatures from 400 °C to 800 °C for about 3 hours in air atmosphere.

XRD patterns were recorded on a PANalytical, PW3040/60 X'pert PRO diffractometer with X-ray tube of 3 kW copper target Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$). FTIR spectra were recorded on a Bruker-Tensor 27 spectrometer with Opus ver. 6.5 software. Raman data were obtained from a Renishaw inVia Raman microscope equipped with He-Ne laser 633 nm laser source. Surface morphology of the sample was observed through VEGA3 SB TESCAN scanning electron microscope. Phase composition was studied by energy dispersive spectrum (EDS), collected with a X-Flash detector (410M) with Bruker ESPRIT QUANTAX EDS analyzing software.

Schematic illustration of Cr₂O₃ base PVA (polyvinyl alcohol) gel electrode fabrication is shown in Fig. S2 (Supplementary data). Nickel foam was used as substrate. Prior to coating of Cr₂O₃, the nickel foam was cleaned with plenty of soap water followed by ethanol and acetone. Finally, the foam was dried in hot

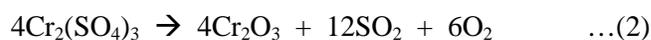
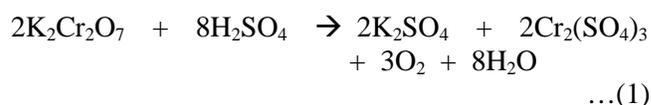
air oven at 60 °C for 3 h. Cr₂O₃ and poly(vinylidene) fluoride binder were mixed in the ratio 90:10 (wt/wt) using *n*-methyl pyrrolidine as solvent. The slurry was coated on the nickel foam substrate and then the foam was dried in the oven at 60 °C. The sensing material was kept at ~50 mg on both sides of the substrate. The PVA-KOH polymer electrolyte was prepared as follows: PVA and KOH (5 g each) were mixed with 50 mL of water and the mixture was heated under constant stirring until a homogenous viscous solution appeared. The resulting homogenous solution was filled in a porous bottom sealed micropipette and then the Cr₂O₃ coated nickel foam was inserted in to the container. Finally, the top portion was sealed with epoxy resin and electrical lead was taken from the top end. To ensure stability and reproducibility, three gel filled reference electrodes (GFRE1, GFRE2 and GFRE3) were fabricated under identical conditions.

The potential stability and performance of the fabricated sensor was measured in aqueous solutions of varying pHs in a two-electrode setup using Rishmulti 18S multimeter (Rishabh Instruments). The impedance spectrum was recorded using Gill AC (ACM Instruments, UK). The frequency range was varied from 100 kHz to 0.01 Hz over 20 mV/RMS amplitude with an additional DC offset of 5 mV. All the electrochemical measurements were carried out at room temperature and potentials were measured with respect to SCE.

Cyclic voltammetric studies were performed using a computer controlled Autolab potentiostat. Reversible characteristics of 1 mM potassium ferrocyanide in 0.1 M KCl solution were analyzed using gold electrode (1 mm dia.) as working electrode and platinum foil (1 cm²) as counter electrode. Conventional SCE, Ag/AgCl reference electrodes were used for comparison with the fabricated reference electrodes. CVs were recorded from -0.4 to 0.6 V at a scan rate of 100 mV s⁻¹.

Results and discussion

In the electrochemical process herein, sulphuric acid acts as a good reducing agent under the applied potential and forms Cr₂(SO₄)₃. The possible reaction of the overall process is given below³².



In the XRD pattern of the product obtained by calcination at 800 °C for 3 h, all the diffraction peaks can be indexed to the rhombohedral phase of Cr_2O_3 (JCPDS No: 38-1479). The average particle size calculated using the Debye-Scherrer formula was found to be 78 nm. In the FTIR spectra, two major peaks observed in the range at around 568 and 643 cm^{-1} may be attributed to the vibration between the metal oxygen bond in octahedral and tetrahedral sites respectively. The oxide phase of Cr_2O_3 was investigated by the Raman spectrum of the synthesized sample. Raman bands at

around 304, 349, 527 and 611 cm^{-1} correspond to the E_{g}^1 s-ph, E_{g}^2 , E_{g}^3 and E_{g}^4 symmetries respectively. The A_{1g} symmetry is observed at 551 cm^{-1} . These results are in good agreement with earlier reports^{33,34}.

