Preparation of PVDF anionic exchange membrane by chemical grafting of GMA onto
PVDF macromolecule

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ABSTRACT

In this research, poly(vinylidene fluoride)(PVDF) anionic exchange membranes were prepared by a method of chemically induced grafting of glycidyl methacrylate (GMA) onto PVDF macromolecule in solution. Various preparation parameters, including initiator, monomer and cross-linker concentrations, grafting time and temperature, drying time of the anionic membranes, were established in correlation with area resistance and anionic permselectivity of the obtained anionic exchange membranes. The chemical and crystal changes of the membranes were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), respectively. Surface morphologies and thermal stability were also evaluated by field emission scanning electron microscopy (FT-SEM) and thermogravimetric analyzer (TGA). The results reveal that a PVDF anionic exchange membrane is successfully prepared by

this method and shows excellent properties with area resistance as low as $4.3 \Omega \cdot \text{cm}^2$ and anionic permselectivity as high as 99%, which are comparable to those of some commercial anionic exchange membranes, such as AHA, AMX, AST and so on. The membranes are homogenous, compact and show great thermal stability up to 171 °C and excellent alkali stability.

Keywords:

Anionic exchange membrane, PVDF, Macromolecular grafting, GMA

1. Introduction

Poly(vinylidene fluoride) is widely considered as a promising base material for preparing ion-exchange membranes due to its attractive features such as sufficient thermal, mechanical and chemical stability, radiation resistance, processability, availability and low cost [1-3]. One effective method to introduce ionic conducting groups to PVDF membranes and prepare PVDF ion-exchange membranes is chemically induced radical grafting polymerization [4–10]. The PVDF membranes are treated in oxidant or alkaline solutions with introduction of active sites to proceed radical grafting polymerization. Monomers or polymers with ion-exchange groups or transformable functional groups are then grafted to the treated membranes serving as ion conducting parts. Chemically induced radical grafting polymerization is one promising method for preparing partially fluorinated ion-exchange membranes because of its simple grafting process, low equipment requirement, as well as low cost.

Xinping Qiu et al. [9] prepared a poly(vinylidene fluoride)-graft-poly(styrene sulfonic acid) (PVDF-g-PSSA) membrane by a solution-grafting method. The membrane exhibits high conductivity with a value $3.22 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at 30 °C and dramatically lowers vanadium ion permeability compared to Nafion 117. PVDF-g-PSSA copolymers with either linear or arborescent PSSA side chains were also prepared using chemically induced radical grafting polymerization by Yu-Huei Su et al. [8]. The arborescent samples exhibit comparable selectivity and low IEC values compared to Nafion 117. Guibao Guo et al. [4-7] had also investigated PVDF-g-PSSA membrane and poly (vinylidene fluoride)-graft- poly (2-acrylamido-2-methylpropane sulfonic acid) (PVDF-g-PAMPS) membrane prepared by the method of chemically induced radical grafting polymerization. In our previous work [10], OMMT/PVDF-based cationic exchange membranes were prepared by two-step chemically induced grafting method. However, for the chemically induced grafting methods reported in references [4-10], the grafting reaction is usually used to introduce cation-exchange groups and almost conducted on the surface of the treated PVDF membrane. The internal grafting reaction is limited and the cation-exchange groups are mainly grafted on the surface of the membranes, which limits the physical and chemical properties of the obtained PVDF cation-exchange membranes.

In this study, a new route of chemically induced grafting PVDF chains is used to prepare PVDF anionic exchange membranes. Firstly, PVDF-g-GMA chains were prepared by alkaline treatment of PVDF chains followed by grafting GMA in

initiator/monomer/cross-linker mixtures. Then PVDF-g-GMA chain solution was directly casted into PVDF-g-GMA membranes which were further quaternized using trimethylamine solution to obtain PVDF anionic exchange membranes. This method grafts ion conducting structures to PVDF chains, rather than to PVDF membranes, thus leading to deep penetration in polymer matrix and uniform formation of active sites for initiating grafting throughout PVDF. The anionic exchange groups can exist not only on the surface but also throughout the interior phase of polymers. The development of a high selective PVDF anionic exchange membrane with a lower manufacture cost and a simple preparation process is interesting and valuable from the viewpoint of practical application as well as academic research. So study on this method may help confirm the merit of the chemically induced PVDF chains grafting process as a promising alternative more economical and environmentally friendly route for preparing PVDF anionic exchange membranes. To our knowledge, this method of chemically induced grafting of GMA onto PVDF macromolecule in solution is the first report for the preparation of PVDF anionic exchange membranes.

