

Na₃SbS₃: Single Crystal X-ray Diffraction, Raman Spectroscopy, and Impedance Measurements

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Dedicated to Professor Hartmut Bärnighausen on the Occasion of His 80th Birthday

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Abstract. Na₃SbS₃ was prepared by the reaction of anhydrous Na₂S, antimony, and sulfur in a ratio of 3:2:3 at 870 K. The pale yellow compound is air and moisture sensitive. A microcrystalline sample was obtained after annealing Na₃SbS₃ for two weeks at 720 K. The crystal structure of Na₃SbS₃ was determined by single-crystal X-ray diffraction at 123 K. Na₃SbS₃ crystallizes in the cubic space group *P*2₁3 (No. 198) with *a* = 8.6420(1) Å, *V* = 645.42(1) Å³ and *Z* = 4. The structure refinement converged to *R* = 0.0099 (*wR* = 0.0181) for 592 independent reflections and 23 parameters. Na₃SbS₃ is isotopic with Na₃AsS₃. Sodium atoms are located on three different sites, which show a

strongly distorted octahedral coordination sphere of sulfur. The coordination polyhedra of equivalent sodium sites share common vertices, whereas those of different sodium sites share common faces. Antimony and sulfur form trigonal SbS₃ pyramids, which coordinate sodium as a mono-, bi-, or tridentate ligand. Raman spectroscopic investigations result in stretching modes *v*(Sb–S) at 334, 321, and 312 cm⁻¹, respectively. Thermoanalytical studies do not show any additional thermal effects up to the melting point of 875 K. Impedance spectroscopy on Na₃SbS₃ in a range from 325 to 570 K shows a temperature dependent Na⁺ conductivity, which is 1.9 × 10⁻⁶ Ω⁻¹·cm⁻¹ at 570 K.

Introduction

Alkali metal pnictogen chalcogenides *M*₃*PnQ*₃ (*M* = Na, K, Rb, Cs, *Pn* = As, Sb, Bi, and *Q* = S, Se, Te) are a well-established group of compounds. Although the homologous elements differ significantly from each other in terms of ion radii and electronegativity, they form a whole series of isotopic crystal structures, and crystallize in the cubic space group *P*2₁3. The structure type is named after the first representative Na₃AsS₃.^[1] Sommer and Hoppe as well as Bronger et al. had a great merit on the synthesis and structural characterization of the corresponding compounds. Sommer described the sodium and potassium containing thioarsenates (Na₃AsS₃, K₃AsS₃) and thioantimonates (Na₃SbS₃, K₃SbS₃),^[2] whereas Bronger and co-workers focused on the selenoarsenates (Na₃AsSe₃, K₃AsSe₃), selenoantimonates (K₃SbSe₃, Rb₃SbSe₃, Cs₃SbSe₃), and the selenobismutates (K₃BiSe₃, Rb₃BiSe₃, Cs₃BiSe₃).^[3–6] The telluroantimonates Na₃SbTe₃ and K₃SbTe₃ were also reported in literature.^[7,8] Jung firstly investigated the conductivity of a compound of this series *M*₃*PnQ*₃, i.e., K₃SbTe₃, which was reported to be a poor semiconductor.^[9] Very recently the thioantimonate Li₃SbS₃ was structurally characterized. It is the first member of this whole group of materials, which crystallizes in a different structure

type. It shows an ionic conductivity of 5.4 × 10⁻⁵ Ω⁻¹·cm⁻¹.^[10] In contrary, Na₃SbSe₃ crystallizes in the well-established Na₃AsS₃ structure type and shows also an enhanced ionic conductivity at elevated temperature.^[11]

Herein, we report on the structural characterization and the ionic conductivity of the corresponding thioantimonate, Na₃SbS₃. To date, only lattice parameters are known, which are based on Guinier powder data, and isotypism to Na₃AsS₃ has been proposed.^[2]