Surface morphological characteristics of the prepared Cr_2O_3 was studied by SEM images of Cr_2O_3 heat treated at 400 °C (Fig. 1(a-d)) and 800 °C (Fig. 1(e,f)). It can be seen that the particles have ball yarn-like sphere structure with a large numbers of rolled yarns. Yarn width was found to be in the range of 0.20–0.25 μm . Increase in the calcination temperature causes the

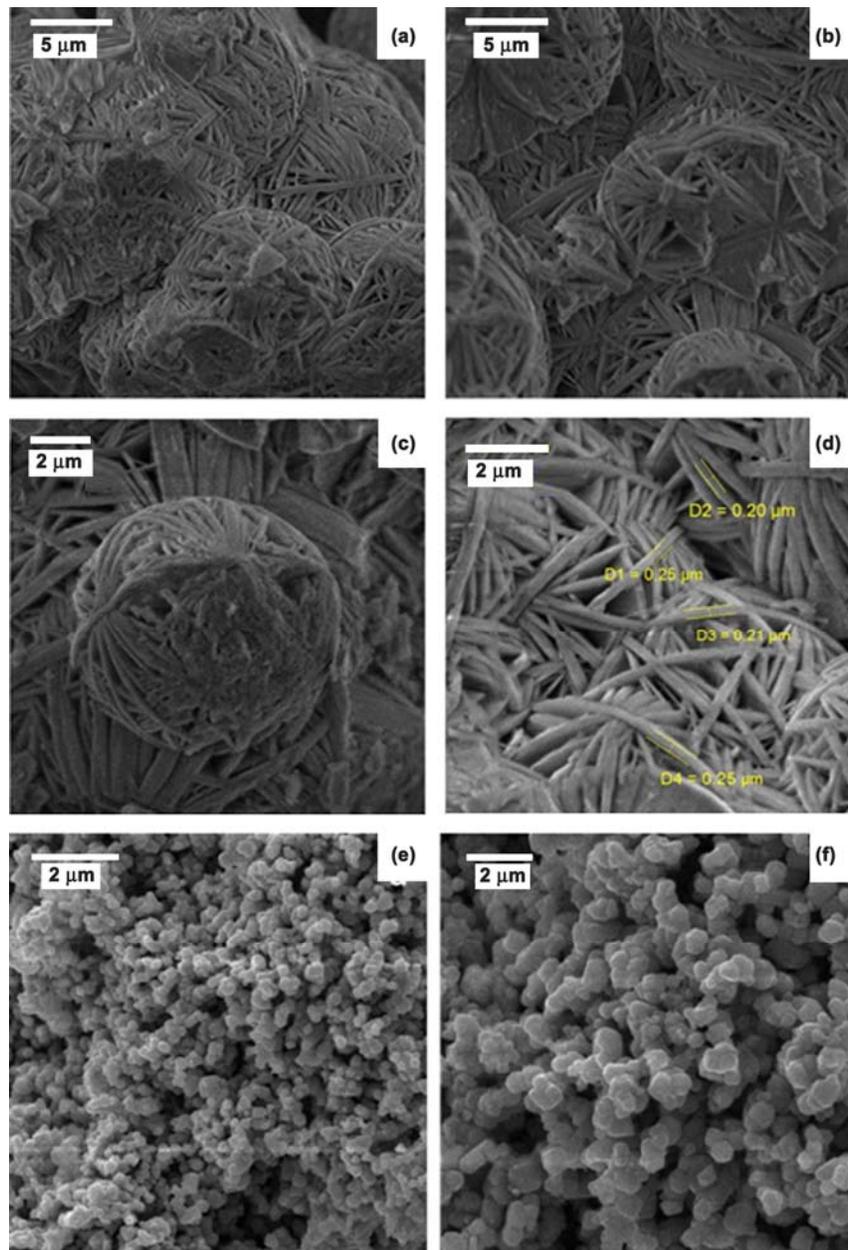


Fig. 1 – SEM images of Cr_2O_3 heat treated for 3 hours at 400 °C (a-d) and 800 °C (e, f) in air.