The objective of this study is to investigate a PVDF anionic exchange membrane prepared by a method of chemically induced grafting of GMA onto PVDF macromolecule under various reaction parameters. The chemical composition, structure, thermal stability and some electrochemical characteristics of the obtained anionic membranes were also investigated by FTIR spectrometer, FE-SEM, XRD, TGA and electrochemical methods.

2. Experimental

2.1. Materials

Poly (vinylidene fluoride) (Mw 5600,000) was kindly supplied by Shanghai 3F New Materials, China. Glycidyl methacrylate, divinylbenzene (DVB) and benzoyl peroxide (BPO) of analytical grade were purchased from Aladdin reagent (Shanghai) Co., Ltd., and used as received. Trimethylamine aqueous solution and N, N-dimethylformamide (DMF), analytical grade, were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. Deionized water was used throughout. All the other reagents are of analytical grade and used as obtained.

2.2. Membrane preparation

The process to produce PVDF anionic exchange membrane is consisted of alkali treatment, grafting reaction, membrane preparation, and quaternization. The process for preparation of the anionic membrane is shown in Scheme 1.

PVDF powder was dissolved in DMF to make a 10 wt% solution. Then a required amount of sodium orthosilicate was added to it and the mixture was stirred for 2 h at room temperature to obtain a dark brown homogeneous solution. Subsequently, BPO, GMA and DVB were added to the dark solution by turn. The solution was further stirred at 65 °C for some time under N₂ atmosphere. The resulting mixture was then cast on a glass plate to a desired thickness and heated at 75 °C to obtain a PVDF-g-GMA membrane. At last the dried grafting membrane was removed from the glass plate by soaking in water, and then cut into small pieces of samples (3×3 cm²).

A piece of above membrane sample was soaked into 30ml trimethylamine aqueous solution at 45 °C for 7 h to complete quaternization reaction, thus a PVDF anionic exchange membrane containing hydroxyl groups was obtained. After rinsing carefully with deionized water to remove residual trimethylamine, the quaternized membrane was lastly stored in deionized water before testing.

2.3. Characterizations

The measurements of the area resistance of the membranes were carried out using a clip cell. This cell was composed of two compartments with two dimensional stability electrodes (DSA). The two compartments of the cell were separated by the PVDF anionic exchange membrane [10]. The active area of electrodes as well as that of membrane S was 1 cm^2 . Before the experiments, the membrane was immersed in deionized water. Area resistance measurements were performed using an alternating low resistance meter with four-electrode mode. Membrane area resistance (r) was estimated by subtraction of the cell resistance (r_2) without the membrane from the cell resistance with the membrane (r_1). The electrolyte was $3 \text{ mol}\cdot\text{L}^{-1}$ NaCl solution.

The area resistance of the membrane r ($\Omega\cdot\text{cm}^2$) is calculated by eq. (1):

$$r = (r_1 - r_2) S \quad (1)$$

The anionic permselectivity was determined from the measured membrane potentials [10-12]. The studied membrane was placed between two compartments of a diffusion cell. The geometrical area of the exposed membrane was 1 cm^2 . A same volume of two KCl solutions of different concentrations ($C_1=0.1 \text{ mol}\cdot\text{L}^{-1}$ and $C_2=0.2 \text{ mol}\cdot\text{L}^{-1}$), was poured in the compartments. The membrane potential that resulted from

the difference in the concentrations in the two compartments was measured with two saturated calomel electrodes. Then, the counter-ion transport number in the membrane phase (t_-^m) can be calculated from eq.(2):

$$t_-^m = \frac{E_m + E_m^0}{2E_m^0} \quad (2)$$

And E_m^0 can be obtained according to Eq. (3):

$$E_m^0 = \frac{RT}{F} (2t_- - 1) \ln \frac{\alpha_1}{\alpha_2} \quad (3)$$

Afterwards, we determine the value of the anionic permselectivity with Eq. (4):

$$P = \frac{t_-^m - t_-}{1 - t_-} \quad (4)$$

Where E_m is the membrane potential between the compartments due to the difference in solution concentrations; E_m^0 is the ideal membrane potential between the electrodes in a same solution concentration; R is the ideal gas constant; T is the temperature; F is the Faraday constant; α_1 , α_2 are the activities of the electrolyte in the two solutions, respectively; t_-^m and t_- are the counter-ion transport numbers in the membrane phase and solution, respectively.