Results and Discussion

Structure Description and Discussion

The crystal structure of Na₃SbS₃ was determined from single-crystal X-ray diffraction data collected at 123 K. The title compound crystallizes in space group *P*2₁3. The cubic cell has the parameters *a* = 8.6420(1) Å, *V* = 645.42(1) Å³ and *Z* = 4. From powder diffraction data of pure powder samples a cell parameter of *a* = 8.7026(5) Å was determined at room temperature. Crystallographic data are listed in Table 1. The structure refinement with anisotropic displacement parameters converged to *R*₁ = 0.0099 [23 parameters, 592 reflections with *I* > 2σ(*I*)] and *wR*₂ = 0.0181 (all reflections). Atomic coordinates and equivalent isotropic displacement parameters *U*_{eq} are listed in Table 2, the anisotropic displacement parameters *U*_{ij} in Table 3.

The Na₃AsS₃ structure type and its relations to the NaClO₃ as well as to the Th₃P₄ structure type has already been discussed in several publications.^[2,6] Thus, we limit the dis-

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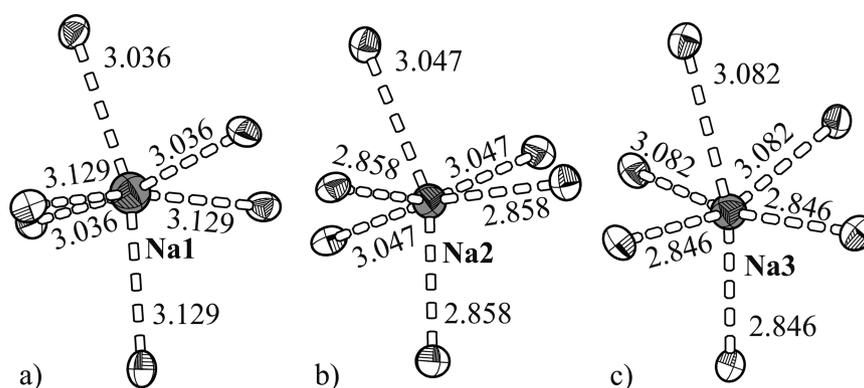
Table 1. Crystallographic data for the structure analysis of Na₃SbS₃.

	Na ₃ SbS ₃
Formula weight /g·mol ⁻¹	286.90
Color	pale yellow
Crystal system	cubic
Space group	<i>P</i> 2 ₁ 3 (No. 198)
Lattice constant <i>a</i> /Å	8.6420(1)
Cell volume <i>V</i> /Å ³	645.42(1)
Number of formula units per unit cell <i>Z</i>	4
Calculated density ρ_{calc} /g·cm ⁻³	2.953
Temperature <i>T</i> /K	123
Wavelength λ /Å	0.71073
Diffractometer	Oxford Diffraction Gemini R Ultra CCD, Mo- <i>K</i> α ($\lambda =$ 0.71073 Å)
Absorption coeff. μ /mm ⁻¹	5.308
Absorption correction	Multi-scan ^[19]
2 θ range /°	6.66 \leq 2 θ \leq 58.68
<i>hkl</i> -ranges	-11 \leq <i>h</i> \leq 10 -11 \leq <i>k</i> \leq 10 -11 \leq <i>l</i> \leq 11
No. of reflections, <i>R</i> _{int}	9385, 0.0337
No. of independent reflections	592
Structure solution	SIR92 ^[20]
Structure refinement	SHELX-97 ^[21]
No. of parameters	23
Final <i>R</i> , <i>wR</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0099, 0.0180
Final <i>R</i> , <i>wR</i> (all reflections)	0.0106, 0.0181
Goof	1.099
Largest difference peak $\Delta\rho_{\text{max}}$ and hole $\Delta\rho_{\text{min}}$ /e \cdot Å ⁻³	0.451, -0.264
Extinction parameter	0.0016(2)
Flack parameter	-0.04(2)

Table 2. Atomic coordinates and equivalent isotropic displacement parameters U_{eq} for Na₃SbS₃.