shrinkage of yarn in the spheres and produces a smooth surface. When the calcination temperature increases, the ball yarn-like sphere structure of Cr_2O_3 changes into smooth sphere due to the internal shrinkage. After calcination, the inter-distance between the yarns is minimized and the pores disappear. Here, the formation of ball yarn-like Cr_2O_3 spheres and Cr_2O_3 spheres is closely related to the Ostwald ripening process³⁵.

In the electrochemical reduction, $\text{K}_2\text{Cr}_2\text{O}_7$ produces $\text{Cr}_2(\text{SO}_4)_3$ spheres initially (which have crystalline ball-like morphology) (Supplementary data, Fig. S3) and followed by the production of ball yarn-like Cr_2O_3 spheres due to homogenous evaporation of sulfur oxides during calcination. Similarly, during strong calcination at higher temperatures of 800°C , the yarns-like spheres shrink together to form smooth spheres as shown in Fig. 1(e,f). It clearly indicates that the surface morphology and size change depend on the calcination temperature. Figure 2 illustrates the schematic formation of ball yarn-like Cr_2O_3 spheres and smooth Cr_2O_3 spheres by the shrinkage of yarns at higher temperature.

Energy dispersive spectrum of prepared sample (Supplementary data, Fig. S4) displays the presence of Cr and O content and absence of peaks due to any impurity, indicating the high purity of the samples.

Electrochemical potential characteristics of the fabricated electrode was studied. The oxidation state of metal and thus the redox potential is dependent upon the redox reactants in solution. e.g dissolved oxygen. In addition, the potential is dependent on pH and H^+ ions change the redox potential of $\text{O}_2/\text{H}_2\text{O}$. Accordingly, the redox potential is considered as a constant, when the pH and oxygen concentration is constant. The potential is constant, even in the absence of oxidizing/reducing agents as well³⁶.

Electrochemical potential response and stability of the fabricated electrodes were measured at various pH with respect to SCE. Here, the preferred pH was achieved by acid base titration of 0.1 M phosphoric acid and sodium hydroxide solution, using a commercial glass pH electrode. As shown by Fig. 3, the measured potential was independent of pH in the range of 1–12 and was stable throughout the studied pH range, indicating its potential use as a good reference electrode.

Standard electrode potential of fabricated electrode was calculated using the equation, $E^\circ_{\text{cell}} = E_{\text{test}} - E_{\text{ref}}$, where E°_{cell} is the measured potential with respect to conventional reference, E_{test} is potential of the fabricated electrode and E_{ref} is used reference electrode potential (here SCE). According to the

systematic series of analytical investigations, the fabricated Cr_2O_3 based gel electrode demonstrates a potential of $-220 \pm 5\text{ mV}$ with respect to SCE.

The addition of acid and base does not change the potential of the Cr_2O_3 alkaline gel electrode due to the insensitivity to pH . Herein, insensitivity towards pH is due to the immobilisable anions and cations. Hydrogen sensitivity is minimized by the high alkaline gel electrolyte environment. The inner alkaline gel behaves like a buffer system and resists the pH changes.

Response time is defined as the minimum time required to attain the maximum stable equilibrium potential of $\pm 5\text{ mV}$ in the testing time. In most cases, fast potential response or sensing characteristics of reference electrodes are questionable since it may be due to external interference such as accidental application of potential or current, or due to polarizable constituents like active electrode material, substrate and electrolytes. Non-polarizable electrodes have the capability of fast response and reproducibility and their potential will not change from the original value even due to large current density/ potential cycle interruption. In the present study, characteristics of the fabricated electrode were

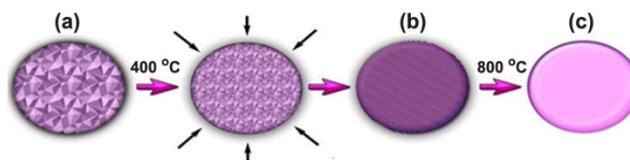


Fig. 2 – Schematic illustration of Cr_2O_3 sphere formation (a) before calcination, (b) calcined at 400°C for 3 hours, and, (c) calcined at 800°C for 3 hours.