Alkali stability was evaluated by immersing the anionic membranes into different concentrations of NaOH solution at room temperature for different time to measure the changes in area resistance and anionic permselectivity. The membrane samples were immersed into NaOH solution at room temperature and then taken out of the solution at regular intervals, and the area resistance and anionic permselectivity of the samples were measured after they were rinsed in deionized water.

Fourier transform infrared spectra of different membranes were obtained using

FTIR spectrometer (NICOLET IS 10, Thermo Fisher Scientific) with the reflection technique. Morphological studies were undertaken with a field emission scanning electron microscope (SU8010, HITACHI). Samples were sputtered with a thin gold film before FE-SEM observation. The changes related to the crystalline phase of the membranes were characterized by X-ray diffraction (PW1700, PHILIPS) using a CuK α radiation under 40 kV voltage. Thermal stability of the membranes was measured by a thermogravimetric analyzer (Q50, TA) under an N₂ atmosphere, with a heating rate of 10 °C ·min⁻¹ from 28 to 800 °C.

3. Results and discussion

3.1. FT-IR spectra

The FT-IR spectra of the PVDF-g-PGMA membrane (a) and PVDF anionic exchange membrane (b) are shown in Fig.1. For the two samples, strong and wide absorption bands appearing between 1400 and 834 cm⁻¹ correspond to C-F stretching vibrations and are characteristic absorption bands of PVDF. The absorption bands at 1721 cm⁻¹ are attributed to C=O stretching vibration of PGMA which confirm that the monomer is grafted onto PVDF. Compared to the PVDF-g-PGMA membrane, the new absorption bands centered around 3400 cm⁻¹ in the spectrum of the anionic exchange membrane are assigned to -OH groups of PGMA after amination and the adsorbed water, proving that quaternary ammonium groups are introduced by the reaction of the epoxy groups of glycidyl methacrylate with trimethylamine.

Fig. 1. FT-IR spectra of the PVDF-g-PGMA membrane (a) and PVDF anionic exchange membrane (b).

3.2. Membrane preparation

Experimental conditions were investigated to determine some optimal preparation parameters of the PVDF anionic exchange membranes. The effect of reaction parameters including initiator (BPO), monomer (GMA) and crosslinker (DVB) concentrations, grafting time and temperature, and drying time were established in correlation with the area resistance and anionic permselectivity of the obtained anionic exchange membranes.

Fig. 2. Effect of BPO concentration on the area resistance and anionic permselectivity of the PVDF anionic exchange membranes.

Fig.2 shows the effect of initiator concentrations on the area resistance and anionic permselectivity of the anionic membranes. It is seen that both conductivity and anionic permselectivity of the membranes initially increase with increasing BPO concentration and attain maximum values when BPO reaches 4.2 g·L⁻¹, respectively. Later, the conductivity and anionic permselectivity decreases with further increasing initiator concentration. The increasing of conductivity and anionic permselectivity with increasing initiator concentration is mainly because more C=C double bonds on alkaline-treated PVDF chains are initiated by the increasing of free radicals, which yields more active sites and gives higher probability of being grafted by monomers [13]. GMA can also be homopolymerized as copolymerized with PVDF. Once GMA is copolymerized with PVDF, more GMA monomers or homopolymers will be

grafted onto the growing chains, which results in an increasing conductivity and anionic permselectivity. However, more free radicals tend to couple rapidly with the active sites if BPO content is further increased to above $4.2 \text{ g}\cdot\text{L}^{-1}$, and there may decrease the amount of active sites on PVDF. As a result, the decreased grafting amount of GMA leads to the decrease of conductivity and anionic permselectivity of the anionic membranes.

Fig. 3. Effect of GMA concentration on the area resistance and anionic permselectivity of the PVDF anionic exchange membranes.