Atom	Wyck.	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Na1	4 <i>a</i>	0.82507(8)	<i>x</i>	<i>x</i>	0.0167(3)
Na2	4 <i>a</i>	0.56826(8)	<i>x</i>	<i>x</i>	0.0117(3)
Na3	4 <i>a</i>	0.05968(8)	<i>x</i>	<i>x</i>	0.0119(3)
Sb	4 <i>a</i>	0.28492(1)	<i>x</i>	<i>x</i>	0.00775(6)
S	12 <i>b</i>	0.01647(5)	0.24997(4)	0.35818(5)	0.01027(9)

a) U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

**Figure 1.** The distorted octahedral coordination of the three sodium sites Na1 (a), Na2 (b), and Na3 (c). Distances are given in Å.**Table 3.** Anisotropic displacement parameters U_{ij} for Na₃SbS₃.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na1	0.0167(3)	U_{11}	U_{11}	0.0005(3)	U_{23}	U_{23}
Na2	0.0117(3)	U_{11}	U_{11}	0.0005(3)	U_{23}	U_{23}
Na3	0.0119(3)	U_{11}	U_{11}	-0.0003(3)	U_{23}	U_{23}
Sb	0.00775(6)	U_{11}	U_{11}	-0.00044(4)	U_{23}	U_{23}
S	0.0092(2)	0.0101(2)	0.0116(2)	0.0005(2)	0.0025(2)	0.0005(2)

discussion herein to the most important details. Distances and angles are based on the data obtained at 123 K.

The crystal structure of Na₃SbS₃ can be subdivided into two structural motifs. Antimony and sulfur are arranged as trigonal-pyramidal SbS₃ units (see Figure 2) with an angle S–Sb–S = 99.40(1)°, the distance $d(\text{Sb–S})$ is 2.4237(4) Å. So-called secondary bonds are formed to three sulfur atoms at a distance of 3.6890 Å. A detailed comparison with isotopic thioantimonates(III) of the other alkali metals is not possible due to a lack of precise structural data for some of them. However, Li₃SbS₃ was synthesized recently.^[10] It represents a completely different structure type as compared with the other compounds of the series M_3PnQ_3 . Nevertheless, the SbS₃ units therein show the typical bond lengths and angles, regardless the fact that they do not have perfect trigonal symmetry in Li₃SbS₃. The trigonal-pyramidal SbS₃ motif was also found in compounds like Cu₃SbS₃, (CuI)₂Cu₃SbS₃, or (AgI)₂Ag₃SbS₃. The distance Sb–S in Cu₃SbS₃ varies between 2.446 and 2.478 Å.^[12] Shorter distances were observed in (CuI)₂Cu₃SbS₃ (2.434 to 2.446 Å).^[13] In silver containing analogue (AgI)₂Ag₃SbS₃, the distances range from 2.418 to 2.426 Å at 173 K.^[14]

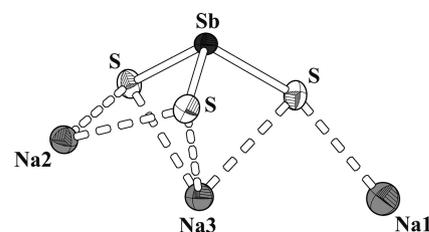
**Figure 2.** Coordination of antimony in the SbS₃ units and sodium in the next coordination sphere.

Figure 1 shows the three different coordination modes of SbS₃ units to the three different sodium sites Na1, Na2, and

Na3 in Na₃SbS₃. Na1 is coordinated exclusively by monodentate and Na2 by bidentate SbS₃ ligands, respectively. Na3 is coordinated by one tridentate as well as by three monodentate ligands. These coordination modes result in three different distorted octahedral environments for the sodium atoms. The interatomic distances in Table 4 quantify the distortions of the NaS₆ units. Several examples of SbS₃ units acting as bidentate ligands to transition metals in competition with amines have been recently reported.^[15–18] However, in these examples only one coordination mode is observed.

Table 4. Selected interatomic distances /Å and angles /° for Na₃SbS₃ at 123 K.