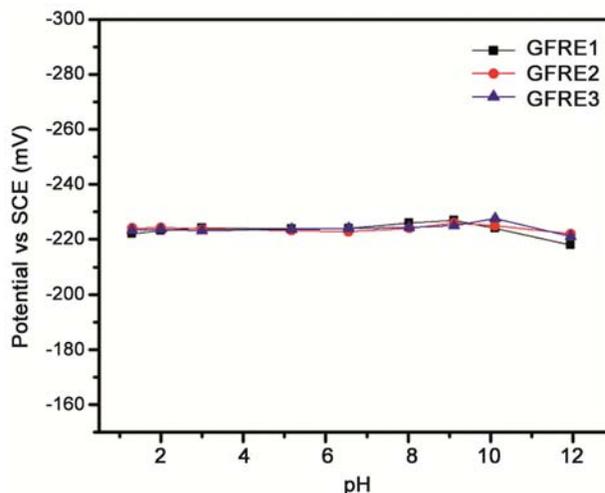


Fig. 3 – Stability of Cr_2O_3 reference electrodes, GFRE1, GFRE2 and GFRE3, in solutions of varying pH s.

analysed by cyclic polarization method from the OCP to ± 20 , ± 100 and ± 200 mV with respect to SCE (Supplementary data, Fig. S5). At the lower potential shift of ± 20 mV, potential deviation between the two half cycles was 11 mV, while at the consecutive shift of ± 100 and ± 200 mV, it was 25 and 41 mV respectively. At the end of each cycle, the potential retained its original OCP within 2 min. It was interesting to note that the higher shifts did not affect the potential stability and reversibility. We observed good stable potential in the same solution after 10 cyclic sweeps. Whenever the original potential of reference electrode was shifted by either positive or negative direction, the original potential was regained. This result is closely interrelated to the pulse current mode reversibility of hydrophobic ion-doped

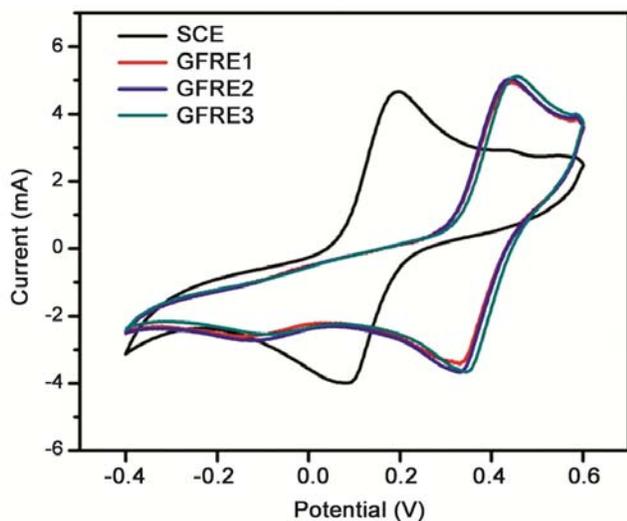


Fig. 4 – Cyclic voltammograms of 0.1 mM potassiumferro/ferricyanide in 0.1 M KCl using gold electrode as working electrode with SCE and fabricated reference electrodes (GFRE1, GFRE2 and GFRE3).

polymeric reference electrode³⁷, and show the good stability and reproducibility of the fabricated electrodes over wide external potential interruption.

The interference of various chloride salts and their influence on the potential of fabricated electrode were measured with respect to SCE in 0.1 M NaCl, KCl and LiCl solutions. No appreciable potential drifts was observed during the measured period, suggesting that the fabricated electrode is insensitive to chloride, metal and other ions and the potential was not influenced by the corresponding ions.