Effect of GMA concentration on the area resistance and anionic permselectivity of the PVDF anionic exchange membranes is shown in Fig.3. The anionic permselectivity is increased with the increased concentration of GMA and reaches a maximum value at concentration of $4.3 \text{ mol}\cdot\text{L}^{-1}$. Thereafter, the anionic

permselectivity falls down at higher concentration of GMA. While the membranes display an increase trend in conductivity as concentration of GMA increases. The increase of total grafting numbers of the monomers can be reasonably attributed to the monomers diffusion rate and their concentration in the grafting solution. With increasing GMA concentration, the amount of the monomer molecules at the active sites is increased and more GMA molecules are available for the grafting reaction, which increases the conductivity and anionic permselectivity of the membranes. However a very high ionic conductivity of the membrane will decrease the anionic permselectivity. When GMA concentration is $4.3 \text{ mol}\cdot\text{L}^{-1}$ (Fig.3), the anionic permselectivity of the membranes shows a maximum value, while the conductivity is also high enough to be used as an anionic exchange membrane.

In order to decrease or diminish free GMA homopolymers, DVB was added to the reaction system to crosslink the free GMA homopolymers to form network structure. Effect of DVB concentration on the area resistance and anionic permselectivity of the PVDF anionic exchange membranes is shown in Fig.4. The anionic permselectivity of the membranes is found to increase with increasing DVB concentration at the beginning until it attains a maximum value at $0.02 \text{ mol}\cdot\text{L}^{-1}$, beyond which it tends to decrease. On the other hand, the increase in DVB concentration is also accompanied by an increase in the area resistance. This phenomenon indicates that crosslinking makes the membranes more compact which suppresses the anion transporting through ion channels, but increases the anionic selectivity. However, an excessively high crosslinking density makes the molecular structure of the membranes so tight that

both anion conductivity and permselectivity may be greatly reduced. When DVB concentration is $0.02 \text{ mol}\cdot\text{L}^{-1}$, the area resistance of the membranes is not the lowest, but still a relatively low and acceptable value as an anionic exchange membrane.

Fig. 4. Effect of DVB concentration on the area resistance and anionic permselectivity of the PVDF anionic exchange membranes.

Effect of grafting time on the area resistance and anionic permselectivity of the PVDF anionic exchange membranes was also investigated. The results are shown in Fig.5. When grafting reaction continues 4 hours, the anionic permselectivity and area resistance of the membranes attain a maximum value and a very low value, respectively, and then the values almost keep stability until the grafting time is increased up to 5 hours, indicating that the grafting reaction is controlled by the diffusion rate of monomers during this period. After 5 hours, the high viscosity of the

system influences the diffusion rate of the monomers to the active sites and ultimately results in the levelling off of the grafting monomers.

Fig. 5. Effect of grafting time on the area resistance and anionic permselectivity of the PVDF anionic exchange membranes.

Fig.6 shows the effect of grafting temperature on the area resistance and anionic permselectivity of the PVDF anionic exchange membranes. The increase of reaction temperature can speed up diffusion rate of monomers, but in the same time also accelerate the decay rate of the free and trapped radicals in the reaction system. Both factors decide the behavior of the curves [14]. As shown in Fig.7, the anionic permselectivity of the membranes is found to increase with increasing temperature until it attains a maximum value at 65 °C, beyond which it tends to decrease. On the other hand, the increase in the temperature from 60 to 80 °C is also accompanied by a decrease in the area resistance. The fact indicates that the increase of grafting

temperature accelerates diffusion rate of the monomers and allows more monomers to react with the trapped PVDF radicals and other free radicals, which results in higher grafting numbers of monomers. When grafting temperature is 65 °C, the area resistance of the membranes shows a relatively low and acceptable value.

Fig. 6. Effect of grafting temperature on the area resistance and anionic permselectivity of the PVDF anionic exchange membranes.