Sb–S	3 ×	2.4237(4)	S–Sb–S	3 ×	99.40(1)
	3 ×	3.6890(4)			
Na1–S	3 ×	3.0355(9)	S–Na1–S	3 ×	83.65(3)
	3 ×	3.1288(9)	S–Na1–S	3 ×	84.49(3)
			S–Na1–S	3 ×	86.79(1)
			S–Na1–S	3 ×	107.385(7)
			S–Na1–S	3 ×	164.53(1)
Na2–S	3 ×	2.8580(7)	S–Na2–S	3 ×	77.46(2)
	3 ×	3.0465(9)	S–Na2–S	3 ×	84.12(3)
			S–Na2–S	3 ×	95.63(3)
			S–Na2–S	3 ×	105.998(7)
			S–Na2–S	3 ×	157.76(2)
Na3–S	3 ×	2.8461(8)	S–Na3–S	3 ×	73.71(3)
	3 ×	3.082(1)	S–Na3–S	3 ×	86.93(2)
			S–Na3–S	3 ×	94.29(3)
			S–Na3–S	3 ×	105.368(8)
			S–Na3–S	3 ×	160.17(3)

The distances $d(\text{Na–S})$ in Na₃SbS₃ vary between 2.846 and 3.129 Å. A calculated distance of $d_{\text{calc}}(\text{Na–S}) = 2.86$ Å results from ionic radii.^[22] Typically compounds adopting the Na₃AsS₃ structure type show two alkali metal sites with bond lengths in the range of those calculated from ionic radii and one with significantly longer distances to coordinating chalcogen atoms.^[11] This is also the case in the title compound with the longer distances observed for Na1, compare Table 4.

Powder X-ray Diffraction

In Figure 3 the pattern, calculated from single crystal structural data, is opposed as inverted intensities to the experimental pattern. A high background in the experimental pattern is due to the measurement in a sealed glass capillary. The comparison between both patterns indicates the purity of the sample, which was subsequently used for impedance measurements. The refined cell constant $a = 8.7026(5)$ Å matches the value, which was presented by Sommer and Hoppe.^[2]

Raman Spectroscopy

The bonding interactions between antimony and sulfur can be estimated by the resonance of the Sb–S stretching vibrations of the SbS₃ units.^[13] In case of Na₃SbS₃ they lead to dominating bands in the range between 334 and 312 cm⁻¹ (see Fig-

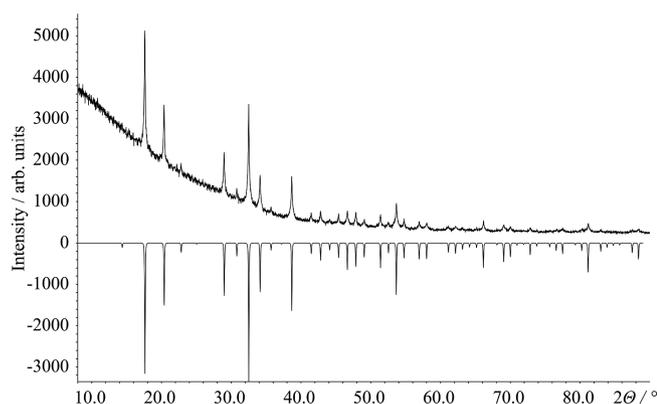


Figure 3. The measured (top) and calculated X-ray powder diffraction pattern for Na₃SbS₃ (down, inverted intensities). All measured lines can be indexed with a cubic primitive cell with $a = 8.7026(5)$ Å.

ure 4). The values agree quite well with the spectra for related compounds like Li₃SbS₃ (333–301 cm⁻¹) or Ag₃SbS₃ (330–303 cm⁻¹).^[10,14] Therein SbS₃ pyramids are not completely isolated from each other, which means corresponding distances $d_{\text{secondary}}(\text{Sb–S})$ are about 3.7 Å. In this case the secondary bonding interactions between the SbS₃ units and the next-nearest sulfur atoms cause a typical red shift in comparison to compounds, in which the SbS₃ units are separated from each other. (AgI)₂Ag₃SbS₃ e.g., shows resonances between 357 and 316 cm⁻¹.^[14]

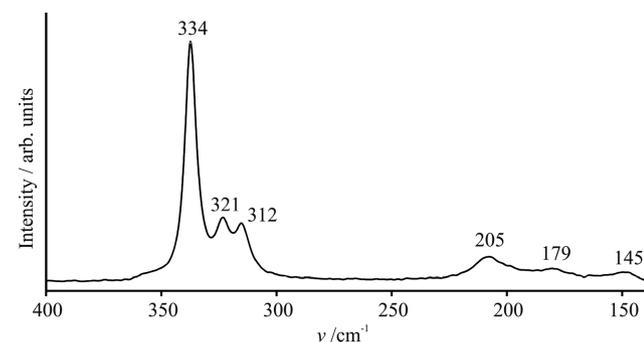


Figure 4. The Raman spectrum shows the bands of the of the Sb–S stretching modes at 334, 321, and 312 cm⁻¹.