The redox reaction with 1 mM of potassium ferrocyanide/ferricyanide was studied in 0.1 M KCl using gold working electrode (dia. 1 mm) with respect to SCE and fabricated reference electrodes (Fig. 4). The peak potential is shifted to ≈ 250 mV in the positive region as compared to SCE. Similarly, the peaks potential differences of three electrodes are found to be ≈ 100 mV, which shows the excellent reproducibility of the as-fabricated gel reference electrode.

Figure 5 shows the Nyquist plots with an equivalent circuit of the fabricated electrode initially and after 75 days stored in synthetic concrete pore solution. Low frequency semicircle or Warburg diffusion line is not seen (Fig. 5a). The absence of the low-frequency semicircle indicates the uniformly covered interface of electrode and PVA-KOH gel electrolyte³⁸. The high frequency half semicircle indicates the bulk resistance of gel electrolyte. This bulk resistance forms double layer capacitance in series at high frequency. Total resistance of the reference electrode is the sum of the solution resistance (R_s) due to the gel electrolyte and charge transfer resistance (R_{ct}) between the electrolyte and electrode surface of equivalent circuit of the reference electrode (Fig. 5b). This phenomena is

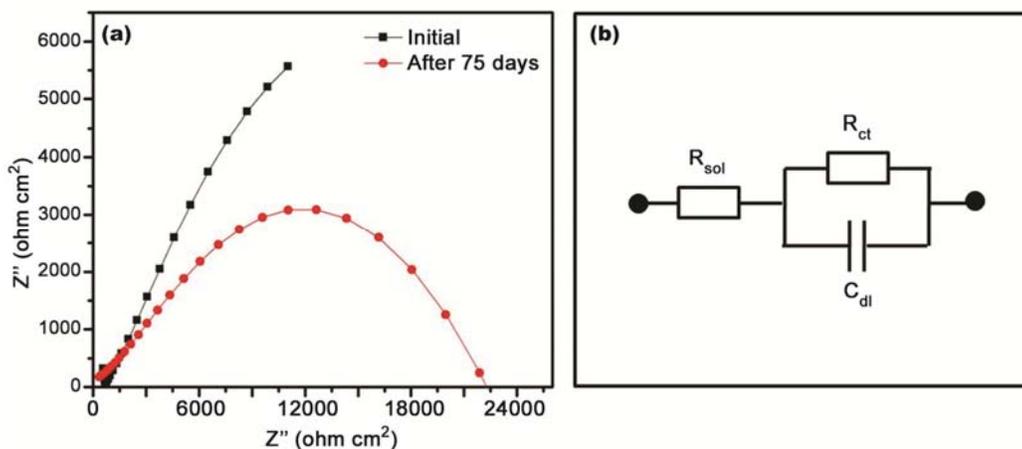


Fig. 5 – (a) Nyquist plot of fabricated gel electrode in synthetic concrete pore solution (pH= ~ 13) initially and after 75 days immersed condition, and, (b) Equivalent circuit model of the reference electrode.

attributed to the polymer electrolyte and the solid surface of Cr_2O_3 electrode interfaces. The derived impedance parameter indicates good stability characteristics before and after stored conditions in high alkaline solution (Supplementary data, Table S1).

Stability of the electrode plays a vital role in electrochemical measurements. Stability of the fabricated gel filled electrode was analyzed by storing it in aqueous solutions for four months and measuring the potential periodically measured with respect to SCE. The potentials appeared the same with minimum drift of ± 6 mV, indicating its good performance for long duration in aqueous medium.

In this study, a polymer alkaline gel filled reference electrode based on non-agglomerated Cr_2O_3 spheres was prepared and characterized. The fabricated electrode shows a stable potential, independent of pH and composition of analyte solutions over exposure period of more than four months. This liquid-free reference electrode exhibits performance comparable with conventional reference electrodes and has maintenance free and multi-orientation usage. The electrode demonstrated excellent reversibility and stable potentials over a wide range of aqueous pH medium. This fabricated electrode/sensor opens up new possibilities of orientation dependent reference electrodes.

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Supplementary data

Supplementary data associated with this article, viz., Figs S1–S5 and Table S1 are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_54A\(10\)1215-1220_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_54A(10)1215-1220_SupplData.pdf).

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