Effect of drying time of the PVDF anionic exchange membranes on the area resistance and anionic permselectivity is shown in Table 1. The drying time decides the amount of residual solvent in the obtained membranes, which can be dissolved into water and leave pores in the membranes when they are soaked in water. The longer drying time shows a more pronounced decrease in the ion conductivity of the membranes. The result may be explained by the lower residual solvent and extremely

compact structure in the obtained membranes, which suppresses the transportation of the ions through the membranes. On the contrary, the shorter drying time often results in a higher residual solvent and a loose structure, which favors the mobility of the ions through the membranes and increases the conductivity. Drying time also influences the anionic permeability through the membranes. Suitable low residual solvent and compact structure in the membranes result in a high anionic permselectivity.

Table1

Effect of heating time on the area resistance and anionic permselectivity of the PVDF anionic exchange membranes

Temperature / °C	Time / h	P / %	R / $\Omega \cdot \text{cm}^2$
75	3	78	4.2
	4	99	4.3
	5	90	5.7

Table2 shows effect of membrane thickness on the area resistance and anionic permselectivity of the PVDF anionic exchange membranes. The thicker membranes show higher area resistance due to the longer transportation route of Na^+ through the membranes. No obvious change is found in anionic permselectivity with increasing membrane thickness.

Table2

Effect of membrane thickness on the area resistance and anionic permselectivity of the PVDF anionic exchange membranes

Thickness / μm	$R / \Omega \cdot \text{cm}^2$	P / %
55	4.3	99
70	5.2	99
90	6.2	97
110	6.8	99

3.3. Morphology

Prior to amination the PVDF-g-PGMA membrane is yellow in appearance. After amination a very obvious color change is observed for the membrane, as shown in Fig.7. The PVDF anionic exchange membrane shows a deep brown color.

Fig. 7. Pictures of the PVDF-g-PGMA membrane (a) and PVDF anionic exchange membrane (b) taken under the same conditions.

Fig. 8. SEM photographs of the surfaces contacting glass plate (a-1, a-2) and air (b-1, b-2) of the PVDF-g-PGMA membranes during preparation.

The morphologies of the two side surfaces of the PVDF-g-PGMA membranes and PVDF anionic exchange membranes are shown in Fig. 8-9, respectively. The first clear observation from pictures is the difference between the two side surfaces of all the membranes: the surfaces contacting glass plate are smooth with just a few small size pores, and the other side surfaces contacting air are rough with bigger and more pores. After quaternization, much more pores are observed on the two side surfaces of the anionic membranes, which should be formed by the reaction of the epoxy groups of glycidyl methacrylate with trimethylamine.

Fig. 9. SEM photographs of the surfaces contacting glass plate (c-1, c-2) and air (d-1, d-2) of the PVDF anionic exchange membranes during preparation.

3.4. XRD Analysis

Crystallization behavior of the PVDF-g-PGMA membrane and PVDF anionic exchange membrane is investigated using XRD. The results are shown in Fig.10. PVDF is typically 50-70% crystalline which imparts the PVDF-g-PGMA membrane and PVDF anionic exchange membrane excellent chemical and mechanical stability which are required for fuel cell application [15-17]. The PVDF-g-PGMA membrane is still a semi-crystalline structure to show several peaks centered at diffraction angle (2θ) of 20.3° , 38.8° and 56.0° , which are associated with the convolution of an

amorphous region and a crystalline region. Quaternization alters the resulting molecular structure and physical network on the surface of the grafting membrane, leading to a decrease in the crystalline peaks at 20.3° and 38.8° , and a disappearance of 56.0° diffraction peak, which manifests that the crystallinity of the grafting membrane structure reduces slightly after quaternization and more amorphous morphology appears on the anionic exchange membrane, which is in good agreement with the morphologies of the PVDF-g-PGMA membrane and PVDF anionic exchange membrane shown in Fig.8-9. It may be explained by the fact that the randomness of the amorphous phase in the membrane is strongly enhanced by introducing quaternary ammonium group side chains, which often perturbs the microstructure of the anionic exchange membrane. The crystallite can maintain mechanical stability of the membranes and also hinder ion transportation through the membranes. So it is very necessary to adjust the ratio of crystalline and amorphism in the membranes in order to obtain ideal properties [16].

Fig. 10. XRD diffraction curves of the PVDF-g-PGMA membrane (a) and PVDF anionic exchange membrane (b).