Differential Thermal Analysis (DTA)

A pure, finely powdered sample of Na₃SbS₃ was used for DTA. The melting and the crystallization curves show one maximum, respectively. The melting point of Na₃SbS₃ is observed at 876 K. The compound crystallizes at 724 K. Similar dystectic behavior was reported for the selenide analogue Na₃SbSe₃.^[11] An additional endothermic effect was reported for heating curves of Na₃SbS₃ and a high-temperature modification was suggested in reference [23] without further characterization. Further experiments, e.g., high-temperature X-ray diffraction will clarify this inconsistency.

Impedance Measurement

For the determination of the total electric conductivity of Na₃SbS₃ frequency dependent impedance spectroscopy was performed in a temperature range from 325 to 570 K. The Nyquist plot in Figure 5 shows the relation between the real and imaginary part of the impedance at 570 K. The linear arc for frequencies below 1 kHz is generated by ionic conductivity, which increases from $1 \times 10^{-9} \Omega^{-1} \cdot \text{cm}^{-1}$ at 325 K to $2 \times 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$ at 570 K.

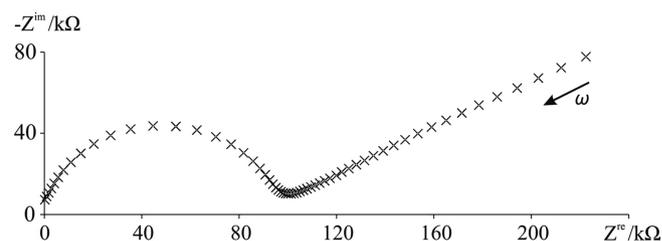


Figure 5. Impedance spectrum of Na₃SbS₃ at 570 K. The spectrum shows the typical frequency dependency in case of an ionic conductor with ion blocking electrodes.

The dependency of ionic conductivity on temperature is illustrated by the Arrhenius plot in Figure 6. The activation energy is 0.49 eV. The presented results for Na₃SbS₃ differ in some case from the recently published values for Na₃SbSe₃. The ionic conductivity of the selenide compound reaches a slightly higher value ($3 \times 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$ at 570 K).^[11] The conductivities of both sodium antimony chalcogenides are well comparable for example to sodium tetrathiophosphate, which shows an ionic conductivity of $4 \times 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$ at 323 K.^[24] However, Na₃SbSe₃ shows a significant higher activation energy of 0.69 eV than Na₃SbS₃. Ionic conductivity was not detectable below 380 K. *Jansen* reported decreasing activation energies of the low-temperature modification for the series Na₃PO₄S_{4-x} ($x = 0, 1, 2, 3, 4$). This observation is explained by the increasing polarisability of the anion lattice from Na₃PO₄ to Na₃PS₄.^[25] Another example for this trend are the silver ion conducting compounds Ag₅Te_{2-y}Se_yCl ($y = 0-0.7$), whose activation energies decrease with an increasing content of tellurium.^[26] Our studies on Na₃SbS₃ and Na₃SbSe₃ result in a contrary tendency so far. Therefore further investigations on compounds with a mixed chalcogenide lattice are in progress.

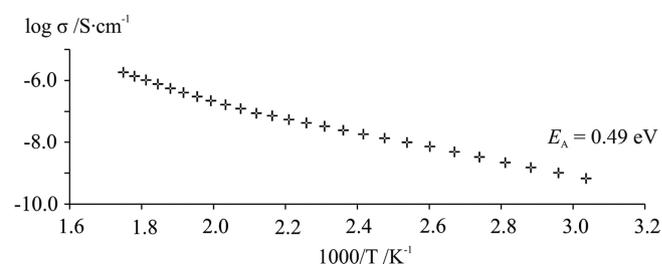


Figure 6. The Arrhenius plot shows an exponential dependency of the specific ionic conductivity on the reciprocal temperature.

Experimental Section

Synthesis: Pure samples of Na₃SbS₃ for X-ray powder diffraction and impedance spectroscopy were obtained from stoichiometric mixtures of Na₂S, antimony (99.9999 %, Chempur) and sulfur (99.999 %, Chempur) in a 3:2:3 ratio, which were heated to 870 K in evacuated silica ampoules for 7 d. The ampoules were coated with graphite by pyrolysis of acetone prior to use. Anhydrous Na₂S was obtained by reaction of stoichiometric quantities of distilled sodium (99 %, Merck) and sulfur in dry ammonia.^[27] Due to their air and moisture sensitivity, all procedures with Na₂S and Na₃SbS₃ were performed in an atmosphere of dry argon. For the structure determination of Na₃SbS₃, pale yellow single crystals were obtained after a second annealing period of two weeks at 720 K.

Crystal Structure Analysis: A transparent, pale yellow single crystal of Na₃SbS₃ was measured in a drop of mineral oil. A nitrogen jet cooled the sample down to 123 K in order to fix the crystal during the data collection. Diffraction data were collected with an Oxford Diffraction Gemini R Ultra CCD with Mo-*K*_α radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption correction was carried out by multi-scans.^[19] The crystal structure was solved by direct methods with SIR92.^[20] SHELX-97 was used for full-matrix least-squares structure refinement, applying anisotropic displacement parameters for all atoms.^[21] An extinction parameter was introduced in the final stage of the refinement. The Flack parameter of almost 0 did not indicate any inversion twinning.

Powder X-ray Diffraction: Finely ground samples were sealed in an argon atmosphere in a glass capillary (diameter 0.2 mm). X-ray powder patterns were measured with a STOE Stadi P diffractometer with monochromatic Cu-*K*_{α1} radiation ($\lambda = 1.540598 \text{ \AA}$) and a Ge-monochromator at room temperature. The intensities were collected in a 2θ range from 8.0° to 90° and evaluated with the STOE program package WINXPOW.^[28]

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, <http://www.fiz-karlsruhe.de/request-for-deposited-data.html>) on quoting the depository number CSD-425458.

Raman Spectroscopy: Raman spectra were recorded with a Varian FTS 7000e Spectrometer with a Nd:YAG laser ($\lambda = 1064 \text{ nm}$) and a germanium detector cooled by liquid nitrogen. Samples were sealed in glass capillaries (diameter 0.5 mm) and measured in back-scattering mode. The signals were Fourier transformed by a Varian FT-Raman module and analyzed with the software Varian resolutions pro.^[29]

Differential Thermal Analysis: The thermal behavior was recorded with a Setaram DTA-TG 92-16.18. A small amount of the powdered sample was filled in a capillary tube (diameter 1.5 mm) and sealed under vacuum. The tube was heated up from 298 to 1073 K and cooled down again to room temperature with a heating/cooling rate of $10 \text{ K} \cdot \text{min}^{-1}$. Onset temperatures of the melting and crystallization process are derived from the respective curves.

Impedance Spectroscopy: Frequency dependent impedance spectroscopy of Na₃SbS₃ was carried out with an experimental set-up described earlier in a silica tube in an atmosphere of dry argon.^[30] The heating cycles proceeded in a temperature range from 325 to 570 K in steps of 10 K. During a measurement the applied frequency was raised from 1 Hz to 1 MHz with an IMd6A from Zahner Elektrik. Data were collected and analyzed with the software Thales Flink.^[31] Na₃SbS₃

was cold pressed (20 min, 7000 kg·cm⁻²) to a pellet with 93% of the calculated density. It was inserted in the spring-loaded conductivity jig according to the scheme Pt|Au|Na₃SbS₃|Au|Pt, where gold acts as ion blocking electrode.

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