3.5. Thermal stability

The TGA and DrTGA thermograms of the PVDF-g-PGMA membrane and anionic exchange membrane are shown in Fig.11. There are both three stages of weight loss for the two membranes. The first weight loss stage for the two membranes is both due to the evaporation of bound water and residue solvent DMF. This is because the two membranes are both hydrophilic and a certain amount of water may remain in the samples even after being dried in oven. Furthermore, the solvent DMF may also remain in the membranes whose bp is 152.8 °C. For the PVDF-g-PGMA membrane, the second weight loss stage shows that the grafting membrane has a satisfactory thermal stability up to 279 °C. It decomposes above 279 °C and attains the maximum decomposition rate at around 365 °C because of degradation of PGMA polymer main

chain. Then the degradation temperature at the maximum degradation rate for the third stage is at about 471 °C because of degradation of PVDF. As shown in the curves of the anionic exchange membrane, the quaternization reaction reduces the thermal stability of the grafting membrane. The anionic exchange membrane exhibits the second weight loss within a range of 171-267 °C which is due to the decomposition of the quaternary ammonium groups. At the third stage above 267 °C, the weight of the anionic exchange membrane is lost rapidly and attains the maximum degradation rate at around 438 °C which is lower than that of the grafting membrane. This is corresponding to the decomposition of the main chain of PGMA and PVDF. The weight loss stage of PGMA overlaps with that of PVDF in Fig. 11(B), which makes the maximum degradation rate of the anionic membrane occur at lower temperature comparing with that of the PVDF-g-PGMA membrane (i.e. 438 °C for the anionic membrane vs 471 °C for the PVDF-g-PGMA membrane). Although the introduction of quaternary ammonium groups decreases the thermal stability of the membrane, the anionic membrane still shows great stability below 171 °C, which is similar to other reported AEMs [18-19].

Fig. 11. TGA and DrTGA thermograms of the PVDF-g-PGMA membrane (A) and anionic exchange membrane (B) with the heating rate of $10\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ under N_2 flow.

3.6. Alkali stability

The alkali stability of the membranes was examined by immersing the membranes into different concentration of NaOH aqueous solutions at room temperature to measure the changes in area resistance and anionic permselectivity. The area resistance and anionic permselectivity of the membranes were measured at different time intervals, and the results are shown in Fig.12. Before the alkali stability experiment, the membranes were soaked in deionized water at room temperature for more than 48 h and measured to determine the area resistance and anionic permselectivity as reference for comparison. As shown in Fig.12, no notable change in area resistance and anionic permselectivity is found after 60 days of exposure in different concentration of NaOH aqueous solutions, indicating the anionic membranes have excellent alkali stability. Maybe, it is due to the special chemical structure of fluoropolymers and the cross-linked network structure. The strong C-F bond is helpful to obtain good thermal and chemical stabilities of fluorinated polymers. Crosslinking also causes significant improvement of chemical stability. The alkali stability of the membranes moderately decreases with increased NaOH solution concentration.

Fig. 12. Changes in area resistance (A) and anionic permselectivity (B) of the PVDF anionic membranes during exposure of different concentration of NaOH solution as a function of time.

4. Conclusions

A PVDF anionic exchange membrane has been prepared successfully by a method of chemically induced grafting of GMA onto PVDF macromolecule in solution which may be useful for design and preparation of ionic exchange membranes based on partial fluorinated polymers with high ionic conductivity and permselectivity. Various experimental conditions including initiator, monomer and cross-linker concentrations, grafting time and temperature, drying time of the anionic membranes were investigated to determine the optimum preparation parameters of the anionic exchange membrane. The obtained optimum preparation parameters are as follows: 4.2 g·L⁻¹, 4.3mol·L⁻¹ and 0.02mol·L⁻¹ for BPO, GMA and DVB concentrations, respectively; 65°C and 4 hours for grafting reaction temperature and time; 4 hours for drying time of the anionic membrane at 75 °C. The PVDF anionic exchange membranes prepared using the above optimum preparation parameters shows excellent properties with area resistance as low as 4.3Ω·cm² and anionic permselectivity as high as 99%, which are comparable to those of commercial anionic exchange membranes, such as AHA, AMX, AST and so on. The PVDF anionic exchange membranes are homogenous, compact and show thermal stability up to 171 °C and excellent alkali stability in NaOH aqueous solution. Thus they are good potentials for application in some alkali battery fields.

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